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Preface

Continuous fiber reinforced composites are a new kind of material with such properties as low density, high strength, high modulus, damage tolerance and safety. They have become very important to the aerospace industry, and found more and more applications in other industries and recreational consumer goods. Polymer matrix composites are the most important type of composite currently in widespread use. Therefore, they are an important subject for college students majoring in materials science and engineering. They have developed rapidly in the last ten or twenty years. New fibers and new matrix resins with better properties and more functions are coming out continuously, as are new molding methods and technologies. This book "Polymer matrix composites and technology" is written according to the cultivating scheme for college students majoring in polymer materials and engineering, and based on two earlier textbooks "Polymer matrix composites" (1986) and "Molding technology of polymer matrix composites products" (1981) and long time teaching practice on the composites course taught by the authors in Northwestern Polytechnical University.

The book was listed as a 21st century textbook project of Northwestern Polytechnical University, and, in the writing process, we try to reflect new developments in the composites field. The authors hope that it accurately reflects the raw materials, technology and performance of polymer matrix composites, and is suitable for course teaching of polymer materials and engineering major so as to meet the demand of knowledge and skill in composites field for technician in the aeronautical industry. There will be some errors in covering such a broad subject, and the authors sincerely ask experts and readers to give them their comments and critiques so that they can amend and supplement the text to make it better.

The book was written to systemically illustrate the essential concept, basic knowledge and elementary property of polymer matrix composites. Structurally, the book consists of an introductory chapter (Chapter 1) and three parts.

Chapter 1 gives an overview of the concept, performance characteristics, application area and development of polymer matrix composites. After reading this chapter, readers should be able to gain some insight of the polymer matrix composites industry and how it affects our daily life.

Part I explores the component of composite material, i.e. fiber, matrix resin and interface, respectively. Discussions include details and examples in each component. The "Fiber" Chapter covers the preparation, structure and property of the main reinforced fibers, and the variety and corresponding special features of each type. It follows with the "Matrix" Chapter where the role, property of matrix resin and its influence on the property of composites as well as formulation design and selection of polymer matrix are explained with great details. Furthermore, in the "Interface" chapter, we discuss the formation, function and damage mechanism of the interface in polymer matrix composites. We also talk about the surface treatment of fiber and research method on interface.

Part II deals with the process and technology for preparing the composite product. Content of the three chapters are respectively the preparation of half-finished product, molding technology of composites, and sandwich structure molding. Specifically, crucial aspects of the topics include the principles of molding, determination of curing process parameters as well as the quality control of composite product.

Part III covers the performance of composites. In the first chapter of this part, micromechanics method is applied to analyze the elementary mechanical properties of composites, the anisotropy of composites and the mechanical properties of multiplied composite laminates. The discussions extend in the following chapter to the basic mechanical properties of composite sandwich structure, composites fracture and damage, impact, fatigue, creep and environment effect. Moreover, in the third chapter of this part, we introduce the high frequency dielectric property of composite and its application in radome. Other properties of composites such as thermal physical properties, chemical properties and etc are covered in the last chapter.

The book was written by Ru-Min Wang, Shui-Rong Zheng and Ya-Ping Zheng who all work in Northwestern Polytechnical University. The work was divided as follows: Ru-Min Wang for Chapter 1, 6, 7, 8, 9; Shui-Rong Zheng for Chapter 2, 5, 10; and Ya-Ping Zheng for Chapter 3, 4, 11. The whole book was unified in structure and content by Ru-Min Wang. In the writing process, we got great support and help from Prof Xi-Zhen Zhou and Prof Man-Ling Sun, and express our acknowledgement to them. The book was chiefly reviewed by Prof Feng-Ji Lu in Xi'an Jiaotong University. She carefully checked and read the book in her busy schedule and put forward many valuable comments and suggestions, and we here express our deep thanks to her.

The whole book was translated and revised by authors Ru-Min Wang and Shui-Rong Zheng. The translation edition of the book was reviewed and proofread by my son Yu-Xiang Wang and his classmate Su Zhou who are now studying in National University of Singapore. Without their reworking on the words, sentence structure and grammar, this work would still be unfinished. We would like to thank many postgraduates of class 2008 who took my course on composite materials, especially my students Chao Yan and Xin-Lin Liu who gave us much help and put a lot of hard work at the beginning of translation process. I would like to express my gratitude to my parents, Bao-Qian Wang and Quan-Sheng Du, for their ever-constant encouragement and inspiration.

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October 2010

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Introduction to polymer matrix composites

1.1 Introduction

Materials are the basis for improving human production and living standards. They provide milestones in human progress. Humans have been accessing and using materials for several thousand years. Looking over the history of human civilization, we will find that its development is about human access and use of materials using social productive forces, science and technology. It reflects human ability to understand and transform nature. Whenever there is a new epoch-making material, productivity will also receive a huge development and human society will leap forward. Therefore, materials have become a symbol of the progress of human civilization, and have become milestones for dividing eras of human history. From the material point of view, human society has experienced the Stone Age, Bronze Age, and Iron Age. High-performance plastics and composites, which appeared in the 20th century, have infiltrated to the national economy and people's lives in various fields with a rare rate of development in the history. They have become the substitutes for traditional materials, showing improved performance. Now, with the rapid development of science and technology, materials play an important role in the national economy and defense. New materials are the basis of new technologies, and materials science, energy technology and information science have become the three pillars of modern science and technology.

Materials science is the integrated discipline. It is closely related to a wide range of other disciplines. It explains the laws of materials' macroscopic properties from the chemical composition and the principle of internal structure, and then develops a set of principles in designing, manufacturing and using new materials with specific properties. It mainly includes three parts contents: ① from the chemical point of view , the relationship of the chemical composition of materials and each component is researched, and the relationship between the composition and performance is researched, and the preparation methods of materials are researched; ② from the physical point of view, the performance of material is studied, and the relationship between the internal structure of materials (the combination of atoms and molecules, the arrangement distribution in space and the state of aggregation) and performance is studied; ③ under the guidance of chemical and physical theory, the technical problems which related to the preparation and application of materials are researched.

There are many different types of materials. Basically, they can be divided into three types of materials with vastly different performance by the way the atoms or molecules are bonded together (the main combination bonds): ① metallic materials, metal elements are combined by metal bonds; ② organic polymer materials, non-metallic elements are bonded covalently to macromolecular compounds; ③ ceramic materials, non-metallic elements and metal elements are combined by covalent bonds, ionic bonds, or a mixture of the two bonds. From the service performance point, there are two main types of materials: ① structural materials; ② functional materials. For structural material, its mechanical properties, such as strength, stiffness, deformation and so on, are majorly considerd, while for functional material, its sound, light, electricity, heat and magnetic properties are mainly used. In this case, we should know the behavior of materials in sound, light, electricity, heat and magnetic field.

As the rapid development of modern science and technology, there are more harsh special requirements for materials. The research of material is gradually breaking away from the track of researching by experiences and fumbling methods. It develops in the direction of material designing according to the designed properties. The composite material which is made of metallic, non-metallic and polymeric material by certain processes, can retain the advantages of the original components, overcomes some shortcomings and show some new properties. The emergence and development of such composite materials is a classic example of material designing.

Composite material is a multi-phase system consisted of matrix material and reinforcing material. Matrix material is a continuous phase, and it includes metal matrix composite materials, inorganic non-metallic matrix composite materials and polymer matrix composites by the different matrix materials. Reinforcing material is a dispersed phase, usually fibrous materials such as glass fiber, organic fiber and so on. We only discuss polymer matrix composites in this book.

Polymer matrix composite material is the one that uses organic polymer as matrix and fiber as reinforcement. Strength and modulus of fiber are much higher than the matrix material normally. This makes fibers the main load-bearing component. However, there must be a matrix material with good adhesion properties to firmly bond fibers together. At the same time, the matrix material can serve to uniformly distribute the applied load, and transfer the loads to fiber. In addition, some properties of composite materials mainly depend on the characteristics of the matrix material. As a result, in composite materials, the performance of fiber, matrix and the interface between them directly impact on the performance of composite materials.

1.2 The definition of composite materials

The term of composite materials was firstly used in abroad in the 1950s, and it has been used domestically from about the 1960s. Composite material is a kind of complex multi-component multi-phase system, and it is difficult to be defined accurately. A concise definition is shown: composite material is a multi-phase combination material of two or more component materials with different properties and different forms through compounding processes, it not only maintains the main characteristics of the original component, but also shows new character which are not possessed by any of the original components. Composite materials should have the following characteristics: ① microscopically it is non-homogeneous material and has a distinct interface; ② there are big differences in the performance of component materials; ③ the formed composite materials should have a great improvement in performance; ④ the volume fraction of component materials are larger than 10%. According to this definition, composite materials in a wide range of areas, straw mud wall, steel bar reinforced concrete, and tire cord, etc. all belong to the scope of composite materials.

From analysis of the composition and the internal structure of composite materials we found that it includes three basic physical phases. One is called matrix phase which is continuous, another is called reinforcement which is scattered and surrounded by the matrix. The other is called composites' interface which is an interface between reinforcement phase and matrix phase. For further study on micro-structure level, we found that, owing to the complex physical and chemical reasons in compounding process, the reinforcement phase and the matrix phase near the interface become a complex structure which is different from both of the matrix phase and the reinforcement phase of their own. And at the same time, we found that the structure and morphology have an impact on macroscopic performance of composites, so the microscopic area near the interface changes in structure and properties. Thus it becomes the third phase of composites, which is called interphase. Therefore, composite material is composed of matrix phase, reinforcement phase and interphase. The structure and the nature of these three phases, their configuration and interaction, as well as the relative content determine the performance of composite materials.

"Material Dictionary" edited by Changxu Shi gave a more comprehensive and integrity definition on composite material: "Composite materials are new materials that are combinations of different types of materials, such as organic polymers, inorganic non-metal or metal and so on, through compound technology. It not only retains the key feature of the original component materials, but also gets the performances that are not depicted by the original components through the combined effects. Materials designing can make the performance of each component to mutual supplement and interrelate to each other, thus produce a new superiority of performance, which has essential differences from general materials mixed simply." The definition stresses the important feature of composite materials that they are designable. In industry, composite materials are usually referred to the materials with excellent integrated performance which is made of reinforcement with high-strength, high modulus and brittleness, and matrix material with low modulus and toughness by a certain processing process. Composite materials discussed in modern materials science are generally referred to as fiber, sheet, and particle reinforced, or self-reinforced polymer matrix, ceramic matrix or metal matrix composites. This definition grasps the essence of the composite materials, namely the enhancing concept by enhancer. The fiber is the most widely used and the most effective reinforcement, so the composite material that people often talk about is a narrow meaning of composite materials, i.e. fiber-reinforced composite materials, which are discussed in this book.

1.3 Naming and classification of composite materials

1.3.1 Naming of composite materials

The development of many new materials is before their scientific name, so traditionally we often firstly use a number of popular names. For example, domestic composite material with glass fiber and resin began to appear in the 1950s, which is called the "glass steel", and its other names are: glass fiber reinforced plastics (GFRP), glass plastics, glass cloth laminates, and glass fiber composite materials. For the same kind of materials, if they have many names and some names are even inaccurate or misleading, it is easy to cause confusion. This is certainly not desirable to the application and development of materials.

Composite materials can be named by reinforcement and the matrix material. According to the type of matrix materials, there are metal matrix composite material, aluminum matrix composites, polymer matrix composite material, and epoxy resin matrix composite material. Polymer matrix composites are often named by the type of their reinforced fiber, such as glass fiber composite material (commonly known as glass fiber reinforced plastics), carbon fiber composites, and hybrid fiber composites. More specifically, the name of the reinforcement is put the front of the name of the matrix material, along with "composite material" on the back. For example, composite material with E-GF and epoxy resin can be named "E-glass fiber epoxy composite material". For convenient writing, it can also be written as abbreviation of the reinforcement and matrix materials, with a "/" separating them, along with "composite material" on the back, and so the former "E-glass fiber epoxy composite material" is briefly called "E-GF/epoxy composite material" (traditionally called epoxy GFRP). Composite material of carbon fiber and metal matrix is called "metal matrix composites", and can also be written as "carbon/metal composite material". Carbon fiber reinforced carbon matrix composite material is called “carbon/carbon composite” or “C/C composite material”. The above-mentioned nomenclature can also be addressed using commodities trademark directly, for example, T300/648, M40/5208, S-GF/5245C, Kevlar49/QY8911, HT3/5405 and so on.

1.3.2 Classification of composite materials

There are many ways to classify composite materials. For example, in accordance with the reinforcing principle, there are diffusion-enhanced composite materials, particle-enhanced composite materials and fiber-reinforced composite materials. Based on different application requirement, there are structural and functional composite materials. Functional composite materials, in accordance with its function, can also be divided into electrical functional composite materials, thermal functional composite materials, optical functional composite materials, and so on. According to different preparation processes, it is classified as laminated composite materials, winding structural composites, pultrusion composite materials, textile structural composite materials and so on.

According to the meaning of composite materials and its naming principles in this book, the classification of composite materials is shown in follows.

(1) Classification in accordance with the type of matrix material. ① Metal matrix composites (MMC’s); ② inorganic non-metallic matrix composite materials; ③ polymer matrix composites (PMC’s). The most important inorganic non-metallic matrix composite materials are ceramic matrix composites (CMC’s) and carbon-based composite materials such as C/C composite materials. In the polymer matrix composite materials, there are thermosetting resin-based composite materials and thermoplastic resin-based composite materials, as well as one-component polymer matrix composite materials and polymer blends matrix composite materials.

(2) Classification in accordance with the form of dispersed phase. ① Continuous fiber-reinforced composite materials; ② fibrous fabric, braid reinforced composite materials; ③ sheet reinforced composite materials; ④ short fiber or whisker reinforced composite materials; ⑤ particle reinforced composite materials; ⑥ nanometer particle reinforced composite materials.

(3) Classification in accordance with the type of reinforcing fibers. ① Carbon fiber composite material; ② glass fiber composite materials; ③ organic fiber composite materials; ④ boron fiber or silicon carbide fiber composite materials; ⑤ hybrid fiber composite materials.

1.4 Molding methods of composite materials

There are many processing methods of composite materials, and big differences in different types of molding processes of composite materials. The molding process about hand lay-up fiber reinforced plastics (FRP) (Fig. 1.1) is a typical process of preparing thermosetting polymer matrix composites. We see that there are many manual labours in process. Compounding of fibers and resins and curing reaction process of resin system are the forming processes of composite materials and at the same time, the formation processes of composite material products. Preparation of materials and products completes in the same process, which is another character that the composite materials are different from metallic materials.

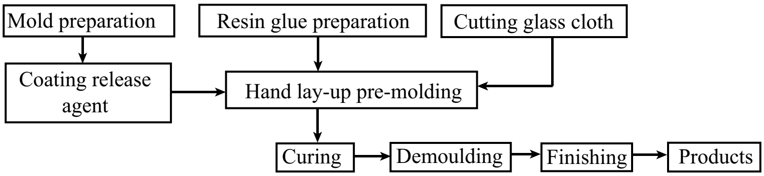

Fig. 1.1 Technique flow chart of FRP by hand lay-up.

1.5 Characteristics of composite materials

From the classification of composite materials, we already know that there's a wide range of composite materials. It is a truism that different types of composite materials have different performance characteristics. However, composite materials also have some common characteristics. Polymer matrix composites, because of their inherent characteristics, have become the fastest growing and most widely used composite materials. Compared with traditional materials such as metals, polymer matrix composites have the following characteristics.

1.5.1 High specific strength, high specific modulus

The prominent advantages of polymer matrix composite materials are their high specific strength and high specific modulus. The specific strength is the ratio of strength and density and the specific modulus is the ratio of modulus and density, and the dimensions or units are both length. Under the premise of equal weight, they are indices of measuring bearing capacity and stiffness properties of the material. Such properties are very important for aerospace structural materials to work in the air or the space. Table 1.1 lists the specific strength and specific modulus of several common structural materials, in which carbon fiber resin matrix composites shows higher specific modulus and specific strength. The high specific strength and high specific modulus of composite materials result from high-performance and low-density of reinforcing fibers. As a result of relatively low modulus, high density of glass fiber, the specific modulus of the glass fiber resin matrix composites is slightly lower than metallic materials.

Table 1.1 Specific strength and specific modulus of some common used materials and fiber composites

Materials	Density (g/cm^3)	Tensile strength (GPa)	Elastic modulus (10^2GPa)	Specific strength (10^6cm)	Specific modulus (10^8cm)
Steel	7.8	1.03	2.1	1.3	2.7
Aluminum alloy	2.8	0.47	0.75	1.7	2.6
Titanium alloy	4.5	0.96	1.14	2.1	2.5
Glass fiber composite materials	2.0	1.06	0.4	5.3	2.0
Carbon fiber II/epoxy composite materials	1.45	1.50	1.4	10.3	9.7
Carbon fiber I/epoxy composite materials	1.6	1.07	2.4	6.7	15
Organic fiber/epoxy composites	1.4	1.40	0.8	1.0	5.7
Boron fiber/epoxy composites	2.1	1.38	2.1	6.6	10
Boron fiber/aluminum matrix composites	2.65	1.0	2.0	3.8	7.5

1.5.2 Good fatigue resistance and high damage tolerance

The fatigue failure of metallic materials is often of no obvious omen to the salience of damage. The interface between fiber and matrix in composite materials can prevent the propagation of crack. The fatigue failure always initiates from the weak links of fiber. Crack growth or damage continues gradually for a long time, so there is a significant harbinger before the final destruction. As we see from the S-N curve of fatigue properties, the fatigue strength of the majority of metallic materials is 30% to 50% of tensile strength, while the fatigue strength of carbon fiber/polyester composite material is 70% to 80% of its tensile strength, the proportion of glass fiber composite materials is between them.

Unlike traditional materials, damage of composite material is not due to the unstable propagation of the main crack and then suddenly happening, but it experiences the development of a series of damages such as matrix cracking, interfacial debonding, fiber pull-out and fiber split or break. A large number of independent fibers in matrix are typical mechanical statically indeterminate system. When a small number of fibers fracture, the part of the load they bore will be transferred via the matrix and quickly diffuse to other fibers. Composite materials will not lose the bearing capacity in short term. Composite material will not fracture with some defects and cracks in it for a sudden development.

1.5.3 Good damping characteristics

The natural frequency of vibration of forced structure relates to the shape of the structure itself, as well it is proportional to the square root of the specific modulus of structural materials. Therefore, composite materials have a high natural frequency, and it's not easy to have a resonance in general. At the same time, the interface between the fiber and matrix in composite materials has a great ability to absorb vibrational energy, resulting in a high vibration damping of materials. Once the vibration occurs, it can be stopped in a short time.

1.5.4 Multi-functional performance

(1) High instantaneous temperature resistance and good ablation resistance. Thermal conductivity of FRP (fiberglass reinforced plastics) is only 1% of metal materials. It can also be made into the materials with high specific heat, high melting heat and high vaporization heat. Thus, FRP can be used as the ablation-resistant protective material for missile nose cone.

(2) Superior electric insulation performance and high frequency dielectric properties. FRP is a superior insulating material in power frequency. Besides insulation property, FRP has good high-frequency dielectric properties as well. It can thus be used as the high-frequency wave-transparent materials for radome.

(3) Good friction property. Carbon fiber has low friction coefficient and self-lubricating property. Its composite materials have good friction-resistance and antifriction properties.

(4) Excellent chemical corrosion resistance.

(5) Special optical, electrical and magnetic properties.

1.5.5 Good processing technics

(1) Fiber, matrix and other raw materials can be chosen in accordance with the use condition and performance requirement of the product, that is, material can be designed.

(2) Molding processing methods can be chosen in accordance with the shape, size, and number of the product.

(3) The integrated molding can reduce the number of assembly parts and thus save time, save material, reduce weight.

1.5.6 Anisotropic and properties designability

Fiber composite materials are characterized prominently by anisotropy, which is related to the designing of performance. The mechanical and physical properties of fiber composite materials are determined not only by the type of fiber and resin type and relative volume fraction, but also closely related with by the direction of fiber arrangement, ply stacking sequence and layer number. Therefore, based on the load distribution and the different application requirement of the engineering structure, we select the corresponding material and ply designing to meet the established requirements. Taking advantage of this feature, we can get the optimal design of parts, to be safe, reliable, economical and reasonable.

There are some shortcomings and problems for polymer matrix composites. First, the degree of the automation and mechanization processes is low. Also, the consistency of the material properties and the stability of product quality are both poor. The methods of quality testing are imperfect too. Moreover, the properties of long-term high temperature resistance and aging resistance are poor and so on. These issues need to be studied and dealt with in order to promote the development of composite materials and produce more mature technology and materials.

1.6 Application of composite materials

In composite materials, the glass fiber polymer matrix composites are the first developed and applied materials. In the 1940s, Americans compounded glass fiber and unsaturated polyester resin firstly, and then produced military radar and aircraft fuel tank by hand lay-up process, which opened the path for the glass fiber composite materials to be applied in military industry. Since then, with the development of glass fiber, resin matrix and composite materials processing, glass fiber composite materials are not only used in the aerospace industry, but also widely used in a variety of civilian industry, and become important engineering materials.

However, after entering the 1960s, people noted that the mass of the glass fiber reinforced plastics is big and the modulus is low. It could not meet the requirements of high-tech products for high specific modulus and high specific strength such as aircraft. Therefore, the lightweight carbon fiber and carbon fiber composite with high specific modulus and high specific strength were developed between the 1960s and the 1970s. Following the carbon fiber, the aromatic polyamide fibers (aramid fiber) and other high-performance fibers were developed. Such new composite materials starting from carbon fiber composite material was known as the advanced composite materials (ACM).

At present, the world's total output of composite materials is in megatons. It is difficult to statistic the accurate output. It was reported that the world's output was 3.9 million tons in 1990, of which 1.503 million tons in the United States, 1.485 million tons in Western Europe, 0.643 million tons in Japan, and 0.106 million tons in China. Nevertheless, the output of composite materials compared with other structural materials is still very small. Now, the world's output of steel is up to thousand megatons, and the production of plastics also reaches hundred megatons. This shows that there is still much room for the composite materials to develop, and there is also need to speed up the development.

Although the first application of composite is in aerospace sector, and its development has been driven by aerospace demand, but the composite materials for aerospace applications are only a small fraction of total output (only $1\%\sim2\%$). Large amount of composite materials are used in transport sector (cars, boats, etc.), construction, chemical corrosion equipment and electric or electronic appliance.

1.6.1 Application in the aircraft and aerospace industry

Although the composite materials of application in the aerospace industry take only a very small share, most of the materials it adopted are advanced composite materials, representing the most advanced technology of composite materials industry. It is worthwhile to discuss this application first.

The root cause for aircraft to use composite materials is to reduce the weight, which can improve aircraft's performance and reduce the costs. Advanced composite materials in the application of military aircraft passed a developmental way that was from small to large, weak to strong, few to many and from structural load to increasing function in the nearly past 40 years.

Most battleplanes in the world that start serving the force after 1980s have some parts made of ACM. Specifically, the components of its wings, tail and other parts are almost all made of ACM, whose weight accounts for 20% to 30% of the body structural weight. The French Rafale, maiden flight in 1980, 50% of its wings, tail, vertical and the fuselage structure were ACM, which took 40% of the body structural weight. The United States B-2 stealth bomber, maiden flight in 1989, the amount of composite materials took 40% of the body structure. Now, ACM has been widely used in the aircraft's primary and secondary structure, such as the vertical tail, horizontal stabilizer, rudder, aileron, frontal fuselage and wing skin and so on. The usage of composite materials in modern helicopter is more than military aircraft, and is currently as high as 50% to 80%. There is the ACAP (Advanced Composites Application Program) in the United States, in which several developing helicopters H360, S-75, BK-117 and V-22 all use largely ACM. For example, the V-22 which cruises in high-speed after vertical take-off, landing and tilting rotor, uses nearly 3,000 kilograms' composite material, accounting for 45% of total structural weight, including most of the structure of the fuselage and wing, joints of the engine and fastening device of blades. In the total weight of the U.S. light reconnaissance and attack helicopters of the latest development, the RAH-66, with stealth capabilities, composite material accounts for about 50%. The length of its keel beam of fuselage is 7.62m, and layer number is as high as 1000. For the Tiger-type helicopter gunship of Franco-German cooperation in the development, the amount of composite materials is as much as 80% of the total weight.

ACM in the application of commercial aircraft is also increasing. Take an example of Boeing, the usage area of composite materials on B707 at 18.5m^2, on B737 at 330m^2, on B747 at 930m^2. For 10 years from B707 to B747, the increase of the area of the fuselage is less than double, but the increase of the area of composite materials used has reached 50 times. The amount of composite materials in B757 is 1429 kg, the amount in B767 is 1524kg, and the amount of the latest development of the B777 has increased to 9900kg, accounting for 11% of structural weight. ACM in European A340 is more than 4 tons, accounting for 13% of the total structural weight. The branch aircraft ATR-72 was developed in cooperation by French and Italian, whose amount of composite materials is up to 20% because of the usage of the wing. Many small aircrafts using all-composite materials are also manufactured, the most famous in the world"Voyager", setting the world record of non-fuel and non-stop flight for 9 days, which couldn't be imagined before the composite materials appear.

Composite materials in space industry are mainly used on the adiabatic shell structures of combustion chamber of solid rocket motor, the inter-segment structure of missile and launch vehicle, structure of liquid hydrogen tanks, module structure of apparatus, missile and satellite fairing structure, heat insulation materials of missile and various satellite structures. Aerospace structural materials have also gone through the metal to fiberglass and then re-developed to the stage of ACM. A typical example is the solid rocket motor casings. The first generation of composite materials used by solid rocket motor is FRP. A successful example is missile engine fiberglass plastics shell of "Polaris A-3" in the early 1960s, which reduces the weight of the alloy steel by 60% and the cost by 66% than "Polaris A-1". The usage of Kevlar-49 (aramid fiber), IM-7 (carbon fiber)/epoxy composite materials for advanced motor shell makes even more significant results of weight saving.

1.6.2 Application of composites in other industry

In addition to aerospace, the composite materials, especially glass fiber composite materials get a wider range of applications in the other economic areas as a result of advantages of their price and performance. They play an important role in the promotion of scientific and technological progress and the development of national economy. In United States, 1,171,000 tons of fiber composites were produced in 1991, of which 324,000 tons were used in transport, 205,000 tons in construction, 169,000 tons in shipbuilding, 163,000 tons in corrosion equipment, 110,000 tons in electronic appliances, 70,000 tons in business equipment, 75,000 tons in daily necessities, only 18,000 tons in aerospace military, and 37,000 tons in others.

(1) In the area of transport, composite materials have been applied in car, train, ship and other transport tools over half a century in history. Composite materials' products have been increased year by year, and the amount within the realm of transportation has the greatest proportion. In the automotive manufacturing industry, composite materials are mainly used in a variety of body components, engine cover, dashboard, door, floor, seat, refrigerated truck, fire engine, box car and other transport tanker. In the railway transport, composite materials are used in passenger carriage, carriage door and window, water tank, toilet, refrigerator car body, storage tank of liquid transportation, container and various equipments of communication. Composite materials have become the champion of the new materials in

transportation.

(2) In the construction industry, CM is widely used in a variety of light house, large building structure, architectural feature and sculpture, sanitary, cooling tower, storage tank, waveform tile, door and window components, hydraulic construction and the ground and so on. Carbon fiber composite as strengthening and repair for infrastructure, has shown a large market in recent years.

(3) In the shipbuilding industry, composite materials are used in the production of a variety of work boat, fishing boat, transport boat, motor boat, lifeboat, cruise, military minesweeper and submarine.

(4) In anti-corrosion equipment, composite materials, especially glass fiber reinforced plastics are highly resistant to corrosive chemicals, and provide the new chemical anti-corrosion materials. Chemical anti-corrosion equipments made by glass fiber reinforced plastics, mainly include large tank, container, various pipes in mass transfer, elbow, three link, such as pipe fitting, ventilation duct, chimney, fan, pump, valve and so on.

(5) In electrical and electronic industry, composite materials are used in the production of laminate, copper clad laminate, insulative pipe, electrical retaining ring, wedge, insulator, street lights, telegraph pole, and tool of live operation.

(6) In ordnance, composite materials are mainly used in the production of fuses, bullets, cartridge cases (coach shells), retaining ring shells, butt, rocket launcher, shield of artillery, and so on.

(7) Composite materials are used in all kinds of sports equipments in sporting goods, such as the vaulting pole, bow and arrow, racing bicycle, skateboarding, rowing, kayak, oarage, and so on.

(8) In the agriculture and fisheries, composite materials are made into all kinds of greenhouse for vegetable, flower, aquaculture, chicken, pig, as well as the granaries, feed store, septic tank, drain, spray, flower pot, milk delivery vehicle, manure transport vehicle and so on.

(9) In the mechanical manufacturing, composite materials have a very wide range of usage, such as fan blades, paper-making machinery accessories (beater parts, the case of hanging roller and roller), diesel engine parts, textile machinery parts, synthetic fiber machinery parts (filters, centrifugal cans, chip sets, etc.), coal mining machinery parts, pumps, mold, food machinery parts, gears, flange, pulley and protective shield and so on.

1.7 The progress of composite materials

As we already pointed out that the composite materials obtain a wide range of applications in various economic fields, the amount of domestic usage is still small. There is a big gap between China and the developed countries in application of composites both in quantity and quality. To promote the development of composite materials, the following main issues should be solved: reduce the price of composite materials in the basis of quality assurance; develop high-performance, in particular multi-functional composite materials; improve the effectiveness of their application; develop new types of more effective molding process; further promote the field of application of composite materials.

1.7.1 Reducing the price of fiber and developing new fibers

Reinforced fiber is the main raw material of composite materials. The current trend is to reduce the price of high-performance fibers and develop the reinforcing fibers with special function. Table 1.2 and Table 1.3 display respectively the estimated demand for advanced fibers and the average price of a variety of fibers between 1970 and 1995 and between 1995 and 2015. It can be seen that the demand for advanced fiber increases year by year, and the price falls. As an example of carbon fiber, the demand increases from 8,000 tons in 1995 to 40,000 tons in 2015, increased by 4 times, and the average price takes from 50US $/kg to 20US $/kg, decreased by 60%. Obviously the decline of advanced fiber prices expands its scope of application of composite materials, for example the application in the

Table 1.2 Estimated demands for advanced fiber in the world between 1970 and 1995[1)]

Fiber type	Demand(ton)				Sales value in 1995(million $)
	1970	1980	1990	1995	
Carbon fiber[2)]	100	1,000	6,000	8,000	400
Organic fiber[3)]	50	5,000	15,000	18,000	500
High-performance glass fiber[4)]	10	500	2,000	3,000	50
Sum total	160	6,500	23,000	39,000	950

Note: 1) Including the total of fiber used in composite materials and other materials.
2) Including the average price of the pitch-based, PAN-based and PAN-based oxidation carbon fiber.
3) The average price of aramid.
4) The average price of high-strength borosilicate glass fiber.

Table 1.3 Estimated demands for advanced fiber in the world between 1995 and 2015[1)]

Fiber types	Demand(ton)				Sales value in 2015(million $)
	1995	2000	2005	2015	
Carbon fiber[2)]	8,000	15,000	25,000	40,000	800
Organic fiber[3)]	18,000	26,000	35,000	45,000	900
High-performance glass fiber[4)]	3,000	8,000	15,000	25,000	200
Sum total	39,000	49,000	75,000	110,000	1,900 0

Note: 1) Including the total of fiber used in composite materials and other materials.
2) Including the average price of the pitch-based, PAN-based and PAN-based oxidation carbon fiber.
3) The average price of aramid and ultrahigh molecular weight polyethylene fiber.
4) The average price of high-strength glass fiber.

cars. On the contrary, the expansion of the amount can promote the decline in prices of material.

The key measure to reduce the price of carbon fiber is to develop pitch-based carbon fiber and large-tow carbon fiber. The price of asphalt is much lower than polyacrylonitrile (PAN) fiber, the performance of current pitch-based carbon fiber has been close to or equivalent to that of the standard type PAN-based carbon fiber, and pitch-based carbon fiber is expected to become the staple products. In the past, the aerospace grade carbon fiber used in military defense technology mainly included 1K, 3K and 6K, but now develops progressively to 12K and 24K, as the small-tow carbon fiber. Commercial grade carbon fiber of more than 48K, which meets the needs of general industrial applications, is called large-tow carbon fiber, and it has been developed to 480K, 540K, and there is absolute advantage in price. As standard type T300 carbon fiber, the price level of the current international market for commercial large-tow has been lowered to 8$\sim$10 \$/1b①, while the price of aerospace-grade is 15 $\sim$ 20 \$/1b.

The organic fiber with high modulus was mainly aramid in the past. A number of new organic fibers have been developed since the 1980s. The ultra-high molecular weight polyethylene (UHMWPE), PBO (polybenzoxazole) and aromatic polyester fiber are representatives. UHMWPE fiber has high strength and modulus, a big potential in the price, and light weight, it is a promising reinforced material.

In order to adapt to the needs of high temperature resistant and multi-functional composite materials, a number of special fibers have also been developed in recent years, of which fibers silicon carbide and silicon nitride are more important, which are characterized by high temperature resistance and semiconductor. Their resin-based composite materials have absorption (stealth) performance.

1.7.2 Expanding the application of composite materials

At present, the application of composite materials is developing toward the industry of high-grade and staple products, such as the automobile industry, shipbuilding, construction and so on.

1) The automobile industry

Composite materials can significantly lower fuel consumption, and have anti-corrosion and anti-vibration performances, so a large number of composite materials will be used in the automobile industry. At present, the application ratio of automotive steel has dropped to 14%$\sim$15%, and it has been reported that in 2000, there were one in five cars which was manufactured using composite materials in the United States. Moreover, in order to reduce environmental pollution, many countries are vigorously developing the usage of natural gas to replace gasoline

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① 1b is illegal unit, 1b = 0.453592kg. The same is in the following.

as motor fuel, and the cylinders of natural gas use FRP structure. The working pressure can go 20∼100MPa, life reaches 10∼20 years, and this cylinder has been in series and into practical application.

Composite materials used in automotive components are mainly glass fiber unsaturated polyester. In the past they were made by hand lay-up and spray-up molding, but in recent years, sheet molding compound (SMC), glass fiber mat reinforced thermoplastics (GMT) compression molding and resin transfer molding (RTM) have been used. The method of making sheet molding compound (SMC) is that chopped glass fiber roving or glass fiber mat is impregnated using the mixture (paste resin) of unsaturated resin system, fillers and other additives, and then wrapped with polyethylene or polypropylene film on both sides of itself to form the sheet type compound. SMC is widely used as a result of continuous production, easy usage and lower price.

In addition to glass fiber composite materials, the application of advanced composite materials in the automotive industry can also be found. The factor of high cost restricts the usage of advanced composite materials, but the good news is that the current price of carbon fiber has dropped to somewhere close to the price that automobile industry can accept.

2) The shipping industry

It's a long history for us to use composite materials in fishing boats, tugs, yachts, boats and minesweepers. The composite materials are light and can withstand the high external pressure, submersibles of composite materials are being developed, which will increase the application of composite materials in submarines.

3) The construction industry

In the construction industry, composite materials are used as a variety of light structural houses, decorative materials, sanitary ware and cooling towers, storage tanks and so on, besides, in recent years they have expanded the application of the reinforced tendons of concrete and the bridge. Composite materials are used as reinforced tendons of concrete instead of steel to create new type of concrete, which has attractive prospects, because it can improve the earthquake resistance and diamagnetism of building structure. The glass fiber, carbon fiber and aramid fiber or hybrid fibers for two-dimensional or three-dimensional woven or braiding are used as reinforcements in reinforced tendons. At present, this new type of concrete has been used in the foundation of bridges and buildings, such as magnetic observatories, high-frequency electrical room and so on, which can extend service life of buildings and play an important role in improving performance.

The application of composite materials in the construction of houses, bridges, tunnels, culverts, subways and their related structures of concrete and other infrastructure projects in recent years have become the fastest-growing civil and one of the most promising areas, and it has become world-wide hotspots of the research and development currently. Composite materials in various forms are used in the field, such as continuous cable, guard rails, handrails, grating; beams, columns, poles, stakes; laminates, wrapped material, short fibers (reinforced cement); ribs. Now, the most widely used are composite materials, especially carbon fiber composite materials for infrastructure repairing, renovating and strengthening, and the application forms are wrapped material (sheet) and laminate. The technology originated in the late 1980s and the early 1990s, was used for the restoration of Osaka earthquake, the Los Angeles earthquake. Thereafter, Japan, the United States and Europe vigorously promote the development of this technology, it has been rapidly developed into many application fields such as civil engineering, masonry, concrete work, and so on, and it has been formed new technology of industrialization and accepted by the world. The technology played a great role in rehabilitation and reconstruction of the "921" earthquake in Taiwan, and further stimulated the Taiwan carbon fiber industry.

1.7.3 Developing new design, preparation methods and new composite technologies

In addition to improving designing and preparation methods of composite materials, it is also necessary to open up the new avenues.

(1) The new designing method. It is such as integrative design of composite materials integrating three aspects of materials-technology-design, the dummy technologies of composite materials and structure.

(2) The new technology of materials compositing. It is such as composite technology including in-situ compositing, self-spreading, and gradient compositing, molecular self-assembly, and super-molecular compositing.

(3) Multi-purpose, low-cost technology. Composite molding process is the key to manufacture component. The choice of forming process depends on the shape, performance, uses of products and technology properties of composite materials. Now the number of developing consecutive and non-continuous molding process is large. In the 1990s, a distinctive feature of the development of molding process is from single to multi-purpose, automation and low-cost. Such as resin transfer molding (RTM) molding technique, resin film infusion (RFI) molding technique, reinforced reaction injection molding (RRIM) forming technique, electron beam curing technique, reinforced thermoplastic sheet (GMT) technique, of which the resin transfer molding (RTM) process is a success example.

RTM process is a closed-molding process. The course of basic process is shown: the liquid thermosetting resin system is immitted into the mold with reinforcing fibers (known as preformed flan), heated to solidify, demolded and post-processed into products.

RTM process has many advantages such as simple equipment, short molding cycle, easy managing in specialization and automation, excellent performance of products, and lower manufacturing costs than other forming processes, which is particularly evident for advanced composite material structures.

In fact, most prominent feature of RTM process is that preformed flan can be specialized in the design and manufacture. Therefore, fibers can be weaved in multi-dimension, which solves the major problems about fiber reinforced in one-dimension by traditional ply-stacking process leads to low strength of interlaminar and in horizontal direction, and greatly improve the mechanical properties of composite materials, especially the damage tolerant properties.

The course of preformed flan manufacture mainly includes arrange manner and density of fiber yarns, interlaminar manner of fabric, overall status of fiber impregnation, in which fibers are braided or stitched. At present, three-dimensional braiding is more mature in multi-dimensional woven fiber technology. Three-dimensional weaving is to get the complete three-dimensional integral structure by intertwining the long fibers one another, characterized by creating a variety of inerratic shape and the solid body and hollow body of abnormity, and will make the structure of versatility.

Three-dimensional weaving technology which appeared abroad in the early 1980's was a new textile technology emerged. The composite materials of the weaving structure which developed by the three-dimensional weaving get great development and application because of their excellent performances. The RTM process is in line with the manufacture of the woven structural composite materials. Thus, RTM process has broader development prospects.

The processing performance of the resin in RTM process has special requirement, which can be summarized in follows: it has low viscosity and a certain storage period at low temperature, and fast solidified at high temperature; and it has a good infiltration, match and adhesion for reinforced fibers. Now for the RTM use, special matrix materials of unsaturated polyester resin, epoxy resin and bismaleimide resin have been developed. At present, RTM process has been widely used to manufacture the composite materials' products in aerospace, automotive, machinery, construction industries.

1.7.4 Developing hybrid fiber composite materials

The characteristic of hybrid fiber composite materials is that different fibers can learn from each other and match in coordination, so that they have excellent performances and lower costs. If we use different mixing ratios and different structures, the adaptability can be broadened, and design freedom can be increased. Hybrid composites designed properly also have certain functionality, even as functional/structural composite materials.

Commonly used hybrid is a mixture of carbon fiber and aramid, in which carbon fiber provides compressive strength that aramid is lack of and aramid improves the toughness of the material. Another popular hybrid is a mixture of the carbon fiber and glass fiber. Carbon fiber provides high specific strength and specific modulus, and glass fiber provides better toughness and lower material cost.

Research and application about hybrid composites have got the great development since the 1970s. Firstly, hybrid composite materials were mainly used for structural materials. The application grows relatively fast, and has an increase of 10 times in 5 years between 1985 and 1990. Its applications popularize in all areas of the national economy. In recent years, the functional structural hybrid composites have been developed successfully, such as absorption/structural composite materials.

Hybrid fiber composite materials are higher-level composite materials than single fiber composites. First of all, the basic problem encountered is the hybrid effect, which involves the match of fiber type, hybrid ratio and hybrid mode. In addition, there are interface issues and manufacture problems. From a wide range of view, there are also the problems of the material strength theory, damage and component design. Further study on these issues is needed. However, one thing is clear, that is, we can manufacture composite materials of multiple applications with lower cost by mixing different types of fibers in different ways and different proportions. Therefore, the hybrid composites are an important development direction.

1.7.5 Developing functional, multi-functional, smart and intelligent composite materials

We have already pointed out that composite materials are the important structural materials. In fact, its design features with a large freedom is more suitable for the development of functional composite materials, especially in functional → multi-functional → smart → intelligent composite materials, that is, the process reflects from the lower forms to higher forms. That the design of composite materials has a large freedom is the result of regulating their multiplicity at random, choosing the connecting form, changing their symmetry and other factors, and the aim is to achieve the optimal value of functional materials.

1) Functional composite materials

Various functional materials can be produced by compounding different materials of function. Such as conductive functional composite materials, magnetic functional composite materials, electromagnetic absorption or permeation functional composite materials (all above are commonly called electromagnetic function composite materials), optical functional composite materials, acoustic damping functional materials, functional materials of friction wear, medical composite materials, etc.

At present, electromagnetic functional materials develop most rapidly and are used most commonly in the functional composite materials, and here we discuss it on focus.

Conductive composite materials and magnetic composite materials were developed earlier. The basic manufacture method is that conductive material (such as carbon black, carbon fiber, metal powder, or other fibers, metal-coated glass fiber) or magnetic powder is compounded with the resin matrix respectively, the abovementioned fillers give material conductive and magnetic properties, and the resin matrix plays adhesive role to give material formability. Therefore, these composite materials can be processed into conductive products and magnetic products with the required shape and the certain mechanical properties by the general forming methods (such as compression molding, laminating, etc.) of polymeric materials.

In order to obtain a good overall performance, we must increase the amount of filler or enhanced material as much as possible, control the interface of composite materials and make composite materials have better processability.

Nowadays, the conductive and magnetic composite materials are used more widely. Conductive composite materials are mainly used for anti-static, electromagnetic shielding materials, integrated circuit materials, and magnetic composite materials as permanent magnets.

2) Multifunctional composite materials

Composite materials have the characteristics of multi-component, so they will certainly develop into the multi-functional composite materials. We could say that the development direction to multi-function is an inevitable trend to play the advantages of composite materials.

First of all, the reinforcing material is applied in functional composite materials, so it can form the composite materials of combination of function and structure, which is a major advantage of composite materials. For the functional and structural integration, the benefits of material are given fully. Therefore, the functional/structural materials are the ideal materials of practical applications. The following are currently in the development of the electromagnetic absorption or permeation the functional/structural composite materials which have very important use in electronic information and military technology.

When incident electromagnetic waves reach the material's surface, electromagnetic waves will be reflected, permeated or absorbed depending on the material's properties. The material that electromagnetic wave can permeate is called wave-transparent material; the material which reflects and absorbs electromagnetic waves is called electromagnetic shielding material; the material that can only absorb the electromagnetic waves is called absorbing material.

Wave-transparent materials are mainly used in the protection structure of radar systems (typically airborne or missile shield of radar antenna), while absorbing materials are mainly used in the "stealth" of aircrafts and warships.

(1) Wave-transparent structural composite materials.

Wave-transparent performance of materials depends on their dielectric properties, in particular the dielectric loss angle tangent (tanδ). The lower the tanδ is, the lower the loss of electromagnetic wave is, and thus leads to high wave penetration rate. Therefore, the fibers and resin matrix of excellent dielectric properties should be chosen to manufacture wave-transparent materials for structural components.

The reinforced fibers used for wave-transparent composite materials are glass, quartz and organic fibers, in which D glass fiber is the commonly used fiber. Quartz fiber with smaller tanδ, as a result of higher prices is applied generally in high-performance wave-transparent materials. Organic fibers are characterized by light, in which aramid is also commonly used. And ultra-high molecular weight polyethylene as a result of light and excellent dielectric properties is a promising type of wave-transparent materials.

Organic polymer generally has good dielectric properties. Previously, as the wave-transparent structural materials, the resin matrix materials are unsaturated polyester resins, phenolic resin and epoxy resin. In recent years, the resin with better dielectric and heat-resistant properties has been developed and applied, mainly bismaleimide resins, cyanate ester resin and a number of high-performance thermoplastic resin. These resin matrix composite materials reinforced by glass fiber have excellent dielectric properties. Among them, the quartz fiber / cyanate ester have best dielectric properties.

(2) Absorbing (stealth) composite materials.

Compared with the wave-transparent materials, electromagnetic wave-absorbing materials convert electromagnetic energy to other forms of energy (heat, electricity, etc.) by electromagnetic loss. Absorbing materials in general are compounded by the resin matrix and the loss media (absorbent). Therefore, the absorbent is the pivotal material. According to the different mechanism of absorption, absorption can be divided into two broad types of electric loss and magnetic loss. The former is such as various kind of conductive graphite, carborundum powder, carbon powder and carborundum fiber, special carbon fiber, aluminum fiber, barium titanate ceramics and conductive polymer, and its main feature is the high dielectric loss angle tangent (tanδ); the latter includes a variety of ferrite powder, carbonyl iron powder, ultra-fine metal powder, which have the high magnetic loss angle tangent (tanδ_m).

The absorbing material compounded by the absorbent powder and resin matrix, is in fact, coating, and it does not belong to the structural composite materials. This kind of absorbing coating can be considered to be the first generation absorbing composite materials, and has been applied on stealth aircraft B-2, F-117, F/A-18E/F and so on.

Ferrite is the most commonly used in absorbers, because it is the dual complex (combination of electric loss and magnetic loss) dielectric material, with high tanδ_m and low price. The absorbing properties of ferrite are closely related to the chemical composition, molding process, particle shape and size, and using frequency, and it is generally believed that the sintering temperature is higher and absorbing properties of ferrite with disc-shaped and moderate size are better.

Another developing absorber is the ultra-fine metal powder with the particle size from nanometer to 10μm. As the particle size reduces, the proportion of external atoms increases rapidly, which leads to a change in band structure, a series of quantum size effect, and the macro-quantum tunnel effect, so that the powder's sound, light, electricity, magnetic, thermal and other properties are obviously different from the macro of the original material. Studies have shown that these powders are of good performance of attenuation for electromagnetic waves, especially electromagnetic waves at the high-frequency even in the scope of light, but its absorption mechanism is unclear. At present, this kind of material has been attached great importance to all countries. It has been reported that currently it is known as the "super black" absorbing material, and its absorption rate on the radar wave is up to 99%, so this absorbing material is most likely to be considered to be nano-scale material.

It must be pointed out that all currently used absorbents exist with the shortcomings of high density, and therefore it is of great practical significance to study a new generation of lightweight high electromagnetic loss absorber.

Although absorbing coating is simple in technics and convenient to use, it bring about the increase of aircraft mass and is easy to break off. Therefore it is better to develop absorbing structural composite materials.

Absorbing structural composite materials are often made of the reinforcing fibers and resin matrix, both of them have absorption feature (also by mixing absorbent powder in the resin). Carbon fiber is a conductor, and it can not only reflect but also absorb electromagnetic waves. If the carbon fiber is modified to semiconductor (resistivity is $10^{-6} \sim 10^{3}\Omega\cdot$cm), it can be a good absorber. In the end, we can get the semi-conductive carborundum fiber. In addition, studies have shown that its absorbing properties can be improved by changing the shape of the cross-section of carbon fiber (such as triangle, square or polygonal cross-section) or its surface properties (such as a layer of carbon particle with tiny holes or silicon carbide membrane deposited on the surface of carbon fiber).

Absorbing structural composite materials are generally used in the form of hybrid composites. Its surface layer is the wave-transparent layer, which is made of glass fiber, aramid and hybrid fiber composite materials; the middle layer is the absorbing layer, which is formed by the wave absorbing composite materials; and the bottom layer is the reflecting layer, which is made of the carbon fiber composite materials or metal film. The middle layer can also be made by honeycomb core or foam plastics core containing the absorbing agents.

Absorbing structural composite materials have been applied to advanced stealth fighter F-22 and bomber B-2, and they are the advanced materials currently for the large military powers to develop.

3) Smart composite materials

Human are expecting that material can have the ability of adapting to the response to apperceive the role of the outside world. We compound sensing functional material and implementing functional material through the matrix, connect the external information processing system, and give the sensor information to the implementing functional material and then it produces the corresponding action. This constitutes the smart composite material and its system. It can perceive the changes of external environment and give the active response, and its role may be manifested in the self-diagnosis, self-adaptive and self-repair capabilities. Smart composite materials is expected to have great applications in sophisticated national defense technology, construction, transportation, water conservancy, medical health, marine fisheries, at the same time also play a lot of role in economizing energy, reducing pollution and improving security.

4) Intelligent composite materials

The intelligent composite materials are the highest form of functional composite materials. It is developed to have the decision-making ability on the basis of smart composite materials, and rely on artificial intelligence systems added to external information processing system, analyze information, give the decision, and direct the implementing material to do the optimizing action. This gives higher demands for the sensitivity, accuracy and response speed of the sensing part and the implementing part of materials. Intelligent composite materials are the pursuit of the objectives in the 21st century.

1.7.6 Developing nano-composite materials and biomimetic composite materials

1) Nano-composite materials

When the size of material is in range of the nano-size, the main components of the material concentrate on the surface. For example, when the particle is 2nm in diameter, the surface atoms will occupy 80% overall. The enormous surface can produce surface energy, and then nanometer-sized objects generate the strong aggregation, which enlarges the particle size. If these nano-cell precursors can be dispersed in a matrix to form composite materials, so that single nanometer-sized individual can be maintained instead of being aggregated (particles or objects of other shapes), it will play the nano-effects. The emergence of this effect is derived from a state of disorder of the surface atoms. This gives rise to several special performances including the quantum size effect, the macro-quantum tunnel effect and surface and interface effects. As a result of the existence of these effects, nano-composite materials have not only excellent mechanical properties, but also produce the function of optics, nonlinear optics, photochemistry and electricity.

Inorganic-inorganic nano-composites were studied earlier, but the speed of development is slow. The reason is that the inorganic nano-particles agglomerate rapidly or grain size grows easily in the molding process, thus the nano-effects lose. Ceramic-based nano-composites and metal-based nano-composites can be made by the method of nano-phase in-situ growth, their performances are improved significantly, but there are still difficulties to accurately control the content of reinforcements and the chemical composition of generated products by in-situ reaction.

At present, the nano-composite materials with organic-inorganic molecular interactions have developed rapidly, because the materials have very good application prospects in both structure and function, and also have the possibility of industrialization. Organic-inorganic molecular interactions have covalent bond type, coordination bond type and ionic bond type, each type of nano-composite material has its corresponding preparation methods. For example, the preparation of nano-composites with covalent bond type adopts the sol-gel method basically. The inorganic components of composite system are the silicon or metal oxide nanoparticles network, which is made from the silicon or metal alkoxy compounds by hydrolysis and condensation reactions, and the organic components are that the polymer monomers are introduced into the network and form nano-composites in situ polymerization. The material can achieve the level of the dispersion of molecular grade, so they get the superior performance. With regard to ligand-based nano-composite materials, the functional organic salts dissolve in soluble organic monomer with ligand and forms coordination bond. Then the material starts to polymerize, so that inorganic compound are dispersed in nano-phase in polymer to form nano-composites. This material has the strong nano-functional effect, and it is a functional composite materials of competitiveness. Recently, the rapidly developed ionic type of organic-inorganic nano-composites are obtained through intercalation to the inorganic lamella, therefore inorganic nano-phase is only one-dimensional nano-size. The negatively charged surface exists between the sheets of lameller silicate, therefore firstly the cation exchange resin is provided to intercalate by electrostatic attraction, while the resin can also have interaction with some polymer monomers or melts, and at last nano-composites are constituted. Research shows that the composite materials can be used not only as structural materials, but also as functional materials, and which have shown the prospect of industrialization.

2) Biomimetic composite materials

Natural biological materials are basically composite materials. From careful analysis on these composite materials, we find that their structure and distribution are very reasonable. For example, the bamboo is made of tubular fiber, with dense outside and sparse inside, and arranges with the anti-spiral, and becomes an excellent long-term used natural material. Another example, the shell is composed of the alternately laminating layers based on inorganic and organic composition, and it is both high strength and good toughness. These are the optimized structure type formed in the long-term biological evolution. A large number of organisms adapt to the test of natural environment by various forms of combination, the survival of the fittest, and provide a way for human to learn. To this end, through the systematic analysis and comparison, we absorb the useful law and form the concept, and combine the knowledge learned from the biological material with the theory and means of materials science to carry out the design and manufacture of new materials. Therefore a new research area, biomimetic composites, is formed gradually. Precisely because of the rich biological information out there and the fact that its mechanism can't be fully understood by the current level, the development has a strong vitality. Although there is a big gap for people to master the mysteries of biological materials of the natural world, it is the surest way for the development of composite materials, and it has a broad prospect.

1.8 The important role of composite materials in the 21st century

Before the discussion of composite materials's role in the 21st century, we should first analyze and forecast the questions that human society will face and the characteristics and needs of the community. The development trend of the world is that people will enter into a highly information-based society. Simultaneously the level of the life quality and the pursuit of health will be higher. In addition, the problems existing in the earth are very serious: environmental pollution is to the intolerable point; extreme population boom tightens the clean fresh water provided by the earth; the arable land for providing food has reached unsustainable situation; the exploited land resources will face the depletion and shortage; community will be plunged into an energy crisis and the lack of raw materials. These will no doubt give composite materials a lot of development opportunities and challenges.

1) Providing services for information technology

Composite materials can be used in all aspects of information technology, such as transducer material for obtaining information, the chip packaging materials and circuit boards in information processing, the magnetic materials for information storage, the composite fiber, sheath tube, and antenna reflector panels for information transmission, and the mechanical structural materials in information implementation.

2) Making contributions to improve the quality of human life

Composite materials are of high-strength and light weight, noise insulation, vibration and noise reduction, and used in construction, transport, improving the houses and comfort of transport tools; composites have good impact toughness, and can be made into the smart composite materials of self-made diagnostics to improve the safety of people's lives; composite materials can be used to repair or substitute human organs to enhance the level of human health.

3) Making contributions to solve the shortage of resources and the energy crisis

In the development of new energy and energy conservation, such as light battery of functional composite materials, wind turbine blade and columns manufactured by composite materials, composite materials can give fully its advantage that its production processes cost less energy. The integrated molding can be nearly no disposable and it can make the transport tools light, so as to save energy. In the development of the oceans and space, the composite material has the distinct advantages, light weight and high-strength, corrosion-resistant, resisting briny erosion and high-pressure in deep water, suitable for manufacturing a variety of spacecrafts and space stations. In taking full advantage of undeveloped resources, plant fiber or minerals whisker reinforced composite materials are developed. By using the composite materials to repair and reinforce, the lives of infrastructures are extended.

4) Composite materials in the role of environment management for example, composites cylinder with high-pressure for natural gas fuel, composite materials made of wastes, which can change harm to benefit, and developing the "green" composite materials of the natural degradation.

Exercises

1. What are the composite materials? What is the main difference compared to metallic materials?

2. How to name composites?

3. What are the advantages of composite materials? What are the main problems?

4. Talk about composite materials in brief, why the interface is also its important part?

5. What are advanced composite materials (ACM)? Talk about the application of ACM in military aircraft and civil aircraft. Why do all countries in the world develop ACM energetically?

6. Give the prospects of composite materials in civilian in brief.

7. Now there is a non-metallic material, the combination contains 100 parts of $618^{\#}$ epoxy resin, 15 parts of $300^{\#}$ and $400^{\#}$ epoxy resin and 80 shares of endomethylene tetrahydrophthalic anhydride, whether the material can be called composite material or not? Adding 40% (weight percent) of chopped glass fiber in the preparation process of these materials, can the product be called composite materials? Why?

8. Talk about the development of composite materials.

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2

Reinforced materials

2.1 Introduction

2.1.1 Additives

In the development process of polymeric materials, it was recognized that only by adding certain additives to the polymer matrix can we obtain the polymer materials with good processing behavior and good using performance, and even produce unique properties that polymer does not have. Therefore, the additives have become the second major constituent of polymer materials, whose importance is no less than the resin matrix. At present, the practical used polymer materials without additives are hard to find.

Additives are also called assistant ingredient or compounding agent. It refers to auxiliary material which is physically dispersed in polymer matrix without significantly affecting the polymer molecular structure. Therefore, the usually crosslinker and catalyst of the thermosetting system are not in this category. According to the functions of additives, they can be summarized into the following categories.

(1) Additives enhancing the stability. Its function is to prevent or delay the aging and degeneration of polymer in the process of storage, processing or using. Therefore, it is also called antidegradant or stabilizer, including antioxidants, light stabilizers, heat stabilizers and fungicides and so on.

(2) Additives increasing the mechanical properties. They improve the strength, modulus, hardness, heat resistance, toughness, etc. They include fiber reinforcing agent, particulate fillers, coupling agents, toughening agents.

(3) Additives improving processing performance. These additives reduce the melting temperature and increase the mobility of materials, but also increase the flexibility of products. They include plasticizers, lubricants, release agents, peptizer and so on.

(4) Additives improving performance and appearance of the surface. These include anti-static agent, anti-fog drop, coloring agent and fluorescent whitening agent.

(5) Additives damping the flammability. That is flame retardant.

(6) Additives changing the other properties. Such as foaming agent and additives which provide polymer materials with special properties such as conductive, heat transfer, magnetic, endothermic, absorbing properties.

2.1.2 Varieties and properties of reinforcing fibers

One component of composite materials is reinforced material or reinforcing agent. Its main function is to significantly improve the mechanical properties of the matrix materials, that is, to provide the mechanical properties to the composite materials, such as high-strength and high modulus. The nature of composite materials is to reinforce using reinforcing agents. Among the various types of agents, such as particles, flakes, fibers and others, the fibrous reinforcing agent is the best. Therefore, most of polymer composite materials used for structures are reinforced with fibrous materials, especially long-fiber reinforcing material. The tensile strength and elastic modulus of the fiber-reinforced materials are several orders of magnitude higher than that of the homogeneous bulk materials. For example, the bulk graphite materials are brittle, and its tensile strength is 689 MPa. The tensile strength of commercial graphite fibers ranges from 1700MPa to 2800MPa. Tensile strength of E-glass fiber is about 3450MPa; tensile strength of nylon fiber is 827MPa; and tensile strength of boron fiber is 3254MPa. They are all higher than the tensile strength of the corresponding bulk materials. When effectively using these high-strength fibers in matrix, we will obtain the composites with strength higher than bulk materials.

With the development and rapid application of composite materials, it is very important to develop the reinforced fiber. Reinforced fibers in varieties are presently widely used which are glass fiber (GF), carbon fiber (CF), alumina fiber, silicon carbide fiber and other inorganic fibers, also aryl amide fiber (aramid such as Kevlar), polybenzoxazole (PBO) fiber, ultra-high molecular weight polyethylene (UHMWPE) fiber and other organic fibers. After the 1990s, in order to meet the demand of composites with high-performance (high strength, high modulus), multi-function, and small size, light weight, intelligence and low-cost, many new technology and new equipment have come about. Development of high-performance fibers is hence promoted. At present, the main type of commercialized fibers, the trade names and manufacturer are shown in follows.

1) Inorganic Fibers

(1) Glass fiber. Including E-glass, Zentron (Owens Corning).

(2) Carbon fiber.

Polyacrylonitrile (PAN)-based carbon fiber: including Torayca (Toray), Pyrofil (Mitsubishi rayon), Besfight (Toho rayon), Thornel (Amoco), Magnamite (Hercules).

Pitch-based carbon fiber: including Granoc (Graphite fiber of Japan), Dialead

Table 2.1 Main typical fiber species and the properties

Properties index	Polymer system					Inorganic system				
	Para-aromatic amide		PE Tekmilon	PBO Zylon	Polyaryl ester Vectran	PAN-based carbon fiber			SiC fiber Hi-Nicalon	Glass fiber E-GF
	Kevlar-49	Kevlar-129				T300	M60J	T800H		
Density (g/cm^3)	1.45	1.44	0.96	1.56	1.41	1.76	1.91	1.81	2.74	2.54
Strength (GPa)	2.80	3.40	3.43	5.80	3.27	3.53	3.82	5.49	2.80	3.43
Modulus (GPa)	109.0	96.6	98.0	280	74.5	230.0	588.0	294.0	270.0	72.5
Elongation (%)	2.5	3.3	4.0	2.5	3.9	1.5	0.7	1.9	1.4	4.8
Specific strength (10^6cm)	19.3	24	36.5	37.2	24.0	20.0	20.0	30.3	10.0	12
Specific modulus (10^8cm)	7.7	6.8	10.4	18.0	5.4	13.0	31.0	16.2	9.6	2.9

(Mitsubishi chemistry), Thornel P100 (Amoco).

(3) Boron fiber.

(4) Silicon carbide fiber. Including SCS-6 (Texton), Nicalon (Carbon Japan), Tyranno (Ube industry Japan).

(5) Alumina fiber. Including Altes (Sumitomo Chemical Co), Safeel (ICI), Fiber-TP (Dupont).

2) Organic fibers

(1) Rigid molecular chain: liquid crystal (dry-jet wet spinning process). ① Para-aromatic amide: including Kevlar (Dupont), Twaron (Akzo Nobel), Technora (Teijin), Terlon, SVM, Armos (Russia) and so on; ② polybenzoxazole: including Zylon (Toyobo-Dow Chemical); ③ polyarylester: including Ekonol (Sumitomo Chemical Co), Vectran (Kuraray-Celanese).

(2) Flexible molecular chain. ① Polyethylene: including Spectra (Allied Signal), Tekmilon (Mitsui Petro-Chemical Company), Dyneema (DSM-Toyobo); ② Polyvinyl alcohol: including Kuralon K-II(Kuraray).

Table 2.1 shows typical types and properties of reinforcing fibers.

The reinforced materials commonly used in polymer-based composites currently such as glass fiber, carbon fiber and Kevlar, etc. The reinforcement function of fibers will be discussed in the chapter of mechanical properties of composite materials. This chapter focuses the composition, preparation, structure and performance of the fiber itself to lay the foundation for design, manufacture and application of composite materials.

2.2 Glass fiber

Glass fiber is an excellent inorganic non-metallic material, with good performance such as uninflammability, heat-resistance, electric insulation, high tensile strength, and excellent chemical stability, and it is an indispensable foundation of high-tech material in modern industry. Glass fiber reinforced plastics have become the main part of composite materials industry. Glass fiber has been more and more widely used in transportation, construction, environmental protection, petrochemical, electronic and electrical appliances, machinery, aerospace, nuclear power, weapons and other traditional industries such as the national defense department and high-tech sector.

In the early 17th century, French invented the preparation of glass fiber. However, it was not until the 1920s, when American invented the fabrication of continuous long glass fiber by using crucible, the glass fiber was used for composite materials. Glass fiber has 80 years of development history abroad. Particularly, since the 1960s to the 1970s, with the emergence of new technologies and new techniques, glass fibers were used more widely, boosting the rapid development of glass-fiber industry. One of the milestones is the wide spread of the new technology of direct-melt drawing. More and more holes drawing process have been largely developed and the diameter of glass fiber used as reinforcement in plastics is enlarged gradually to the range of 14 $\sim$ 24μm, even up to 27μm. Mass production of alkali-free fiber and non-woven glass fiber fabric has been carried out. The proportion of chopped untwisted roving glass fiber mat is increasing. Research on fiber-resin interface has been stressed and the variety of coupling agents is increasing. Pre-treatment of glass fibers has been commonly used. Now there are more than 30 countries in the world produce glass fiber and there are up to 5000 different types of glass fibers. The total production grows in an average annual rate of $3\% \sim 5\%$. The output of the world was 2.3 million tons in 1996. China's glass fiber industry was born in 1950, at that time we only produced primary fibers for insulation. After 1958, especially after the reform and opening to the outside world, with the development of GFRP industry, glass fiber industry has developed rapidly to a considerable scale. Output of China's glass fiber was 172,000 tons in 1996, being the fifth in the world.

Molten glass liquid is drawn into filaments at a rapid speed in order to get glass fiber. Because it is very fine, it also has some new features besides the ordinary features of the bulk glass. For example, losing the brittleness of glass and becoming soft, flexible, elastic, and can be strand-collected, twisted, weaved to a variety of glass fabric, etc.

2.2.1 Glass fiber composition and classification

1) The composition of glass fiber

Glass is a silicate-type mixture consisting of SiO_2 and various metal oxides, which belongs to the ion structure of amorphous materials.

(1) SiO_2. SiO_2 is the main component of glass, it is the basic skeleton in the formation of the glass, and it has a high melting point.

(2) Metal Oxide. Such as Al_2O_3, CaO, MgO, Na_2O (K_2O), BeO, B_2O_3, etc. The function is shown in the following: ① improve process conditions of glass fiber fabrication (at the cost of reduction of glass fiber properties), such as lower melting point, reduce the tendency to crystallization of the components, so that there is a suitable liquid glass viscosity to facilitate drawing. For example, usually glass fibers contain alkali metal oxides Na_2O (K_2O). These oxides lower the melting temperature and viscosity of the glass, so that bubbles in the liquid glass could be removed easily. Production then becomes easier, so it is known as flux oxide. However, it has harmful effects on performance such as water-resistance, electrical properties, etc. ② Make glass fiber have certain characteristics, such as BeO, which improves the modulus, but also yields high toxicity. Adding B_2O_3 can improve the acid resistance of glass fiber and improve the electric performance, reduce the melting point and viscosity, but decline the modulus and strength.

Different components lead to different properties of glass fiber and different price. Table 2.2 shows chemical composition of commonly used glass fibers for composite materials.

Table 2.2 Chemical composition of common used glass fibers

Types of Glass fiber	Chemical composition of glass fiber (mass fraction) (%)										
	SiO_2	K_2O	Na_2O	Al_2O_3	MgO	CaO	ZnO	B_2O_3	ZrO	BaO	CaF_2
Non-alkali 1#	54.1		<0.5	15.0	4.5	16.5		9.0			
Non-alkali 2#	54.4		<2.0	13.8	4.0	16.2		9.0			
Electrical non-alkali E	53.5	0.3		16.3	4.4	17.3		8.0			
Ordinary alkali A	72.0	14.2		0.6	2.5	10.0		SO_3 0.7			
Ordinary medium-alkali	64.5		12.5	4.0	3.5	8.5	4.0			3.0	1.5
Medium-alkali 5#	67.5	<0.5	11.5	6.6	4.2	9.5					
Alkali-resistant G_{20}	71.0	2.49		1.0					16.0		
Acid resistant C	65.0	8.0		4.0	3.0	14.0		6.0			
High strength S	64.3	0.3		25.0	10.3						
High modulus M	53.7	BeO 8.0	TiO_2 7.9	Li_2O 3.0	9.0	12.7	CeO 3.0	Fe_2O_3 0.5	2.0		

2) The classification of glass fibers

(1) Classification according to chemical composition.

Usually this is done by content of alkali metal oxides. ① Alkali glass fiber, content of alkali metal oxide is higher than 12%; ② medium-alkali glass fibers, alkali metal oxide is in a range of 6% ∼ 12%; ③ low-alkali glass fiber, alkali metal oxide is in a range of 2% to 6%; ④ micro-alkali glass fiber, content of alkali metal oxide is less than 2%. Micro-alkali glass fiber is also called non-alkali glass fiber.

Usually, if alkali metal oxide is of a high content, the glass is easily fusible and easily melting and filature which ruduces the cost of production; and this kind of glass fibers are seawater corrosion resistant. They could meet the requirements of common applications. Many low-alkali or alkali glass fibers are used in civil constructions. And we select non-alkali glass fiber for electrical or the military-industrial products.

(2) Classification according to using performance of fibers.

According to application characteristics, glass fibers include: ① ordinary alkali glass fibers (A-GF); ② glass fibers for electrical purpose, called E glass fibers, whose content of alkali metal oxide is less than 1%, applied extensively; ③ glass fibers with high strength, called S or R glass fibers, whose content of alkali metal oxide is less than 0.3%, 33% higher than E-GF in strength, 20% higher than E-GF in modulus, they have good retention at high temperature and are only used in situations of high strength; ④ high modulus glass fibers (M-GF), content of alkali metal oxide is close to 0, 60% higher than E-GF in modulus, the same as E-GF in strength; ⑤ glass fibers with chemical resistance, called C glass fibers, particularly have good acid resistance, which are suitable for corrosion-resistant parts and storage battery jar and other parts; ⑥ alkali-resistant glass fibers, called AR glass fiber; ⑦ low dielectric glass fibers, are called D glass fibers, they have good electric insulation and good wave penetration properties and suitable for reinforcing materials for radome; ⑧ high silica oxide (glass) fibers, they are used for ablation-resistant materials; ⑨ quartz (glass) fibers.

(3) Classification by product characteristics.

We usually classify the fibers basing on quite a few metrics: ① according to the length of fiber, there are fixed-length fibers and continuous fibers. The length of fixed-length fiber is about 6 ∼ 50mm. The majority is obtained from short-cut fibers from continuous fiber and a little amount obtained from blow process, which can be made into glass wool or glass fiber mat. They can be used as thermal insulation materials, and also used as reinforcing material of molding plastics. Continuous long fibers are drawn from marble or tank furnace. They can be twisted, strand-collected and weaved. This type of fiber used for reinforcement of composite materials. ② By the fiber diameter size, there are crude fiber (single filament is 30μm in diameter), the primary fibers (single fiber is 20μm in diameter), intermediate fibers (single fiber diameter is in a range of 10 ∼ 20μm), advanced fiber also known as textile fibers (single fiber diameter is in a range of 3 ∼ 9μm). Filament diameter is less than 4μm, which is called the ultra-fine glass fiber. In general, filament with diameter in a range of 5 ∼ 10μm is used as a textile fiber products; fiber filament with diameter in 10 ∼ 14μm is used for the roving, non-woven fabric, chopped fibers mat. In general, the slighter the fiber is, the fewer defect and the higher strength. ③ By the appearance of fibers, there are continuous fiber (untwisted roving, twisted yarn), chopped fiber, hollow glass fiber, ground granulated fiber and glass powder.

2.2.2 Glass fiber and preparation of glass fiber products

1) Preparation of glass fiber

At present, the most common methods of producing glass fiber are marble process (crucible drawing) and direct-melting process (tank furnace).

(1) Crucible drawing method.

Crucible drawing method production process is composed of two parts that make the ball and drawing. In accordance with requirements of the fiber quality, we dry-mix sand, limestone, boric acid in a certain proportion, loading in the melting furnace at around 1260°C, molten glass flows through a mechanism built into the glass ball with diameter of 15 ∼ 18mm (weight for 10g) for drawing.

The prepared glass ball is washed by hot water, and is decontaminated and selected into the platinum crucible (or clay pot) for heating melting. Temperature of glass liquid is about 1300°C, which outflow from leakage plate or spinneret at the bottom of the crucible by its weight. The numbers of holes on the leakage plate are 102, 204 or 408 (currently holes 3000∼4000 abroad), aperture is 1.5∼ 2mm. The temperature of effluent glass melt is about 1190 °C. In the rapid cooling process, with high-speed (1000 ∼ 3000m/min) rotation, glass fiber is pulled into a very small diameter (3 ∼ 20μm). Each fiber pulled out from the crucible is named monofilament. All the monofilaments from the crucible are collected into a strand after through the sizing agent tank. The strand is winded on the spool and then it is ready if it passes a quality inspection. Schematic diagram of the crucible drawing method is shown in Fig. 2.1.

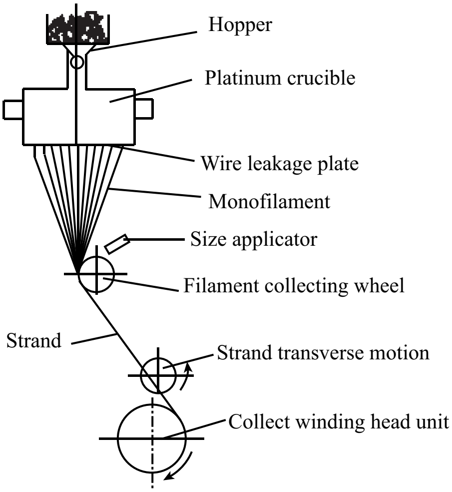

Fig. 2.1 Schematic of the crucible drawing method.

(2) Direct-melting process.

Put the glass batch into the tank furnace for melting, and then pull it directly to a variety of counts continuous glass fibers. This is a new process to produce continuous glass fibers. Compared to crucible drawing method, it has the following advantages. ① It omits the process of marble making, simplifies the process, and improves the efficiency; ② tank furnace has large capacity, high production capacity; ③ tank furnace temperature, hydraulic, pressure, flow and temperature of leakage plate can be automatically controlled in the centralized manner, so that the products have stability quality; ④ suitable for producing bulky glass fibers by using leakage plate with more orifices; ⑤ easy to recycle waste products.

2) The manufacture of glass fiber products

Glass fiber can be made into various products by unwinding from strand, such as rovings, chopped strand mat, various types of cloth and so on, for the preparation of composite materials. The major equipments to produce glass fiber products are spinning machine and loom machine, the process is shown in Fig. 2.2.

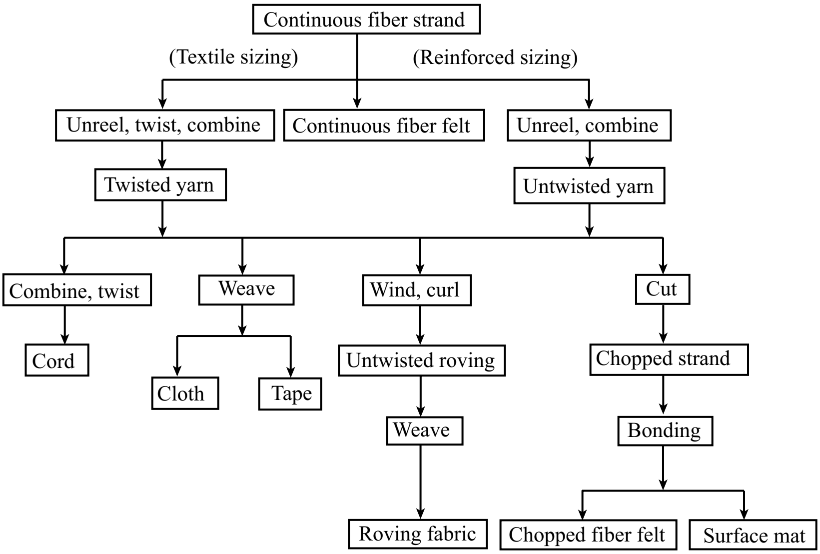

Fig. 2.2 Flow chart of glass fiber product technological process.

3) Sizing agent of glass fiber

In the process of drawing glass fiber, the single fiber surface is coated by an emulsion component composed of film formers, lubricants, antistats, and the surfactants, which is called sizing. The role of sizing is to collect monofilaments, for ease of the subsequent processing, etc; to prevent the fibers bonding with each other when the yarn wound into a roll, and to protect the fiber surface from wearing out to reduce strength of fiber when woven.

Types of size are classified in following.

(1) Textile size.

Textile size has good properties such as the cluster, lubrication, filming and antistatic. It is mainly used in textile processing of glass fiber products. Paraffin-based size is often used as textile size in China, but starch-oil size is widely used in international community. For textile size, in particular paraffin emulsion, it will impede bonding of glass fibers and adhesive, so in the preparation of glass fiber composites, we should take off the sizing agent firstly, that is dewaxing treatment.

The main components of paraffin-based size are paraffin wax, petrolatum, mineral oil, stearic acid, fixing agent, surfactant and so on.

The major components of starch-based size are starch, animal and vegetable oils, cationic amines, water-soluble resin and so on.

(2) Reinforcing size.

Reinforcing size is developed for the product of reinforcing fiber, mainly in order to improve the fiber impregnation of resin, and enhance the bonding force of resin with fiber. Film-former is the main agent component of the reinforcing size. Generally there are five series of emulsion or solution, polyester, epoxy, polyvinyl acetate, polyurethane and polyacrylate. Nevertheless, this category also includes components of coupling agent, lubricant, wetting agent, anti-static agent and so on.

(3) Chemical treatment agent.

In the preparation process of glass fiber, we directly use the chemical treatment agent of glass fiber, that is the coupling agent as a sizing agent, and this is the pretreatment method of glass fiber, commonly used in products of untwisted glass fiber yarn with high-performance and so on.

2.2.3 The structure of glass fiber

Glass fiber has the same composition and structure as the bulk glass, which is a kind of amorphous supercooled liquid, and its primary structure is inorganic ion substance based on SiO_2 as basic skeleton, secondary structure is amorphous structure of isotropy.

The structure of glass fiber has been a controversial problem. However, analyzing the temperature parameters of drawing glass fibers, we found that for the E-glass fiber, the crucible temperature is above $1300 \sim 1400°C$, and drawing temperature is about 1190°C, while the upper limit temperature T_c for crystallization of the glass is $1135 \sim 1140°C$, the glass transition temperature T_g is around 600°C. The drawing temperature is $50 \sim 55°C$ higher than the crystallization upper limit temperature. We can use the ideal glass volume (or specific volume) of the drawing process V-temperature T curve (Fig. 2.3) to describe the preparation of glass fiber, the glass liquid at point A draw out from the drain hole to form fiber. If the cooling rate is very slow, V-T curve is $AabE$, produce crystalline glass, T not change at T_c when crystal. If faster cooling at the rate of 1°C/min, on the V-T curve, glass volume will change with curve $ABCD$. In fact, when glass liquid is

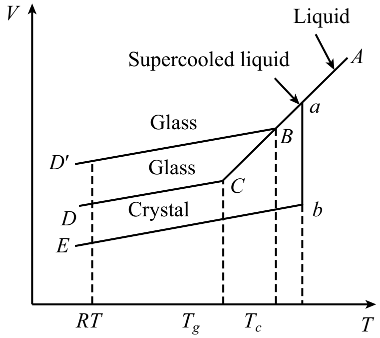

Fig. 2.3 V-T curve of glass fiber in drawing process.

pulled into fibers from the drain hole, because of the extremely fast drawing, fibers are in a small diameter (6 $\sim$ 8μm), so when cooling from drawing temperature 1190°C to the glass transition temperature 600°C, it almost only needs 10 $^{-5}$s. In the V-T curve, glass volume will change as curve ABD'. The results of the experiment show that density of bulk e-glass is 2.58 g/cm^3, and the density of glass fiber is 2.52g/cm^3. It is similar to the density of liquid glass at drawing temperature. This is because cooling rate $\uparrow\rightarrow$ the glass transition temperature T_g $\uparrow\rightarrow$ free volume V $\uparrow\rightarrow$ density ρ_f $\downarrow$. Therefore, glass fiber drawn out is in an unstable state where it will shrink again when heating. Its structure should be similar to the common glass structure, which is an amorphous ion structure.

2.2.4 Properties of glass fiber

1) Mechanical properties

(1) The stress-strain relationship of glass fiber is a straight line until the break, no significant yield and plastic stage showing the characteristics of brittle materials.

(2) The tensile strength of glass fiber is higher, but a lower modulus. Glass fiber has high tensile strength. Glass fiber with less than 10μm in diameter has a tensile strength over 1000MPa; less than 5μm in diameter is over 2400MPa. These data not only exceed the strength of natural and synthetic fibers, but also overrun the strength of ordinary steel. The strength is many times of the tensile strength of bulk glass whose tensile strength is about 40 $\sim$ 100MPa, because defects of glass are reduced after drawing into thin fibers.

According to the Griffith theory of micro-cracks, during the manufacturing process of brittle materials, many micro-cracks may be introduced. The crack tip stress concentrates after loading. When the stress reaches a certain value, crack propagation leads to material break. Therefore, the greater the defect size is, the more serious the stress concentration is, resulting in lower strength. Bulk glass has larger size than the glass fiber itself, and the probability of the existence of defects internal and on the surface is higher. The material break is caused by the most dangerous or the biggest size cracks, so the strength of the bulk glass is much lower than glass fiber. And thus the strength of glass fiber has the following characteristics: ① the smaller diameter (d_f) of monofilament, the higher tensile strength (σ_{fu}). $d_f = 50$μm, $\sigma_{fu} = 855$MPa; $d_f = 8$μm, $\sigma_{fu} = 2.21$GPa; $d_f = 3.4$μm, $\sigma_{fu} = 3.32$GPa; ② the larger of the test gauge length l of the specimen is, the lower the tensile strength σ_{fu} is. For the fiber with d_f at 5μm, $l = 4.5$mm, $\sigma_{fu} = 2.86$GPa; $l = 18.6$mm, $\sigma_{fu} = 2.33$GPa; $l = 87$mm, $\sigma_{fu} = 1.71$GPa.

The two results are called size effect or volume effect of glass fiber strength, that is, the greater the volume or the size, the lower the tested strength. Therefore, when testing the strength of glass fiber monofilament or the yarn cloth, the regulated size of the sample should be given.

The strength of glass fiber is of large dispersion. When the fibers component is given, the glass fiber surface and internal defects depend on the control in the production process, such as the crystal impurities and air bubbles existed in the glass liquid, glass fluid and drawing temperature fluctuations, the diameter of leakage orifice, reel speed and so on. Because so many factors influence the strength of glass fiber, the dispersion of strength is large. Generally, it is believed that the strength of glass fiber obeys the Weibull distribution of the strength of brittle materials. The strength or breaking force data of glass fiber products are generally the statistical average of a large number of tests.

The strength of glass fiber is affected by humidity. Strength declines after absorbing water.

Glass fiber has the lower tensile modulus, which is about 70GPa, which is similar to the modulus of aluminum, only one-third of ordinary steel. This is one of the main disadvantages of glass fiber. Elongation at break of the glass fiber is about 2.6%. Its density is 2.50 $\sim$ 2.56g/cm^3; the Mohs hardness is 6.5.

Table 2.3 shows the main properties of high-strength glass fibers which are produced by some countries. The main component of high-strength glass fibers is aluminum-magnesium-silicon glass which is ternary composition of Al_2O_3, MgO and SiO_2, the upper limit temperature for crystallization is between 1442°C and 1453°C, fiber forming temperature is up to 1500 °C.

Table 2.3 Properties of high-strength glass fibers produced by some countries

Types	America S-2	Japan T	France R	Russia BMП	China high strength 2#	China high strength 4#
Tensile strength of virgin filament (MPa)	4580	4655	4400	4500~5000	4020	4600
Tensile elastic modulus (GPa)	85.6	84.3	83.8	95	83.4	86
Density (g/cm^3)	2.49	2.49	2.55	2.56	2.54	2.53

2) Thermal properties

Glass fibers are inorganic amorphous substance, and the relationship between mechanical properties and temperature is similar to amorphous organic polymers, for the transformation may happen at both T_g and $T_{f.}$. Because of the high T_g, about 600°C, and non-combustion, they have better heat resistance compared with polymer matrix. We can see that the heat resistance of glass fiber reinforced plastics mainly depends on the resin matrix.

Even if below T_g, the tensile strength of glass fiber is influenced largely by temperature, such as E-glass fibers, which is 3450MPa at 22°C, is 2620MPa at 371°C, and reduces to 1720MPa at 538°C. When the glass fiber is treated at high temperature, its strength will decrease significantly, and the longer time the glass fiber is treated, the more the strength will be decreased. Usually under

200 ∼ 250°C, there is no obvious changes when it is treated; At 300°C for 24 hours, the strength drops by about 20%; at 400°C for 24 hours, the strength will reduce to half. However, because of the higher melting temperature of glass fiber (about 1200 °C), it has excellent short-term high temperature thermal properties.

Glass fibers have low thermal conductivity. It is about 0.86 kcal①/(m·h·°C) in the range of 20 ∼ 200 °C, while thermal conductivity of aluminum alloy is 108∼144 kcal/(m·h·°C), which shows good thermal insulation properties.

Glass fiber has low thermal expansion coefficient, which is 4.8×10^{-6}/°C in the range of 20 ∼ 200 °C; but 4.9×10^{-6}/°C at 300°C; 4.52×10^{-6}/°C at 400°C, its specific heat is 0.19 cal/(g·°C).

3) Chemical corrosion resistance

After immersion in water, strength of glass fiber will be reduced. After drying, the strength recovers partly, but the loss part of strength can not be restored. The former strength loss is caused by the physical role of water on glass fiber, so it has reversibility; the latter is chemical reaction between water and glass fiber, which caused irreversible loss of strength. Chemical reaction process is shown in follows:

$$\text{— Si — O — Na} + \text{H}_2\text{O} \longrightarrow \text{— Si — OH} + \text{Na}^+ + \text{OH}^-$$

$$\text{— Si — O — Si —} + \text{OH}^- \longrightarrow \text{— Si — O}^-\text{—} + \text{— Si — OH}$$

$$\text{— Si — O}^-\text{—} + \text{H}_2\text{O} \longrightarrow \text{— Si — OH} + \text{OH}^-$$

From the above equation, we see that the greater the amount of alkali, the faster the rate of water erosion on glass fiber. In addition, there are micro-cracks in fiber, so synergistic effect of stress and water at crack tip, causes crack to propagate, leading to a permanent strength loss of glass fiber.

In general, glass is an excellent anticorrosion material. Except for hydrofluoric acid, it has corrosion resistance to almost all acids, alkalis, salts and organic solvents. Nonetheless, because of the increased surface area, the corrosion resistance of the glass fiber is worse than the bulk glass.

4) Electrical properties

(1) Good electrical insulation. Volume resistivity of the glass fiber ρ_v is$10^{11} \sim 10^{18}\Omega$·cm, so a large part of FRP are used for insulating materials.

The electrical properties of glass fiber are related to its components, particularly, the amount of alkali. This is because the alkali metal ions in the structure of glass do not have solid combination. They are in large migration and they are good current carrier. The conductivity of glass depends on mainly the conductivity of alkali metal ion, so the higher the alkali content, the lower of its resistivity, such as: alkali-free $1^{\#}$ ($Na_2O < 0.5\%$) ρ_v is $1.23\times10^{12}\Omega\cdot$ cm, and alkali-free $2^{\#}$ ($Na_2O=2\%$) ρ_v is $1.06\times10^{11}\Omega\cdot$ cm; the higher humidity, the lower resistivity;

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① Cal is illegal unit, 1cal=4.1868J,the same in the following.

the higher temperature, the more active the alkali metal ions are, and the lower resistivity.

(2) Good high frequency dielectric properties. Glass fibers have smaller dielectric constant, low dielectric loss, so good high-frequency dielectric properties. FRP can be used as microwave antenna radome.

Table 2.4 shows the relationship between the high-frequency dielectric properties and the components of glass fiber. See Table 2.4, different varieties of glass fiber, its dielectric properties are different, which are also related to the frequency of the electric field. In addition, the dielectric properties of glass fiber are greatly influenced by the environmental temperature and humidity.

Table 2.4 High frequency dielectric properties of glass fibers

Types of fiber or resin	Dielectric constant ε		Dissipation factor tanδ	
	1MHz	9.375GHz	1MHz	9.375GHz
E-glass fiber	5.80	6.13	0.001	0.0039
S-glass fiber	4.35	5.21	0.002	0.0068
D-glass fiber	3.56	4.00	0.0005	0.0026
High silica fiber	—	3.78	—	0.0002
Polyester 307	3.4∼3.6	—	0.015∼0.016	—

2.2.5 Varieties and specifications of glass fiber products

As marketable glass fiber products, there are glass fiber yarns, glass cloth, glass fiber mat, special fabrics and so on.

2.2.5.1 Glass fiber yarns

Glass yarn is used for preparation of nonweft fabic or tape, and for reinforced fibers in filament winding, pultrusion and spray-up molding, or is chopped into short fibers.

1) Commonly used terms and parameters

(1) Strand (original yarn). The strand refers to a single cluster after the monofilament collecting together in glass fiber manufacturing process; and the glass yarn for purchase or for woven is generally a bundle or group of twisted or untwisted filaments from unwinding original yarns.

(2) The index representing the size of yarn (strand or roving). The indices representing the size of yarn are β, *tex* and *den* (denier).

① The count β refers to the length (m) of 1g yarns. If the count β of one kind of strand is 160, this means that 1g weight of the strand corresponds to the 160 meters long. The greater the β, the slighter the strand, it means that the slighter monofilament or the less number of monofilament of the strand.

② Tex refers to the weight (g) of 1000m long yarns, which reflects the linear density of yarn. The larger the tex is, the thicker the yarn is.

③ Den (denier) refers to the weight (g) of 9000m long yarns. The larger the den, the bigger size the yarn is.

Their conversion relationship is given by

$$\beta = \frac{1000}{tex} = \frac{9000}{den} \tag{2.1}$$

(3) Twists. The twists mean the degree of twisting, that is the number of turn per meter strand, turns/m. Use S to stand for the direction of twist in right; Z stand for the left. Twisting can make yarns hold together strongly and weave easily.

(4) Plied number N. It refers to the number of strands that constitute plied yarn. Plied number based on single strand for one, and if several strands combine into plied yarns the number of strands (N) is the plied number N. Nominal count of glass yarn is the strand count divided by N $(\beta = \beta_0/N)$.

2) Varieties and specifications of yarns

(1) Varieties. There are two types of glass yarn which are untwisted yarn and twisted yarn. With the difference of the plied number N, there are roving and yarn. Generally, roving is a parallel bundle composed of a great number of untwisted strands or tows, and yarn is a number of strands or tows collected into a parallel bundle with twist. Filaments of the untwisted roving are in parallel, looser and have good infiltration for the resin, but they are easy to break, pilling and difficult to be woven. Characteristics of twisted yarn are on the contrary, which is mostly used for weaving.

(2) Specifications. Specifications of yarns are the technical index, mainly include monofiber diameter d_f, the strand count β_0, the yarn nominal count β, tensile breaking force P_b, twists and so on. ① Monofilament diameter d_f at 4μm, 6μm and 8μm; ② the strand count β_0 is 40, 80 or 160; ③ plied number N stands for twisted yarn at 2∼8, of untwisted yarn at 5∼60; ④ the count of plied yarn β_0/N; ⑤ twists; ⑥ breaking force of the yarn P_b (kg or g); ⑦ fiber types of alkali, alkali-free and high-strength; ⑧ types of sizing agent.

Table 2.5 and Table 2.6 list the performance specifications of several types of Chinese-made twisted glass yarns and untwisted glass rovings.

Table 2.5 Specifications of several Chinese-made twisted glass yarn

Trademark	Filament diameter (μm)	Plied number	Nominal count	Tensile breaking force (g)	Twists- (turns/m)
Alkali-free yarn 4-600/2	4	2	300±30	150	120±15
Alkali-free yarn 4-360/2	4	2	180±20	250	150±15
Alkali-free yarn 5-250/2	5	2	125±10	400	120±15
Alkali-free yarn 6-160/2	6	2	80±8	500	120±15
Alkali-free yarn 6-80/2	6	2	40±4	1000	110±15
Alkali-free yarn 6-80/4	6	4	20±2	2000	110±15
Alkali-free yarn 6-80/8	6	8	10±1	3500	110±15
Alkali-free yarn 8-40/2	8	2	20±2	1600	110±15

Table 2.6 Specifications and breaking strengths of several Chinese-made twisted glass rovings

Trademark	Filament diameter (μm)	Plied number	Nominal count	Tensile breaking force (kg)
Alkali-free untwisted 8-40/5	8	5	8.0±0.8	3
Alkali-free untwisted 8-40/10	8	10	4.0±0.4	6
Alkali-free untwisted 8-80/14	6	14	5.7±0.6	8
Alkali-free untwisted 8-40/20	6	20	2.0±0.2	12
Alkali-free untwisted 8-40/40	8	40	1.0±0.1	22
Alkali-free untwisted 8-40/60	8	60	0.67±0.07	30

(3) Representation of grade. Grade for non-alkali yarn 4-600/2 indicates that non-alkali glass yarn with monofiber diameter d_f is 4μm, the count of strand β_0 is 600, the plied number N is 2. Size of the glass yarn can also be indicated by "metric numbers", the metric number, namely strand *tex* multiplied by N. For example, grades for EC5.5-6 × 1 × 2S yarn, E indicates non-alkali glass fiber; C indicates continuous fiber; 5.5 indicates monofilament diameter; 6 indicates tex number of strand (6 tex is equal to 160 count); 1 indicates rewinding plied number; 2 indicates plied number of yarn; S indicates twisting on the right direction. EC10 2400 indicates E (non-alkali), C (continuous fiber yarn), d_f=10μm, 2400 tex; EC10 40 × 60 indicates $d_f = 10$μm, 40 tex, 60 plies continuous fiber rovings.

3) Converting from tensile breaking force to fracture strength

In Table2.4 and Table 2.5, we use tensile breaking force P_b to represent the strength of the yarn. The break load of the glass yarn per unit area can be obtained by conversion, i.e., convert to the fracture strength σ_b (kg/cm^2). Thus it is easy to compare the strength of yarns in different sizes.

According to definition of count, we get cross-sectional area of yarn A(cm^2):

$$A = \frac{1}{100 \times \beta \times \rho_f} \tag{2.2}$$

So, we convert it to the fracture strength:

$$\sigma_b = \frac{P_b}{A} = \frac{1000 \times \rho_f \times \beta_0 \times P_b}{N} \tag{2.3}$$

Here ρ_f is density of glass fiber, usually for 2.54 g/cm^3.

4) The reasons that yarn's strength is lower than the monofilament strength

By calculating, we find the converted fracture strength of yarn much lower than the strength of monofilament, the reasons are shown in following. ① Different testing gauge length of them, monofilament is about 10mm, while the yarn is 200mm; ② the different straightness of all monofilaments, it is impossible for them to load and break at the same time, but break in batches, the final fracture monofibers are only those with highest strength; ③ twisting makes fiber to bear additional torsion force, but the experiment has shown that glass fiber, only if the turns are greater than 300, will be affected obviously.

2.2.5.2 Glass fabrics

1) Varieties and specifications of cloth

(1) Varieties of glass cloth. Majority of glass fiber reinforced plastics products are made of glass cloth. Cloth is woven by the warp yarn and weft yarn. According to different weaving methods, there are plain weave, twill weave and satin cloth (Fig. 2.4).

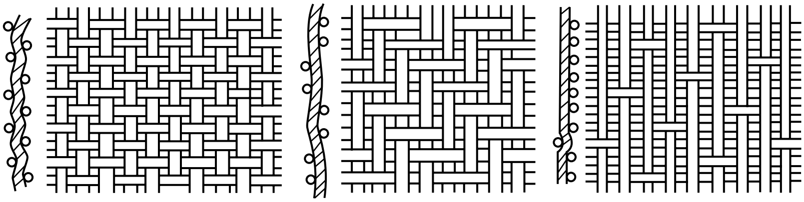

(a) (b) (c)

Fig 2.4 Schematic diagram of fabric weave:

(a) plain weave; (b) twill weave; (c) satin fabric.

Plain weave. Each warp fibre passes alternately under and over each weft fibre. The fabric is symmetrical, with good stability and reasonable porosity. However, it is the most difficult of the weaves to drape, and the high level of fibre crimp imparts relatively lower mechanical properties compared with the other weave styles.

Twill weave. One or more warp fibres alternately weave over and under two or more weft fibres in a regular repeated manner. This produces the visual effect of a straight or broken diagonal rib to the fabric. Superior wet out and drape is seen in the twill weave over the plain weave with only a small reduction in stability. With reduced crimp, the fabric also has a smoother surface and slightly higher mechanical properties.

Satin fabric. Satin weaves are fundamentally twill weaves modified to produce fewer intersections of warp and weft. The harness number used in the designation (typically 3, 5, and 7) is the total number of fibres crossed and passed under, before the fibre repeats the pattern.Satin weaves are very flat, have good wet out and a high degree of drape. The low crimp gives good mechanical properties.

Specifications and properties of common used E-glass cloth are shown in Table 2.7.

Unidirectional cloth refers to one that load at break has great difference between the longitudinal and latitudinal direction of the glass cloth, of which the warp yarn is dense or strong yarn, weft yarn is thin or weak yarn. Unidirectional cloth has the transverse fiber, which is different from non-woven (non-weft fabric), the latter is prepreg soaked with resin, no weft, and the parallel longitudinal fibers are sticked together by the resin.

Table 2.7 Specifications and properties of non-alkali glass cloth

Grade	Thickness (mm)	Width (mm)	Filament diameter (µm)	Count of strand/plied number β_0/N		Warp density b_L and filling density b_T(end/cm)		Tensile breaking force of 25×100mm^2 specimen (kg)		Twists (turns/m)	Weight of per square meter (g/m^2)
				Warp	Weft	Warp	Weft	Warp	Weft		
Tabby -80	0.08±0.01	450±10 900±15 1000±20	6	160/4	160/4	18±1	20±2	50	26	120±15	72±8
Tabby -100	0.10±0.01	900±15 1000±20	6	80/2	80/2	20±2	20±2	55	55	110±10	105±15
Tabby -150	0.15±0.02	900±15	6	80/4	80/4	16±1	12±1	99.2	74.7	110±10	200±20
Tabby -200	0.20±0.02	900±15	6	80/5	80/5	18±1	14±2	110	90	110±10	200±20
Tabby -210	0.21±0.02	900±15	6	80/6	80/6	16±1	12±1	120	100	110±10	
Tabby -300	0.30±0.03	900±15 1000±20	6	80/8	80/8	16±1	10±1	175	105	110±10	290±20
Tabby	0.09		6	160/4	160/4	18	16	50	45		
Twill	0.21		6	80/8	80/8	18	12	130	50		
Satin	0.35		6	80/8	80/8	22	14	250	160		
Unidirectional 14:1	0.35		6	80/14	80/2	24	12	280	20		

Untwisted cloth or woven roving consists of continuous rovings woven into a heavy, coarse, but drapable fabric of usually plain weave. Input rovings, compatible with most hand lay-up resins, are designed to provide rapid wet-out and high laminate properties. In multi-layer laminates woven roving is alternated with chopped strand mat to increase in-plane shear and "peel" strength. Woven roving is available in various strength orientations, widths to 3.5m, and weights 270∼1350g/m^2.

(2) Main specifications. See Table 2.7, the structural parameters and specifications of cloth are including: weaving method - plain, twill, satin weave; the thickness of cloth reflects the bending degree of fiber and the width of cloth at 900mm, 1000mm; specifications of warp and weft, the monofilament diameter of warp yarn and weft yarn, count of yarn (strand count/plied number), and twists, etc; warp density and filling density b_L and b_T which refer to how many yarns on the length of 1cm wide cloth in warp and weft direction, reflecting the extent of density of the warp and weft; fabric areal density (fiber areal weight) G_f is fiber weight of per unit area cloth, g/m^2; tensile breaking force in longitudinal and transverse directions P_b refers to force at break of sample with width at 25mm and with testing gauge length at 100mm, which is expressed by kg .

See Table 2.7, because of different sizes of warp and weft, different arrangement density of yarn, there will be great differences of breaking force in longitudinal and transverse direction. Such fabric is called unidirectional cloth. Unidirectional clothes of 4:1, 7:1, 11:1, and 14:1 are commonly supplied.

(3) Representation of grades. Grade plain weave-100 represents thickness of plain weave is 0.1mm; Grade EW100A-90 represents non-alkali (E), cloth (W), thickness is 0.1mm, category (A), width is 90 cm.

2) The fracture strength of cloth

Given tensile breaking force P_b (kg) of cloth, cross-sectional area of the cloth specimen F (cm^2) and the converted fabric breaking strength σ_b (kg/cm^2) can be calculated according to the following formulas (2.4) and (2.5) respectively.

$$F_{cloth} = 2.5 \times b \times A = \frac{2.5 \times b}{100 \times \beta \times \rho_f} \tag{2.4}$$

$$\sigma_b = \frac{P_b}{F_{cloth}} = \frac{100 \times \rho_f \times \beta_0 \times P_b}{2.5 \times N \times b} \tag{2.5}$$

3) The reasons for cloth's strength is lower than yarn's strength

Break strength σ_b of the cloth actually means the tensile strength of fiber in the cloth. Because of weaving, glass fibers in the cloth are in the state of bending and distortion, so its tensile strength is far lower than the strength of yarn.

4) Using characters of fabrics

(1) Weaving situation. Table 2.8 lists the weaving method of cloth (plain weave, twill and satin weave) and its influence on the using characters of fabrics. Drape or

deformability means if glass fabric can joint with the mold when laying up on the curve surface, i.e., it is deformable ability of the glass cloth, which influences the shape complexity of components. Plain cloth is compactable, poor flexibility, so it has a poor drapability; satin cloth has the least dense, good flexibility, and the best drapability. Therefore, plain weave is only suitable for the FRP product with single curved surface or a large radius of curvature, and satin weave can manufacture FRP products with complex mold surface.

Table 2.8 Comparison of influence on using characters of weaving method of glass cloth

Projects	Plain weave	Twill weave	Satin fabric
Weaving number	More	Intervenient	Few
Fiber bending	Big	Intervenient	Small
Tensile strength	Low	Intervenient	High
Impact strength	High	Intervenient	Low
Drapability, deformability	Compact , poor flexibility	Intervenient	Good

(2) Fabric thickness. The thinner the cloth is, the smaller the fiber bending and higher tensile strength of the fiber; the thinner the cloth, the easier for soaking, but more plies.

(3) Fabric count. It reflects the density of the yarn, the larger the density, the more difficult for resin to soak.

2.2.5.3 Other glass fiber products

Except for glass fiber yarn and glass cloth, there are other glass fiber products.

1) Three-dimensional braiding

Three-dimensional braiding is the need of the shape and performance requirement of product, for example, braided cover for radome, three-dimensional fabric with the specific requirements.

2) Glass fiber mats

(1) Chopped strand mat. Untwisted rovings was chopped into short fibers about 25∼50mm long and became uniformly random distributed mat, which is felted by the latex adhesive or heating powder adhesive, such as chopped fiber mat for SMC.

(2) Continuous strand mat. Glass strand formed from fiber drawing process or continuous strand unwinding from the spool is placed in 8-shaped on continuous shift zone, also felted by the powder adhesive. Areal density G_f is 150∼650g/cm^2. Continuous strand mats can be used in pultrusion, RTM molding, or manufacturing GMT (glass mat reinforced plastics).

(3) Suture felt. It refers to the chopped fibers or continuous fibers stitching by sewing machine, in stead of chopped fiber or continuous fiber mat by adhesive bonding.

(4) Surface mat (monofilament felt). It refers to the middle-alkali corrosion resistant (C) glass fiber monofilaments which is 10∼20μm in diameter, being randomly cross placed and we use a small amount of adhesive for bonding to form the

fiber felt with low areal density. It can be used for the surface of glass fiber reinforced plastics. There are two methods for manufacturing surface mat, dry (steam injection method) and wet (paper-making process). Its surface density G_f is 30$\sim$ 150g/cm^2.

3) Stitch-bonded fabric

Stitch-bonded fabric or knitted glass felt refers to one layer of weft and warp overlapping together, through stitching the warp and weft be woven together to form fabric. It consists of three sets of yarn: parallel warp, deviated weft from the standard oblique (angle) and fine seams. Stitch-bonded fabric has both direction (intensity) of weaving fabric and the sponginess and impregnability of mats.

4) Non-weft fabric (tape)

The non-weft prepregs are sheet materials with certain thickness which is formed by using uncured adhesive to fix fibers in orderly direction.

2.3 Carbon fiber

Considering that glass fiber has low modulus and heat resistance is not enough, it is difficult to meet the requirements of structure application in aerospace industry. In the 1960s, carbon fiber, boron fiber and other fiber materials with high-strength, high modulus and low-density were developed. Carbon fiber is made from carbonization heat treatment of organic fibers such as rayon fiber, polyacrylonitrile fiber, or pitch fiber in the protection atmosphere (N_2 or Ar), and its carbon content is 90%$\sim$99%. The invention of the carbon fibers can be traced back in 1880, Edison used cotton, flax and other fibers to manufacture carbon filament as wire for lamp, but due to its big brittleness, easily oxidation, and too low brightness, at last he used tungsten filament as wire. It was not until the 1950s, the development of carbon fiber began to draw attentions as new engineering materials. In 1959, Union Carbide Corporation developed industrial production of carbon fiber using rayon as raw materials and its trademark is named as Thornel. In 1962, Shindo Akio who worked in government industrial research institute in Osaka, Japan, use polyacrylonitrile (abbreviated as PAN) fiber as raw materials to develop PAN-based carbon fiber. In 1964 Watt and others in the Royal Institute (RAE) produced carbon fiber with high strength and high modulus, by imposing drawing stress on the PAN fiber in the process of its pre-oxidation and carbonization. In 1963, Otani Sequoia Lang from Japan had successfully developed carbon fiber using asphalt as the raw material. Since then, carbon fiber is developed towards high-strength and high modulus. After 40 years of unremitting efforts, the carbon fiber technology has matured in mechanical properties, industrial production, variety and applications, far ahead of other new materials. Annual output of carbon fiber all over the world is 100 tons in 1969, which increased to 4700 tons in 1985, about 20,000 tons in 2000. At present, Japan is the largest country of carbon fiber manufacture (particularly in manufacturing technology and production output of the PAN precursors), and the United States is the largest user of carbon fiber. In 1970s China began to produce carbon fiber, but as a whole, with a slow development speed and less varieties, common properties and a low output.

2.3.1 Classification of carbon fiber

At present, carbon fiber has the rapid development, and there are many types of carbon fiber production at home and abroad. Generally, they can be classified by the type of fiber precursor, carbon fiber property and purpose.

1) Classification according to the type of precursor fiber materials

① PAN-based carbon fiber; ② pitch-based carbon fiber; ③ rayon-based carbon fiber; ④ vapor-grown carbon fiber.

The performance of carbon fiber which prepared with different raw materials is shown in Table 2.9.

Table 2.9 Properties of carbon fiber which prepared with different raw materials

Properties	PAN-based carbon fiber	Pitch-based carbon fiber	Rayon-based carbon fiber
Tensile strength (GPa)	2.5～3.1	1.6	2.1～2.8
Tensile modulus (GPa)	207～345	379	414～552
Density (g/cm^3)	1.8	1.7	2.0
Break elongation (%)	0.6～1.2	1	

2) Classification of carbon fiber according to different manufacture methods

They are carbon fiber (800～1600°C), graphite fibers (2000～3000°C), oxidative fibers (preoxidation fiber at 200～300°C), activated carbon fiber and vapor-grown carbon fiber.

3) Classification of carbon fiber according to mechanical properties

According to the mechanical properties of carbon fiber, they are general grade carbon fiber (GP) and high performance carbon fiber (HP); HP includes middle strength type (MT), high strength type (HT), ultra-high strength type (UHT), intermediate modulus type (IM), high modulus type (HM), ultra-high modulus type (UHM). Table 2.10 shows the performance of carbon fiber.

Table 2.10 Performance of carbon fiber

Performance	Carbon fiber				
	UHM	HM	UHT	HT	IM
Tensile modulus (GPa)	>400	300～400	200～350	200～250	180～200
Tensile strength (GPa)	>1.7	>1.7	>2.76	2.0～2.75	2.7～3.0
Carbon content (%)	99.8	99.0	96.5	94.5	99.0

4) Classification of carbon fiber according to application field

They are commercial grade carbon fiber and aerospace grade carbon fiber. Generally, commercial-grade carbon fiber is large tow, and refers to a bunch of monofilament yarn is more than 24K (1K=1000). In order to reduce the cost, it has been gotten into large-tow fibers of 360K, 480K, and 540K. Aerospace grade, such as the composite materials structure of national defense applications, aerospace grade carbon fiber is small tow (<12K), and more of 1K, 3K in the past, now developed to 6K, 12K. For the current standard modulus carbon fiber T300 3K used in aerospace applications, the international bidding is 30~40$/kg; and the price of civilian large-tow carbon fiber T300 has been reduced to 15~16$/kg, which is close to the accepted price 11$/kg of the automobile industry; the price of large tow AS4 carbon fiber with standard modulus has been lowered to 18$/kg. Performance and price of commercial-grade carbon fiber and aerospace-grade carbon fiber are presented in Table 2.11. See the table, the higher the fiber modulus, the higher the price. The price of high modulus carbon fiber which used in aerospace industry is much higher than that of high strength carbon fiber pursuited in aviation industry.

Table 2.11 Performance and price of commercial-grade carbon fiber and aerospace-grade carbon fiber

Types of carbon fiber		E_f(GPa)	Price/($/kg)
Commercial-grade		210~230	17~26
Aerospace-grade	Standard modulus	231~245	39~44
	Medium modulus	255~310	68~72
	HM	336~490	132~143
	UHM	490~980	264~1028

5) Classification of carbon fiber according to the function

It includes: ① load structure using carbon fiber; ② flame resistant (fire) carbon fiber; ③ activated carbon fiber (adsorption activity); ④ conductive carbon fiber; ⑤ carbon fiber used for lubrication; ⑥ wear-resistant carbon fiber; ⑦ corrosion-resistant carbon fiber.

2.3.2 Preparation of carbon fiber

Carbon fiber cannot be manufactured using a general production method of synthetic fiber, because we have not found the solvent which dissolves the element C so far. To melt C, we must put it under 10MPa and higher than 3800°C.

Organic fiber with a high content of C is used as a precursor in manufacturing carbon fiber under the protection atmosphere of N_2 or Ar and imposing traction force, a majority of non-carbon elements are removed by heating (carbonization), we get the fiber material, its main body is the graphite crystal structure of carbon.

As a precusor, it satisfies the following requirements: ① it does not melt in carbonization process and fiber morphology can be maintained; ② higher carbonization yield; carbonation yield is the mass ratio of the prepared carbon fiber to the original precursor; it is an important economic and technological index in the carbon fiber manufacture; ③ strength, modulus and other properties of carbon fiber meet the requirements; ④ stable and continuous filament could be obtained.

There are three kinds of raw yarns which meet the above four requirements and have the industrialization meaning and are shown in following:

(1) Viscose fiber (regenerated cellulose) $(C_6H_{10}O_5)_n$. Preparation of carbon fiber by the viscose fiber is one of the first industrialization manufacturing methods. Because it needs the process of traction graphitization at high temperature, the technology is difficult, the equipment is complex, cost is high and carbonization yield is low (20%~40%). Now it has gradually been eliminated, the retained is only part production for ablation resistant material application.

(2) Pitch fiber. Pitch is abundant in the earth, carbonation yield is high (70%~90%), and new technics are developing unceasingly, with a very good prospect, especially in improving the fiber modulus.

(3) PAN fiber $(C_3H_3N)_n$. PAN fiber can be made into high-performance carbon fiber, with a high carbonization yield (40%~60%), and the manufacturing method is simpler than other methods, and it is the most mature manufacturing method at present with the highest yield, the largest species, and the fastest development.

1) The manufacture of polyacrylonitrile-based carbon fiber (PAN-CF)

Fig. 2.5 shows the flow chart of the PAN-based carbon fiber production process. Generally the preparation process of carbon fiber using polyacrylonitrile fiber to manufacture has four steps: pre-oxidation, carbonization, graphitization and surface treatment.

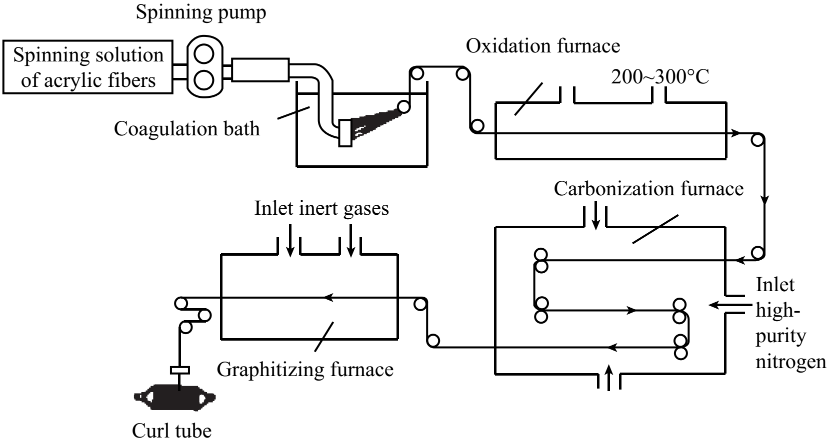


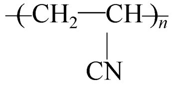
Fig 2.5 Schematic of the production process of PAN based carbon fiber.

The preparation process of CF with the method of PAN

PAN fiber→Preoxidation→Carbonization→Graphitization→Surface treatment
precusor preoxidation CF-II, high strength CF CF-I, high modulus CF
yarn Carbon fiber GrF, graphite fiber
High σ, low E High E, low σ

(1) The pre-oxidation treatment of PAN precursor.

① Structure and properties of PAN fiber.



$$\left(\mathrm{CH_2}-\underset{\mathrm{CN}}{\underset{|}{\mathrm{CH}}}\right)_n \xrightarrow{\text{Drawing}} \text{PAN precursor}$$

Two-dimensional ordered structure

Linear random structure (A good lateral sequences order in two directions vertical to main chain)

Thermal properties of PAN: because of the strong polarity of —CN, the intermolecular force is great, and the T_g is about 120°C, T_m is 326°C, and it has good heat resistance; At the same time, $T_d < T_m$, the thermal stability is poor, so the filature cannot melt. We can only use solvent wet spinning or dry spinning. To promote cyano cyclization, we often introduce comonomer components into system such as acrylic ester and propylene derivative, because they have similar reactivity rate with acrylonitrile and have nucleophilic group. Lower T_m of copolymers can facilitate the spinning process and reduce the temperature forming ladder structure in the pre-oxidation.

② Role of pre-oxidation.

PAN fiber is a linear polymer structure and has poor heat resistance, because it will decompose at a high temperature, so it cannot undergo the high temperature of carbonization process and become carbon fiber. However, if heating PAN fiber at a lower temperature (200∼300°C), through oxidation reaction, the β-C will be partially oxygenated into hydroxyl and carbonyl, which could form hydrogen bond inter-molecular or intra-molecular. The inducement action of hydroxyl and carbonyl can cause the cyclization of CN under a low temperature so as to get a conjugated six-membered ring trapezoidal structure with a better heat stability. Then it can withstand the high temperature of carbonization process to form carbon fiber. This is the function of pre-oxidation. In the pre-oxidation process of PAN fiber, the main chemical reactions are cyclization reaction of oxidative dehydrogenation. See Fig. 2.6, dehydrogenation and cyclization make the structure of PAN fiber from a linear structure to a six-membered ring trapezoidal structure.

$$\text{PAN fiber} \xrightarrow[\mathrm{O_2},\text{tension}]{200\sim300^\circ\mathrm{C}} \text{Structure with hexatomic ring}$$

The trapezoidal structure is in Fig. 2.6A. It enhances the softening temperature, so it can withstand high temperature carbonization, not melt, and maintain fiber morphology; the trapezoidal structure in Fig. 2.6B has a good thermal stability, which can improve the carbonization yield; the trapezoidal structure in Fig. 2.6C reduces molecule pyrolysis in the carbonization treatment process.

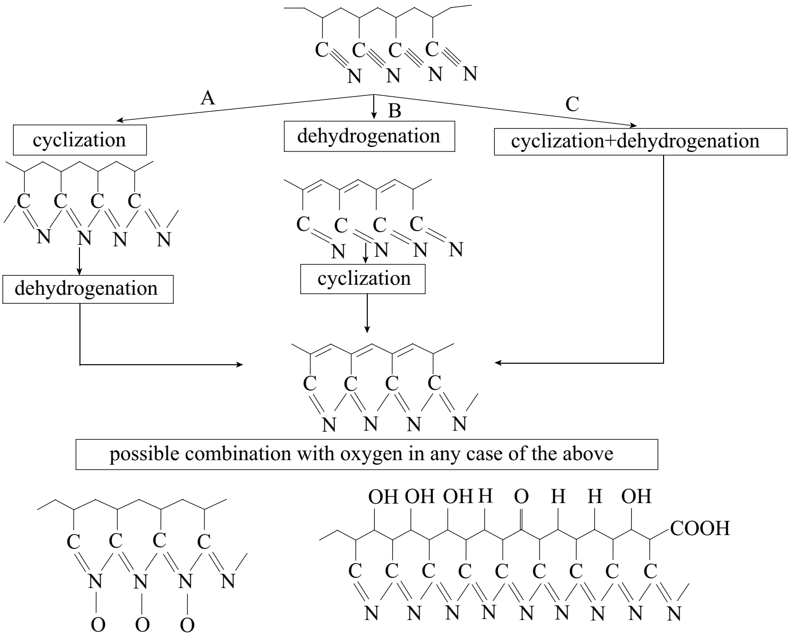


Fig. 2.6 Possible reaction of PAN in pre-oxidation process.

③ Molecular structure character of the fiber after pre-oxidation.

The trapezoidal structure after pre-oxidation in Fig. 2.6A, its main chain is primarily made of trapezoidal structure, but it retaines the random structure of the PAN; the trapezoidal structure in Fig. 2.6B, it is mainly composed by the element C, H, N; the trapezoidal structure in Fig. 2.6C, it contains oxygenic groups, such as —OH and —CO— in the trapezoidal structure, and the oxygen content of it is between 5% and 10%.

④ Pre-oxidation process conditions.

PAN fiber pre-oxidation process is carried out at four segments of controlled temperature, 200°C, 230°C, 250°C and 280°C, and pre-oxidation process is continuous. PAN fiber stays two hours in the pre-oxidation furnace, and tension is exerted in two segments: PAN fiber elongates about 10% in the stage of 200∼230°C; and in the stage of 250∼280°C, fiber maintains fixed-length or stretches at 3%. The pre-oxidation process is carried out under the condition of ventilation, so it helps get rid of by-products and hold the uniform temperature.

Imposing tension in the pre-oxidation stage is to orient the formated trapezoidal structure in the fibers. The PAN fiber will shrink in the major axis direction on heating when the temperature is higher than its glass transition temperature. In the earlier period of the pre-oxidation process, it is physical contraction, which showing a sharp decline of orientation degree; and it is chemical shrinkage in the later period, which characterized by the emergence of hollows. Whether it is physical or chemical shrinkage, the mechanical properties of the fiber will be significantly weakened. Therefore, imposing tension to restrain contraction is advantageous to orientation qualification of the polymer chain. It is propitious to cis-isotactic arrangement of cyano, so as to promote the cyclization of cyano, get the stable cyclization structure, increase the orientation degree of the trapezoidal structure, and ultimately enhances the tensile strength and elastic modulus of the fiber significantly.

In the pre-oxidation process, a skin-core structure appears on the fiber transect. The cover structure is sturdy while the core structure is soft. The skin has a higher stability while the core has a lower stability. The strength and modulus of carbon fiber are mainly decided by the volume of the cover; and if volume of the core is big, many hollows or empty will be formed in the carbonization process. Generally, it is believed that the pre-oxidation has been completed when the volume of cover skin reaches above 86%.

The pre-oxidization of PAN fiber makes use of the principle that below its melting temperature (326°C), the polyacrylonitrile has molecular cyclization and at the same time molecular decomposition occurs. In order to improve the preparation of carbon fiber as well the previous polyacrylonitrile spinning, a small number (0.05%∼10% mol) of the acrylic acid ester and propylene derivatives are used as the second, third monomer in the preparation of the dual or ternary copolymer of polyacrylonitrile. These copolymers have a lower melting point of about 317°C and good plasticity, which are good for the fiber spinning and increasing the fiber orientation. And the activation energy to form the ladder structure is also low, so the pre-oxidation temperature is reduced, the time is shortened, the performance and the yield of carbon fiber are all improved.

(2) Carbonization treatment.

$$\text{Pre-oxidized fiber} \xrightarrow{300\sim1500^\circ\text{C, N}_2\text{, Tension}} \begin{array}{c}\text{Chaotic layer graphite}\\ \text{structure CF-II}\\ \text{(Two-dimensional hexagonal}\\ \text{network structure,}\\ \text{interlayer disorder,}\\ \text{carbon content} > 92\%)\end{array}$$

Carbonization is the thermal decomposition reaction of pre-oxidized fibers under the tension at the temperature of 300∼1500°C and under the protection of nitrogen (purity>99.99%), with the unstable part of the structure and non-carbon atoms (such as N, H, O, etc.) being pyrolyzed out. At the same time intermolecular condensation occurs (transverse cross-linking reaction), and finally we get the carbon fibers with the carbon content more than 92%. Its structure transforms towards to graphite crystal. Fig. 2.7 shows condensation and pyrolysis process. At the temperature of 300∼400°C inter-molecular dehydration crosslinking reaction will happen, and at the temperature of 400∼600°C denitrogenation and dehydrogenation crosslinking reaction will occur and go further at the temperature of 600∼1300°C. By now the carbon fibers have formed two-dimensional hexagonal network of graphite layers parallell each other, with comparatively regular spaces among layers. But laminated layers are still messy and in disorder, so it is called chaotic layer graphite structure.

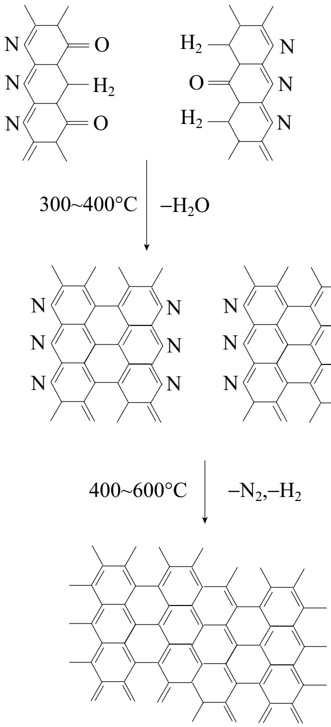


Fig. 2.7 Schematic diagram of transverse crosslinking in carbonization process.

Carbonization takes about 40 min and the imposed tension is about 50g/bundle. Tension makes the graphite crystal orientate along the fiber direction and suppresses the contraction in the transverse cross-linking reaction. With the increase of heat treatment temperature (HTT), the modulus of carbon fiber increases and strength has maximum (Fig. 2.8). In the carbonization process, apart from the release of hydrogen, nitrogen, oxygen, there are methane, carbon dioxide, ammonia, hydrocyanic acid and so on. These gases must be quickly eliminated, otherwise they will condense and then stick to the fiber, which not only hinder fiber self-cleavage products excluded, but also bond fibers together and cause overheating. This results in fiber breakage, increasement of broken filament and significant reduction of strength and modulus. In order to exclude these pyrolysis products, we have to make the nitrogen to flow in oppositive direction of the tow smoothly.

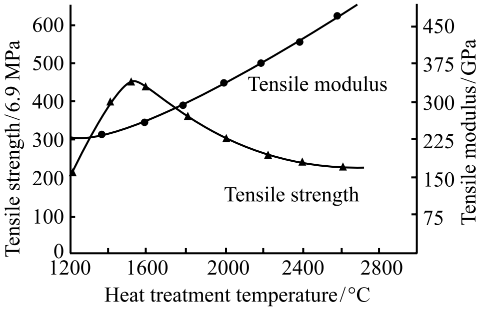


Fig. 2.8 The effect of heat treatment temperature on properties of carbon fiber.

(3) Graphitization treatment.

The structure of carbon fiber obtained in the carbonization process belongs to chaotic layer graphite structure. In such structure, the orientation of lamellar graphite along the fiber axis is relatively low, and so is the elastic modulus. In order to obtain high modulus fiber, we must carry out high temperature treatment at 2000∼3000°C at the basis of carbonation. This is the so-called graphitization.

$$\text{CF-II} \xrightarrow{2000\sim3000^\circ\text{C, Ar, large tension}} \text{CF-I}$$

Graphitization treatment is carried out in argon and not in nitrogen, because nitrogen reacts with carbon to generate cyanide at above 2000°C. In the graphitization process, the residues of nitrogen, hydrogen and other non-carbon elements are further excluded. Carbon-carbon rearranges, so the number of aromatic ring increases in the layer. The size of lamellar layer and the content of crystalline carbon are increased. At high graphitization temperature and applying large tension (100∼200g/bundle), carbon fiber displays sufficient plasticity. The graphite layers orientate along the fiber axis (the angle between graphite layer and the fiber axis is called orientation angle θ), and layer spacing d_{002} is decreased. Through the graphitization treatment, carbon fiber structure is further converted toward the graphite crystal structure and the degree of graphitization is improved. It shows that the graphite crystal size ↑, crystallinity ↑, the orientation angle θ ↓, layer spacing d_{002} ↓, which largely improves the modulus of the fiber.

With the increasement of graphitization temperature, carbon fibers have a linear increase of elastic modulus, lower break elongation and lower tensile strength (Fig. 2.8). The decrease in strength is mainly because the surface carbon of the carbon fiber may be evaporated during graphitization treatment at high temperature, resulting in uneven defects, causing reduction of weight and strength. In addition, because carbon fiber has a skin-core structure, as increasing of the degree of graphitization, the original gap size increases, which results in a decrease in strength. Because polyacrylonitrile fiber has relatively regular structure after carbonization, graphitization time is just for tens of seconds or a few minutes. In order to limit the rate of decline in strength, we usually adopt pulling graphitization or graphitization under high atmosphere pressure. When the pressure in graphite furnace is more than 2 times of atmosphere pressures, the strength of carbon fiber is about 40% higher than that under normal pressure.

(4) Sizing and surface treatment.

Surface activity of carbon fiber is low, so surface treatment (oxidation, sizing) is needed for improving it and thus improving the performance of composite materials. Sizing is the last process to manufacture carbon fiber, whose function is to protect the carbon fiber, to prevent it from damaging and pilling, and also serves as a coupling agent between carbon fiber and resin.

2) Manufacture of pitch-based carbon fiber

Except for natural pitch, there are many other sources of pitches to prepare pitch-based carbon fiber. They are: coal tar pitch from by-product of coal coking, petroleum pitch from the residue after fractionation of petroleum crude oil, pyrolysis pitch from by-product from petroleum distillating pyrolysis system at the time of check-products of ethylene. There is also pure synthetic pitch with narrow molecular weight distribution obtained by polycondensation of synthetic resin such as PVC or pure aromatic such as naphthalene, anthracene, but its cost is higher.

There are two main types of pitch-based carbon fiber: one is the common carbon fiber with lower mechanical properties, which is also called isotropic pitch carbon fiber; the other is the mesophase pitch carbon fiber with higher mechanical properties. Their main difference in the structure and properties depends on the composition of pitch. Therefore the modulation of pitch is the key to control the properties of carbon fiber.

Pitch is a mixture of a wide range of aromatic ring polycondensate. Its softening point is 100∼200°C molecular weight distribution is very wide and average molecular weight is more than 200. Its carbon content is large than 70%. Pitch materials for preparing carbon fiber must have certain rheological properties and chemical reactivity to facilitate the spinning and non-melting treatment, and meet the needs of containing high carbon content and low quinoline insoluble compounds, free carbon, S, N, O and metal-organic or less complex. Fig. 2.9 shows the flow chart of manufacturing pitch-based carbon fiber.

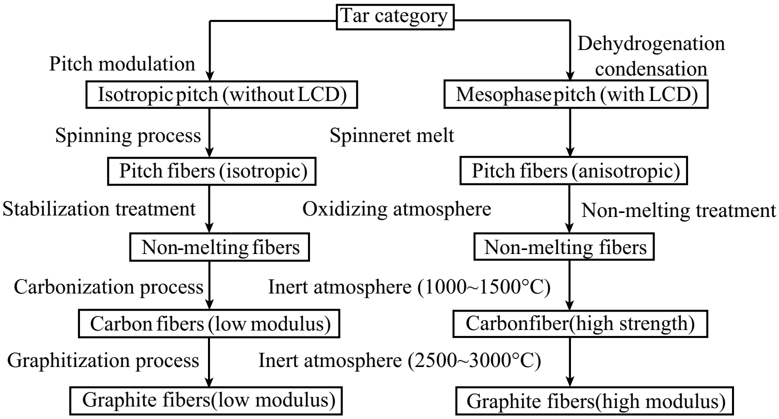


Fig. 2.9 Fow chart of manufacturing process of pitch-based carbon fiber.

(1) Manufacture of isotropic pitch carbon fiber.

① Modulation of pitch. Modulation methods include solvent extraction, distillation, hydrogen treating, adding appropriate compounds and so on. Through the modulation, its chemical composition, molecular weight and its distribution will be able to meet the preparation requirements of carbon fiber and pitch also has certain fluidity.

② Melt spinning. Spinning temperature is generally 50∼150°C higher than softening point of pitch, so that pitch will change from glass state into viscous flow state, and spinning forming is in the viscous flow state.

③ Stabilization treatment. In order to protect the pitch fiber after spinning from melting and binding together in the carbonization process, non-melting treatment must be carried out (acid gases at 250∼400°C).

④ Carbonization treatment. After stabilization treatment, carbonization treatment of pitch fibers can be done under the protection of inert gas at 1000∼1500°C in order to remove H, N and other non-C elements and transfer the structure to polycrystalline graphite lamellar structure.

⑤ Graphitization treatment. Graphitization treatment is carried out under the protection of the inert gas at 2500∼3000°C.

(2) Preparation of mesophase pitch carbon fiber.

① Mesophase pitch's modulation. Dissolve pitch in quinoline (or pyridine) solution at 80∼120°C, filter to remove the quinoline insoluble compounds which are not conducive to the growth of mesophase small balls; and then get the mesophase pitch with appropriate viscosity and high orientation along the fiber axis by condensation and dehydrogenation in an inert atmosphere at 300∼350°C.

② Spinning. Melting spinning, we should strictly control the spinning temperature, shape of spinneret orifice, the surrounding atmosphere temperature.

③ Non-melting treatment of the mesophase pitch fiber. Handling in the air (or with NO_2, O_2) at 275∼350°C, or liquid-phase oxidation (hydrogen peroxide, sulfuric acid, nitric acid, etc.) treatment.

④ Carbonization treatment. Dehydrogenation, dehydration and condensation among the aromatic molecules in fibers. This is to remove non-carbon elements.

⑤ Graphitization treatment.

2.3.3 The structure of carbon fiber

Carbon fiber has high strength and high modulus, which is inseparable from its structure. Carbon fibers' structure is similar to graphite crystal. For the discussion of the structure, we first intruduce the structure of the ideal graphite crystal composed of pure carbon.

1) Ideal graphite crystal structure

Graphite crystal is a three-dimensional ordered hexangular crystal lattice structure. Its features are shown in following:

(1) Carbon atoms within the layer have sp^2 hybridization bonds, that is, each carbon atom has three σ bonds to combine with the other three carbon atoms, each carbon atom gives one p-orbital to form a large conjugated π bond. Between layers, however, the atoms are linked via van der Waals' force. The distance is larger. The valence bond nature of carbon atoms in graphite crystals is shown in Table 2.12.

Table 2.12 Valence bond nature of carbon atom of graphite crystal

Location	Valence bond	Bond length (nm)	Bond strength (kcal/mol)	E(GPa)
In-plane	Covalent bond	0.142	150	1035
Interlayer	Secondary bond	0.335	1.30	36

(2) The location of C atoms between adjacent layers has a fixed relationship between layers.

Therefore graphite crystals are three-dimensional ordered anisotropic materials, having a very high modulus along the layer. And this enlightens us an idea to develop fiber material with the fiber axial in the layer direction, and it is sure to have a high modulus. Then carbon fiber came out.

2) The structure of CF

$$\text{Graphite lamella} \rightarrow \text{Graphite microlite (chaotic layer structure)}$$
$$\rightarrow \text{Graphite fibril (ribbon structure)} \rightarrow \text{Carbon fiber}$$

The structure of carbon fiber is chaotic layer graphite structure, as shown in Fig. 2.10.

A carbon fiber with 6∼ 8μm in diameter is composed of fibrils. Fibril is thin strip structure with about 20nm at width and a few hundreds nm at length. It is a tertiary structure unit of carbon fiber and can be observed with a high resolution electron microscope. In carbon fiber, fibril (band) is not straight along the fiber

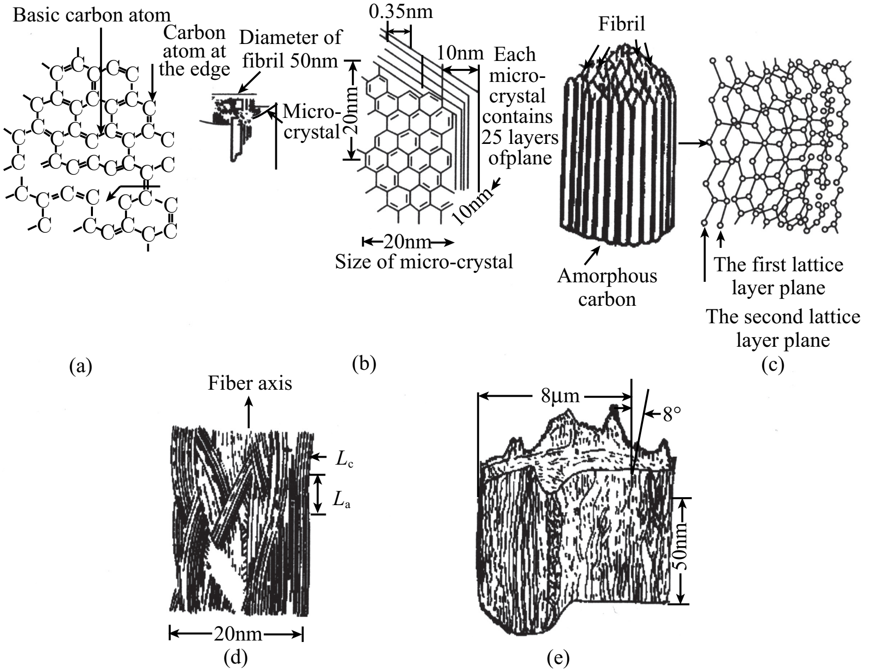


Fig. 2.10 Schemic diagram of chaotic layer structure of carbon fiber:
(a)defects and carbon atom at the edge of graphite lamella;
(b)graphite microlite; (c)fibril; (d)ribbon structure; (e)stereo structure.

direction, but bent, folded, crossed to each other in a monofilament. There exists needle-shaped gap with width of 1.0nm to 2.0nm and length of several tens nm in those bands. Gaps and fibrils in the long axial direction generally arrange parallelly to the fiber axial direction, and show a certain angle (approximately at 8°). The value of this angle determines the modulus of carbon fiber. As heat treatment temperature increases, the orientation angle decreases. In the fibril, the graphite microlite may be separated by some amorphous structures.

Fibril is composed of many graphite microlite units with secondary structures of carbon fibers. Microcrystalline graphite is a parallel superposition structure formed by several to dozens of lamellar graphite layers. The difference between microcrystalline graphite and ideal graphite crystal is that it is not three-dimensional orderly lattice structure, but two-dimensional orderly chaotic layer structure; the distance between the layers is larger than ideal crystals. The size of graphite crystallite (crystal length or diameterL_{a}, crystal thickness L_{c}), layers' spacing d_{002} and degree of graphitization γ are related with the heat treatment temperature (HTT) and time in fabrication process (See Table 2.13). HTT $\uparrow\rightarrow L_{\mathrm{a}}\uparrow$, $L_{\mathrm{c}}\uparrow$, $d_{002}\downarrow$, $\gamma\uparrow$.

Calculation of the degree of graphitization is given by

$$\gamma = \frac{0.3440 - d_{002}}{0.3440 - 0.3354} \tag{2.6}$$

Where 0.3440 is the interlayer distance of amorphous carbon's graphite crystal, nm;

0.3354 is the interlayer distance of ideal (natural) graphite crystal, nm;

d_{002} is the interlayer distance of graphite crystal tested, nm.

Table 2.13 Relationship of graphite crystallite size, lamellar spacing, the degree of graphitization and the heat treatment temperature

HTT(°C)	L_a(nm)	L_c(nm)	d_{002}(nm)	γ(%)
1000	3.9	1.4	—	—
1500	5.6	2.2	—	—
2000	—	—	0.39	—
2500	11.0	6.4	0.342	23
2800	—	—	0.340	45
3000	20.0	8.6	0.337	81

Graphite lamellar is the primary structure unit of carbon fibers and the most basic structural unit with a length (diameter) L_a of less than 20nm, which contains the basic carbon atoms in composition of the hexatomic ring, edge carbon atoms and defects.

For a carbon fiber (monofilament), it is a skin-core structure. The size of surface crystallite is large, fibril is arranged neatly and orderly, degree of orientation is high and the orientation angle is small. From the cortex to the inner core, crystallites become small and fibrils become more disordered and sparser, structure inhomogeneity is thus more significant.

3) The relationship between structure and properties of CF

(1) Impact of heat treatment temperature (HTT) on the strength and modulus of CF. In Fig. 2.8, with the increase of heat treatment temperature (HTT), the modulus of carbon fiber enhances and the strength reaches the peak value.

HTT $\uparrow \rightarrow E \uparrow$. Since HTT$\uparrow \rightarrow L_a \uparrow L_c \uparrow$ (crystallite size $\uparrow$), $d_{002} \downarrow$ (compact structure) $\rightarrow E \uparrow$, HTT $\uparrow$ (tension) $\rightarrow \theta \downarrow \rightarrow E \uparrow$.

$\theta/(°)$	0	90	13
E/GPa	1035	36	400

σ has a ultimate value. On the one hand, HTT $\uparrow$, the number of cross-linking bond increases in fibrils or in crystallites, and $\theta \downarrow$, $d_{002} \downarrow$, graphite crystallites$\uparrow$, which causes carbon bond density increased (the number of carbon bond per unit area) $\rightarrow \sigma \uparrow$. On the other hand, there are the following possible reasons for σ to drop when HTT increases: ① $T \uparrow \rightarrow$ crystallite size $\uparrow \rightarrow$ the number of gaps $\downarrow$ but the size of gap $\uparrow \rightarrow$ stress concentration $\uparrow$; ② crystallite size is small: when this happens, crystal boundary area is large and energy consumption of crack propagation is large; ③ high-temperature drawing: it is possible to pull off the cross-linking bond in fibrils, weaken the bonding between crystals' boundary;

④ in skin-core structure the thermal expansion coefficient of the skin and core is different: the higher the temperature, the greater the residual stress; ⑤ under high temperature carbons on carbon fibers' surface evaporate. This will cause surface defects.

(2) Wetting and bonding. Because of the well crystallization of carbon fibers, neatly arranged carbon atoms, large grain, and small crystal edge, small surface defects, the wettability of resin on carbon fiber is not good, so surface treatment is necessary.

(3) Quality of PAN precursor itself. The performance of carbon fiber is affected by defects of PAN precursor. Carbon fibers' defects are mainly from precursor fiber and the carbonization process; the quality of PAN precursor affects the performance of carbon fiber. Moderate molecular weight, small dispersion, a great degree of orientation is in favor of enhancing carbon fibers' performance. Gaps and impurities in the precursor will become carbon fibers' defects. Furthermore, the non-uniform diameter of precursor will lead to uneven degree of pre-oxidation and an uneven skin-core structure, both will affect the performance of carbon fiber.

2.3.4 The performance of carbon fiber

1) Mechanical properties

The strength of carbon fiber σ_{fu} is high, modulus E_f is large. Because of the small density ρ_f, it has high specific strength σ/ρ and high specific modulus E/ρ. Table 2.14 shows the mechanical properties of several carbon fibers.

Modulus of carbon fibers increases with the increase of treatment temperature in carbonization process. It is because the carbonization temperature increases and the crystal "grow up". Regular array region of carbon hexatomic ring enlarges, and the degree of crystal orientation rises. By high-temperature treatment at 2500°C (is also called graphitization treatment), it yields high modulus carbon fiber (or graphite fiber): carbon fiber of type I. Its elastic modulus is up to 400 ~ 600GPa, the minimum fracture elongation is about 0.5 %.

Table 2.14 Mechanical properties of several carbon fibers

	Type A (Common, Medium strength)	Type II	Type I
HTT (°C)	1000	1500	2500
ρ_f(g/cm^3)	1.73	1.75	1.9~2.0
σ_{fu}(GPa)	2.1	2.5	1.4~2.1
E_f (100GPa)	2	2.2~2.5	3.9~4.6
ε_{fu} (%)	1.2~1.5	1.0	0.5

With the treatment temperature increasing, the strength of carbon fiber increases and the highest value lies in the range of 1300~1700°C (see Fig. 2.8). The strength reduces after treatment more than 1700°C. This is because defect in the fiber increases and enlarges. The strength of carbon fibers is relative to the internal defects, which can be confirmed by testing tensile strength of fiber at different lengths. The longer the fiber tested, the greater the emerging probability of the internal defects, so the lower strength is. Carbon fiber treated between 1300°C and 1700°C is called high strength CF, or carbon fiber of type II.

We can see, CF of type I has the maximum modulus, the minimum strength, and the lowest break elongation, the highest density; CF of type II has medium modulus, the maximum strength, the largest break elongation and the lowest density. The cost increases with the increase of HTT.

Compared with glass fiber, σ_{fu} of S-GF is the highest, $\sigma_{fu}$of type I CF is the minimum, σ_{fu} of E-GF is similar to that of type II; E_f of type II is 3 times more than that of GF, E_f of type I is 5 to 7 times more than that of GF; CF has a small density and a low fracture elongation. Elastic modulus of carbon fiber is higher than that of glass fiber, so the strain of carbon fiber composite materials is lower under the same external load. The stiffness of the parts is higher than glass fiber composite parts. Break elongation of high modulus carbon fiber is about 0.5$\%$, of high-strength carbon fiber is about 1$\%$, of glass fiber is about 2.6$\%$, and of epoxy resin is about 1.7$\%$. So the strength of fiber in the carbon fiber composite materials can play the role fully.

The brittleness of carbon fiber is very large, thus has bad impact performance. Its tensile damage is in the brittle mode without obvious plastic deformation before break, and its σ-ε curve is a straight line. This is similar to glass fiber, but modulus E_f is higher than glass fiber, break elongation ε_{fu} is less than glass fiber. The strength of CF has a big dispersibility and has a size effect. Use kg/cm^2 and MPa to express the strength unit of CF as well g/den and cN/dtex. The anisotropy of CF structure determines its anisotropy of mechanical properties and thermal properties.

The density of carbon fiber is 1.5$\sim$2.0g/cm^3, depending on the nature of raw materials and heat treatment temperature, for example, density of PAN-based carbon fiber after treatment at 1000°C is 1.7g/cm^3, it is about 2.01g/cm^3 after treatment at 3000°C.

For carbon fiber, σ and E are not only affected by HTT in the manufacturing process, but also the level of manufacturing technology (like age). With the development of technology, the defects in fiber reduce, the strength σ_{fu} of brittle carbon fiber enhances. Even the same brand, different age has different performance. At present, Japan Toray's high-strength carbon fiber T300: σ_{fu} is 3530 MPa, E_f is 230GPa, ε_{fu} is 1.5$\%$, ρ_f is 1.76g/cm^3; medium-modulus high-strength carbon fiber T800H: σ_{fu} is 5590MPa, E_f is 294GPa, ε_{fu} is 1.9$\%$, ρ_f is 1.81g/cm^3; medium-modulus high-strength carbon fiber T1000: σ_{fu} is 7060MPa, E_f is 294GPa, ε_{fu} is 2.4$\%$, ρ_f is 1.82g/cm^3; high modulus carbon fiber M40: σ_{fu} is 2740MPa, E_f is 392GPa, ε_{fu} is 0.6$\%$, ρ_f is 1.81g/cm^3; high-strength and high-modulus carbon fiber M60J of MJ series: σ_{fu} is 3820MPa, E_f is 588GPa, ε_{fu} is

0.7%, ρ_f is 1.94g/cm^3.

2) Physical properties

(1) Thermal properties. Carbon fiber has good resistance to high and low temperature. It still has strength at 2000°C when isolated from the air (inert gas protection); it has no brittle fracture under liquid nitrogen.

Carbon fiber has good thermal conductivity performance. Thermal conductivity is high, but decrease with temperature increasing. Thermal conductivity is anisotropic, and thermal conductivity along the fiber axial direction is much higher than that vertical to fiber direction. Thermal conductivity of high strength carbon fiber is much lower than that of high modulus carbon fiber, for example, the thermal conductivity of T300 is 6.5W/(m·K), while that of M40 is 85W/(m·K).

Its linear expansion coefficient along the fiber axial direction has a negative temperature effect, so with the rise of temperature carbon fiber has the trend of contraction. We can make use of this property to design zero expansion composite materials with good dimensional stability and good fatigue performance. The linear expansion coefficient along the fiber axial direction is about $-0.9\times10^{-6} \sim -0.72 \times 10^{-6}$/°C, that perpendicular to fiber axial direction is about $22\times10^{-6} \sim 32 \times 10^{-6}$/°C, and the expansion coefficient of resin matrix is about 45×10^{-6}/°C. There is a larger difference between them, so for the carbon fiber composite material after curing if cooling too quickly, or undergoing great temperature change, crack is easy to come forth. Table 2.15 lists the thermal conductivity and linear expansion coefficient of glass fiber and carbon fiber.

(2) Bad bonding performance of CF with resin. Carbon fiber has a low surface activity, whose bonding with matrix material is worse than with glass fiber, so carbon fiber composite has lower interlaminar shear strength (ILSS). The higher the degree of graphitization is, the more inert of the carbon fiber surface is. Carbon fiber used in resin-based composite materials should enhance their surface activity by surface treatment.

Table 2.15 Thermal conductivity and linear expansion coefficient of glass fiber and carbon fiber

Projects	Thermal conductivity λ [W/(m·K)]	Linear expansion coefficient α (10^{-6}/°C)
GF	1.0	4.8
CF axial direction //	16.7	$-0.72\sim -0.9$
CF transverse direction ⊥	0.84	22～32

Short beam shear strength (ILSS)of carbon fiber composite before and after surface treatment are measured: ILSS of untreated type I is 245kg/cm^2, of type II is 385kg/cm^2, of type A is 560～670kg/cm^2; ILSS of surface treated type I is 840 kg/cm^2, of type II is 1050kg/cm^2.

3) Chemical properties

(1) Oxidation. Oxidation reaction of carbon fiber will happen in the air at 200～

290°C. It will be showing obvious signs of oxidation when the temperature is higher than 400°C and oxides leave in the form of CO, CO_2 from the surface. Therefore in the air the heat-resistance of CF is worse than that of GF. Oxidation resistance of high-modulus carbon fiber is significantly superior to that of high-strength CF. Oxidation resistance of carbon fiber on the surface with protective slurry is not as good as that without it. If treat it with 30% H_3PO_4, its oxidation resistance will be enhanced. Using strong oxidants (concentrated sulfuric acid, concentrated nitric acid, hypochlorite, and dichromate) to make the surface carbon oxidate into groups containing oxygen can improve the interface bonding performance.

(2) Corrosion resistance. Apart from strong oxidants such as concentrated nitric acid, hypochlorite and dichromate oxidation, the general acid and alkali have little effect on carbon fiber. CF has better corrosion resistance than glass fiber. Put carbon fiber in 50% hydrochloric acid, sulfuric acid and phosphoric acid for 20 days, its elastic modulus, tensile strength and diameter have no change.

Unlike glass fiber hydrolysis in the wet air, carbon fiber has better water resistance than GF, so carbon fiber composite material has good water resistance and good wet and heat aging resistance. Carbon fiber also has oil resistance, anti-radiation, as well neutron deceleration.

4) Other properties

Carbon fiber has good conductivity along the fiber direction, and the specific resistance is related to fiber types. At 25°C, specific resistance of high modulus fiber is 755μΩ·cm and of high-strength fiber is 1500μΩ·cm. Electromotive force of carbon fiber is positive and of aluminum alloy is negative. Therefore, if carbon fiber composite materials combine with aluminum alloy, electrochemical corrosion will happen.

The friction coefficient of carbon fiber is small and has self-lubrication property.

2.3.5 Types and specifications of carbon fiber

Like glass fiber, carbon fiber products in different forms include long fiber, short fiber, cloth, mat, twisted or braided rope, three-dimensional fabric and so on. Table 2.16 lists the major species and performance of carbon fiber.

There are three ways for producing carbon fiber fabric (cloth): weaving carbon cloth with the carbon fiber yarn in warp and weft; weaving cloth with pre-oxidation fiber, and then carbonized; weaving cloth with precursor fiber, then pre-oxidation, and carbonization.

Domestic carbon fiber and its fabrics are not yet formed a strong production capacity and the usage of carbon fiber mainly depends on imports. Most frequently used and the most common CF is the Japanese Toray high-strength carbon fiber, such as Torayca T300B 3000-40B, the number of monofilament is 3000.

Table 2.16 Major species and performance of carbon fiber yarns

Fiber type	Filament count	Tensile strength (MPa)	Tensile modulus (GPa)	Break elongation (%)	Density (g/cm^3)	The mass in 1000 m *Tex* (g/km)
T300	1K3K6K12K	3530	230	1.5	1.76	66/198/396/800
T300J	36K12K	4410	230	1.9	1.82	198/396/800
T400H	3K6K	4410	250	1.8	1.80	198/396
T700S	12K	4800 (700ksi)	230	2.1	1.82	800
T800H	6K12K	5590 (814ksi)	294 Medium-modulus high-strength	1.9	1.81	243/445
T1000G	12K	6370 (928ksi)	294 Medium-modulus high-strength	2.1	1.80	485
T1000	12k	7060 (1029ksi)	294 Medium-modulus high-strength	2.4	1.82	448
M35J	6K12K	5000	343	1.6	1.75	225/450
M40J	6K12K	4400	377	1.2	1.77	225/450
M46J	6K12K	4200	436	1.0	1.84	225/445
M50J	6K	4020	475	0.8	1.87	215
M55J	6K	3630	540	0.7	1.93	212
M60J	3K6K	3820	588	0.7	1.94	100/200
M30	1K3K6K12K	3920	294 Medium-modulus high-strength	1.3	1.70	53/160/320/640
M40	1K3K6K12K	2740	392	0.6	1.81	61/182/364/728
M46	6K	2550	451	0.5	1.88	360
M50	1K3K	2450	490	0.5	1.91	60/180
HM40	6K	2740	380	0.7	1.84	375
UM46	12K	4705	435	1.1	1.82	385
UM68	12K	3330	650	0.5	1.97	315
UHM, Celion GY-80		1860	572		1.96	
UHM, Thornel P-120S		2200	827		2.18	

The demand for carbon fiber is mainly in developed countries. For example, the United States aerospace technology is in a leading place and carbon fiber composite materials have been widely used. Its demand for carbon fiber accounts for 50% of the world total demand; European demand accounts for 20%, of which 50% in aerospace, 30% in sport goods; and Japanese in recreation accounts for 70%, Taiwan, Korea also needs carbon fiber mainly in sport goods.

CF manufacturers are mainly in Japan and the United States, Table 2.17 lists production capacity of major PAN carbon fiber manufacturers in 1991. There are five manufacturers which have the annual production capacity of more than 1000 tons, two in Japan (both more than 2000 tons) and three in the United States.

Table 2.17 Production capacities of major manufacturers making PAN carbon fiber in 1991 (12000 tons in total)

Country or area	Manufacturer	Brand name	Production capacity (t/a)	Source of PAN precursor
Asia	Toray	Torayca T300, M40	2250	Self production
	Toho Rayon Co	Besfight IM-40	2020	Self production
	Mitsubishi Rayon	Pyrofil	500	Self production
	New Asahi Kasei carbon fiber	Hi-Carbon	450	Self production
	Taiwan Plastic	Tairyfil	230	Courtaulds-Grafil
	Korea Steel Chemical	Kosca	150	Courtaulds-Grafil
U.S.A.	Hercules	Magnamite AS4, IM-6	1750	Sumika-Grafil
	BASF Structural Mater (Celanese)	Celion Celion G-40-600	1485	Toho Rayon
	Amoco Performance Products (Union Carbide Corp)	Thornel Thornel 300	1000	
Holland	Akzo Courtaulds-Grafil	Fortafil	360	Du Pont Rayon
Britain	Courtaulds-Grafil	Grafil	350	Self production
	R K Carbon	Sigrafil	230	Courtaulds-Grafil
Germany	ENKA	Tenax	350	Toho Rayon

2.3.6 The development of carbon fiber

The development of carbon fiber in the 1980s shows continuous improvement in performance and constant introduction of new varieties. In the 1990s, the performance didn't have much development and market demand was mainly on costs reduction, so commercial large-tow carbon fiber were developed and carbon fiber composite materials were most widely applied in the construction, transportation and other areas.

1) Constant improvement of product performance

The performance of the old varieties is continuously improved, taking Toray T300 of Japan as an example: tensile strength σ_{fu} of T300 was 2450MPa in the early 1970s; it increased to 2940$\sim$3140MPa in the early 1980s; 3300$\sim$3430MPa in the middle 1980s; and since 1988, σ_{fu} is stable at around 3530MPa.

Like Toray T300, the standard modulus high strength carbon fiber accounts for 90% of high-performance carbon fiber in the world. Similar species are Thornel T300 of Amoco, AS4 of Hercules and Celion G 30-500 of BASF and so on. The performance is that E_f is 207$\sim$235GPa, σ_{fu} is 3450$\sim$3800MPa, ε_{fu} is 1.6%.

2) The development of medium-modulus high-strength carbon fiber

Mechanical properties of composites mainly depend on the mechanical properties of reinforcing fibers. Therefore, improving the performance of fiber plays a key role in improving the performance of composite materials. Improving performance of carbon fiber is particularly important for they have been widely used in aviation industry. In fact, with the improvement of properties in the plane as well as the expansion in application of composite materials in plane parts, composite materials designers soon found that the properties of the typical T300 are low (mainly low tensile strength and low fracture strain), which can not meet the new design idea to reduce the weight of the aircraft structure, improve aircraft performance, reduce costs, save energy and other requirements. Specifically, it fails for the primary structures, such as wings, fuselage, etc. So the development of medium-modulus high-strength carbon fiber better than the T300 is extremely important.

With increasing awareness of the relationship between structure and properties of carbon fiber, remarkable development and improvement of the carbon fiber manufacturing technology emerges. To meet the aviation needs, since the 1980s, the developed countries have developed and produced a number of medium-modulus high-strength carbon fibers, which have a certain modulus, high strength, and high strain ($E_f > 270$GPa, $\sigma_{fu} > 4000$MPa, $\varepsilon_{fu} > 1.5\%$). If these kinds of carbon fibers are compounded with high toughness resin, the compression strength after impact (CAI) reflecting the toughness of composite materials will be greatly enhanced. These kinds of carbon fibers are: Hercules IM-6, 7, 8, 9 series; BASF Celion G40-600, 700,800; Toho Rayon IM-400, 500, 600, 700; BPAC company Hitex 46-8; Amoco T650/42 (E_f is 290GPa, σ_{fu} is 5037MPa); Toray F-40 (E_f is 290GPa, σ_{fu} is 5670MPa); Toray T800H (in 1984), the strength is higher than T300 of 80%; Toray T1000 (in 1986), d_f is smaller, the strength is higher (E_f is 295GPa, σ_{fu} is 7060MPa).

Table 2.18 lists grades and performance of medium modulus carbon fiber of the

Table 2.18 Properties of medium modulus carbon fiber

Companies	Grades of CF	Monofilament number of per bundle fiber (thread)	Tensile strength (MPa)	Tensile modulus (GPa)	Fracture strain (%)	Diameter of monofilament (μm)	Density (g/cm^3)
Toho	IM-400	3K6K12K	4510	295	1.5	6.4	1.74
	IM-500	6K12K	5100	300	1.7	5	1.76
	IM-600	12K	5790	285	2.0	5	1.80
Toray	M30	3K6K	3920	294	1.3	5	1.70
	T800H	6K12K	5590	294	1.9		1.81
	T1000	12K	7060	294	2.4		1.82
Hercules	IM-2	12K	4800	276	1.75	5	1.75
	IM-6	6K12K	5100	300	1.75	5	1.75
	IM-7	6K12K	5400	300	1.85	5	1.80
	IM-8	12K	5200	310	1.63	5	1.80
	IM-9	12K	6300	310	2.2	4.5	1.80
Toray	T300	6K	3530	230	1.5		1.76

three largest companies in the world. For comparison, the table also lists properties of carbon fiber T300.

See Table 2.18, compared with T300, medium modulus carbon fiber has these characteristics: ① high strength, it is higher than T300 by 50%∼100%; ② fracture strain has been largely increased, for example, IM-7 and T800H mostly used in current, it is higher than T300 by about 25%; ③ 30% higher than T300 in modulus. These indicate that medium modulus carbon fiber is the preferred reinforcing fibers, particularly T1000. However, T1000 has not been largely used because of the high cost.

Since medium modulus carbon fiber has higher fracture strain, in order to play the full role in reinforcing effect, composite matrix resin should have high toughness, including modified epoxy resin, modified bismaleimide resin and thermoplastic resin. Table 2.19 lists the performance of the typical medium modulus carbon fiber composite materials. See from the table, the compressive strength and interlaminar shear strength of medium modulus carbon fiber composite is similar to T300 composites, while tensile properties of medium modulus carbon fiber composite are significantly higher than the latter. The strength is almost doubled, modulus is increased by 20%, and fracture strain increased is by 1/3. The composite materials are outstanding in toughness. Its compression strength after impact CAI is bigger than 220MPa, and it has good damage tolerance, which suits for primary structures in bearing loading.

Table 2.19 Performance of typical medium modulus carbon fiber composite materials

Performance	Unit	T1000/ 3620	T800/ 3620	T300/ 3620	IM7/ 8551-7	IM7/ 8552	IM7/ 5245	IM7/ 5260
Tensile strength in 0°	MPa	3490	2950	1700	2863	2656	2550	2672
Tensile modulus in 0°	GPa	158	160	135	165	172	165	167
Fracture strain in 0°	%	2.0	1.7	1.2	1.6	1.6		
Compressive strain in 0°	MPa	1700	1600	1600	1600	1690		1660
Interlaminar shear strength	MPa	110	120	125	106	128		
Tensile strength in 90°	MPa	60	60	60	77		66	
Tensile modulus in 90°	GPa	9.0	9.0	9.0	8.3		9.2	
Fracture strain in 90°	%	0.7	0.7	0.7	0.9			

3) High-strength high-modulus carbon fiber of MJ series

Toray developed the corresponding MJ series with high strength and high modulus on the basis of M series in 1989. The strength of carbon fiber with high modulus was enhanced largely (see Table 2.15). The development is based on the optimization of the crystallite orientation in carbon fiber to achieve high modulus and the minimization of defects within fiber to reach high strength. Such as M40: E_f is 392GPa, σ_{fu} is 2740MPa, ε_{fu} is 0.6%; M40J: E_f is 377GPa, σ_{fu} is 4400MPa, ε_{fu} is 1.2%; the strength of M40J is higher than M40 by 63%. M65J has the highest modulus in MJ series: E_f is 640GPa, σ_{fu} is 3630MPa.

4) High-modulus pitch-based carbon fiber

In the development of high-modulus carbon fiber, thermal treatment temperature of PAN-based fiber is higher than pitch-based fiber by hundreds of degrees to get the same modulus. Union Carbide Corporation of the USA (now belongs to the Amoco Corporation) developed the pitch-based carbon fiber of P series, following P-55 (E_f is 380GPa, σ_{fu} is 2100MPa), P-75 (E_f is 500GPa, σ_{fu} is 2000MPa), P-100 (E_f is 690GPa, σ_{fu} is 2200MPa), they developed P-120 (E_f is 820GPa), P-130 (E_f is 897GPa), P-140 (E_f is 966GPa). Modulus of carbon fiber is close to the theoretical modulus. In addition, there are the Mitsubishi K-139 (E_f is 784GPa); the Dupont E-130 (E_f is 896GPa, σ_{fu} is more than 3000MPa). At present, the price of pitch-based carbon fiber with E_f more than 500GPa is 700$\sim$2200$/kg.

2.4 Aramid

Glass fiber's E is low, carbon fiber's ε_{fu} is small (brittle), organic fibers have good toughness but low strength and low modulus. Later on aromatic polyamide (PA) fiber was discovered with high strength, high modulus and good toughness. The meta-aromatic polyamide fiber (Nomex) was developed by Dupont USA in 1960, which began the development of para-aromatic polyamide fiber in 1968 and industrialized in 1972, taking merchandise known as Kevlar. Aromatic polyamide fibers are collectively referred to as Aramid, with Dupont Kevlar as a typical one. Kevlar fiber is a low-density, high-strength, high-modulus organic fiber with good corrosion resistance. It is currently the most widely used high modulus organic fibers in composite materials.

2.4.1 High modulus organic fiber

The high performance fibers have three common characteristics in the structure: very high molecular orientation (crystallinity); orderly lateral arrangement and very low content of axial defects. Any kind of organic polymer, as long as it has the above structural characteristics, can become a high performance fiber. Successful and commercialized high-performance organic fibers are mainly shown in the following.

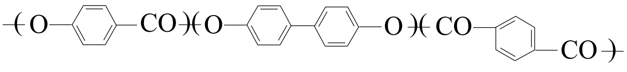
1) Organic fibers with rigid molecular chain

(1) Aromatic polyamide fibers (aramid). Aromatic polyamide is connected by

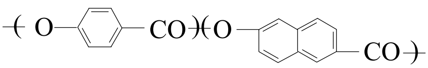
single bond. The main commodities have Kevlar (Dupont), Twaron (Akzo), Technora (Teijin), Armos (Russia) and so on.

(2) Aromatic polyester fiber. Terephthalic acid (ester) and hydroquinone condensation polymerize into aromatic polyester. Because it has a bad fibrillation and co-component is often introduced, so in fact the full-aromatic polyester is copolymer fiber, also known as polyarylester fiber. Its main commodities are Ekonol (Sumitomo Chemical Co), (E_f is 136GPa, σ_{fu} is 3822MPa, ρ_f is 1.40g/cm^3, ε_{fu} is 2.6%, T_m is 350°C); Vectran (Kuraray- Celanese), (T_m is 250°C); Vectran/high-strength (E_f is 74.5GPa, σ_{fu} is 3270MPa, ρ_f is 1.41g/cm^3, ε_{fu} is 3.9%); Vectran/high-modulus (E_f is 106GPa, σ_{fu} is 2658MPa, ρ_f is 1.37g/cm^3, ε_{fu} is 2.4%). The maximum use temperature of aromatic polyester fiber is 150°C.

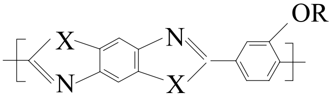
Ekonol:



Vectran:

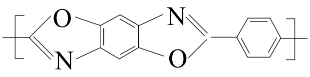


(3) Polybenzoxazole (PBO) fiber. Poly (p-phenylene benzobisoxazole) (PBO) belongs to aramatic polymer with multiple (double) bonds connected. The similar ones are poly (p-phenylene benzobisthiazole) (PBZT), poly (p-phenylene benzimidazole) (PBI). The main commodities are Zylon (Toyobo -Dow Chemical): E_f is 280GPa, σ_{fu} is 5800MPa, ρ_f is 1.56g/cm^3, ε_{fu} is 2.5%. Both Akzo and DuPont have PBO fiber merchandise.

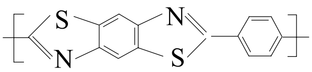


X=O, S, NH

PBO



PBZT



2) Organic fibers with flexible molecular chain

(1) Polyethylene (UHMWPE) fiber.The main commodities of UHMWPE fibers are Spectra (Allied Signal), Tekmilon (Mitsui Petro-Chemical), Dyneema (Toyobo-DSM), and so on. Such as Spectra1000 (E_f is 172GPa, σ_{fu} is 3090MPa, ρ_f is 0.97g/cm^3, ε_{fu} is 3.0%).

(2) Polyvinyl alcohol fiber. Kuralon K-II (Kuraray).

2.4.2 Types of aramid

Aramid includes meta-aromatic polyamide fibers and para-aromatic polyamide fiber. The latter has a prominent high strength and high modulus and is used for advanced composite materials. Kevlar fibers belong to this category.

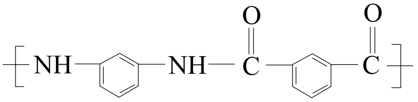
Kevlar fibers have a lot of varieties, including Kevlar, Kevlar-29, Kevlar-49, Kevlar-68, Kevlar-100, Kevlar-119, Kevlar-129, Kevlar-149 and Kevlar M/B and so on. These different kinds of products are for different purposes, the main species are Kevlar, Kevlar-29 and Kevlar-49. Kevlar is mainly used to reinforce plastics and rubber products; Kevlar-29 is mainly used in ropes, cables, and bullet-proof device; Kevlar-49, Kevlar-119, Kevlar-149 are applied in composite materials, in which Kevlar-49 is the most widely used.

Besides Kevlar series, there are SVM and Armos which were produced by the former Soviet Union; HM-50 of Japan Teijin company, etc.; Kevlar-1414 was developed by Shanghai Synthetic Fiber Research Institute in China in 1985. It is estimated that total production capacity of aramid in the world has reached 36,000t/a, Dupont Group (including the three plants in the United States, Britain and Japan) accounts for 29,250 t/a.

Aramid fiber is mainly used in space, aviation, national defense industry, shipbuilding and other fields, such as rocket motor casing, bullet-proof glass, aircraft interior materials, radome, high pressure cylinders, high pressure corrosion containers, hull and so on.

1) Meta-aromatic polyamide

The structure of poly (m-phenylene isophthalamide) is given by



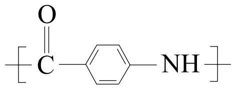
The trade names are Nomex by Dupont in the United States, Teijinconex by Teijin Japan, Kevlar-1313 by China and so on. Compared with ordinary organic fiber, which is characterized by good high temperature properties (maintain high strength in high temperature), good insulation properties (small thermal conductivity), good dimensional stability (small thermal expansion coefficient), with self-extinguishing flame retardant, and good oxidation, good hydrolytic stability, good chemical corrosion resistance, good anti-static properties; but strength and modulus are still relatively low, so it can not be used as the reinforced fiber for structural composite materials, which is mainly used as Nomex honeycomb.

2) Para-aromatic polyamide

P-aramid (p-aromatic polyamide) has two kinds of molecular structures.

(1) Poly (p-benzamide).

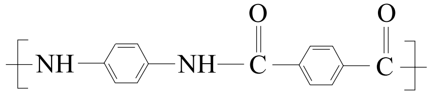
Poly (p-benzamide) fiber is made from polycondensation of p-aminobenzoyl chloride through spinning, and its molecular structure is shown.



This kind of fiber are "B" fiber which was produced by Dupont in the United States early, PRD-49-1, HGA of the former Soviet Union and aramid I in China (aramid -14).

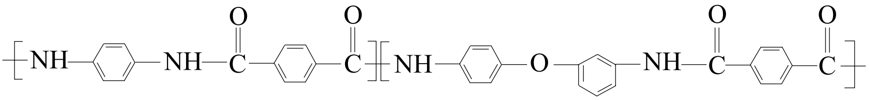
(2) Poly (p-phenylene terephthalamide).

Poly (p-phenylene terephthalamide) is made from polycondensation of p-phenylenediamine and terephthaloyl chloride through spinning, abbr. PPTA fiber. Its structure is shown:

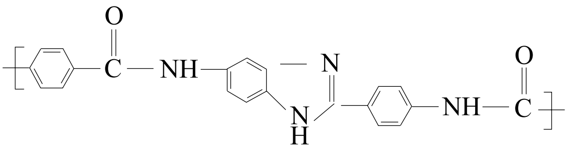


Goods of this fiber type are Kevlar of Dupont, Twaron of Netherlands Akzo, Aramid II of China (Aramid-1414) and so on. Others with similar structures are Teijin Technora of Japan, Armos of the former Soviet Union. Kevlar-49 has good performance as the reinforced fiber of structural composite materials; Kevlar-29, Kevlar-129 for civilian using, such as rubber cord; Kevlar-149 is the second generation of lightweight, high-strength Kevlar fiber, its modulus is higher than Kevlar-49 by 40% and specific modulus almost reaches the level of high-strength CF.

Technora used 3, 4 '-diamino diphenyl ether to modify poly(p-phenylene terephthalamide), the base polymer is copoly(1,4-phenylene/3,4'-diphenylether terephthalamide), and its structure is shown:

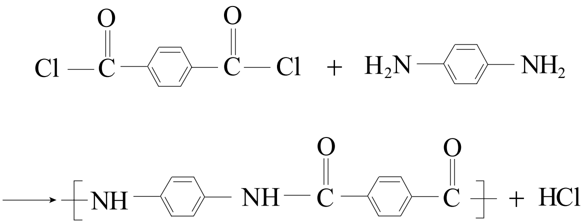


Armos (F-12 fiber called at home) is nitrogen heterocyclic aromatic polyamides or polyamide benzimidazole. The base polymer is copoly[p-phenylene/5-amino-2-(p-aminophenyl)benzimidazole terephthalamide] and its structure is shown:



2.4.3 Preparation of kevlar fiber

Preparation of aramid fiber has two steps, polycondensation and spinning. Poly (p-phenyleneterephthalamide) (PPTA) is from polycondensation of para-phenylene diamine and terephthaloyl chloride, the chemical reaction is expressed:



There are three typical polycondensation ways for producing Kevlar in Dupont Group which are intermittent polycondensation, continuous polycondensation and gas polycondensation. For intermittent polycondensation, the monomer solution is put into the reactor, and then the polymer is obtained after the polycondensation under nitrogen. This method uses intermittent process and has low equipment utilization, which halts large-scale production. DuPont developed the continuous polycondensation, which largely reduced the cost of polymer. The produced polymer is then spinned once more. Both of the technologies include the polycondensation (two steps of condensation reaction in continuous polycondensation) of p-phenylenediamine, terephthaloyl chloride and solvent after they are put into the reactor and the removal hydrochloric acid and solvent afterwards. For gas polycondensation, we get the product from gas polycondensation of p-phenylenediamine, terephthaloyl chloride and nitrogen after they were put into the reactor. This approach does not need solvents, thus the product has a high purity, and the obtained fiber has good properties.

The obtained polymer by the mentioned ways above will turn into final fiber after spinning process. Spinning process includes preparation of spinning solution, jetting, dry-wet spinning, solution extraction and washing, drying and other steps. Spinning solution is prepared with concentrated sulfuric acid and poly (p-phenyleneterephthalamide), so after drawing out the fiber, the solvent extraction and washing should be carried out to remove sulfuric acid. Kevlar-29 can be obtained after drying. Kevlar-49 can be obtained if heat treatment goes under nitrogen at 550°C. The fiber has further improvement in strength, particularly in modulus. The production technological process of Du Pont typical Kevlar fiber is shown in Fig. 2.11.

1) Technique flow of spinning

$$\begin{array}{c}\text{Polymer}\\ \text{PPTA}\end{array} \xrightarrow{\text{Dissolved in concentrated sulfuric acid}} \begin{array}{c}\text{Spinning}\\ \text{solution}\end{array} \xrightarrow{\text{Dry-wet spinning}}$$

$$\begin{array}{c}\text{Washing, drying}\\ \text{(Kevlar-29)}\end{array} \xrightarrow{\text{Heat treatment}} \text{Kevlar-49}$$

2) Spinning solution

The spinning of PPTA usually uses concentrated sulfuric acid as solvent to form macromolecules with liquid crystal nature for spinning. This lyotropic liquid crystal system can be changed from isotropic into anisotropic under certain conditions, also said liquid crystal state solution. Polymer will orient in the solution, under the outside shear stress the polymer molecules orient easily along the direction of shear stress, which is conducive to spinning.

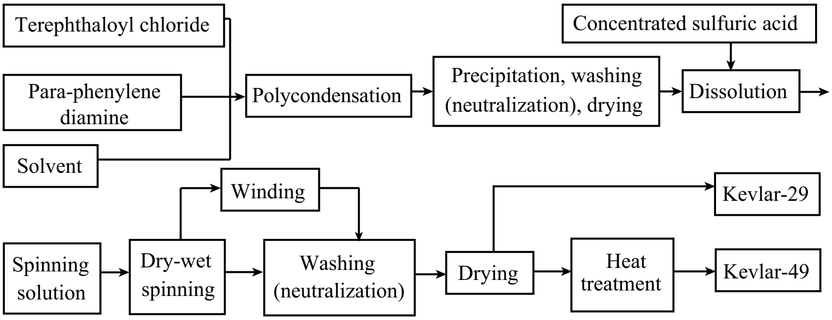


Fig. 2.11 Production technique process of Kevlar fiber.

Liquid crystal (LC) is the middle phase between crystal and liquid, which has mobility and continuity of liquid on the macro and order of crystal on micro view, and anisotropy in light, electricity, and force on the nature. LC has three categories. Nematic liquid crystal: molecular arrange in axial direction; smectic liquid crystal: molecular layered arrangement; and cholesteric liquid crystal: molecular layered arrangement with spiral structure. Solution for the spinning is nematic liquid crystal, whose molecular chain arranged in accordance with a direction in the liquid (because PPTA has a big rigid molecular chain, and it is in rod-like order). This is just like match in the matchbox, matches can roll or slide back and forth in the matchbox, but always parallel to the long axis of the matchbox. Such nematic liquid crystal molecules flow easily through each other, and lower viscosity than the isotropic liquid; under the outside shear stress the molecules can easily go orient along the stress direction, very favorable to fiber forming.

LC is the thermodynamic steady state, so orientation would not be lost after spinning. But the temperature and concentration should be in good control in order to ensure that the spinning solution is a very good LC solution.

Fig. 2.12 shows the relationship between viscosity and the solution concentration. We see that there is a critical concentration: when the concentration is lower than the critical concentration, viscosity will be increased with the increase of concentration; but when it is equal to the critical concentration, the viscosity will be decreased (because the molecular chain arranges along the flow direction). Since at the critical concentration, the solution will change from isotropic to anisotropic. At the largest concentration of liquid crystal, the viscosity began to increase with the increase of solution concentration. We can see that PPTA solution has the characteristics of high concentration and low-viscosity.

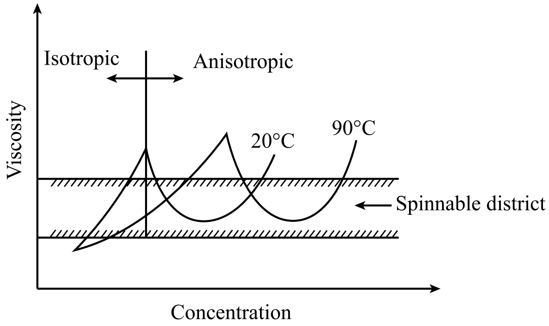


Fig. 2.12 The relationship between viscosity and concentration of PPTA solution.

Relationship of solution viscosity and temperature is the same with that in the above, the temperature increases, the viscosity of LC solution drops, but after dropping to a minimum value, the temperature increases again the viscosity has a substantial increase, at the same time the solution changes from the anisotropy to isotropic.

Visibly, PPTA dissolved in concentrated sulfuric acid in a certain temperature and a certain concentration to form the nematic liquid crystal solution, with high concentration and low viscosity, which is conducive to spinning.

3) Dry-wet spinning

The technique process to prepare the Kevlar fiber using dry-wet spinning method is shown in Fig. 2.13. During the process, liquid crystal solution goes through dry

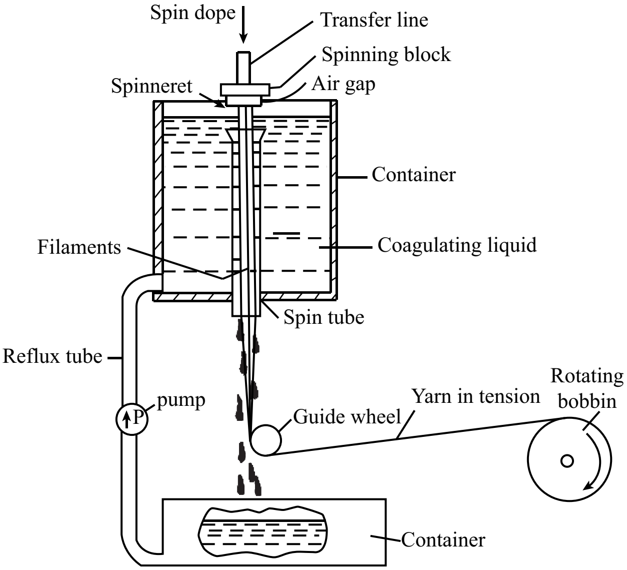


Fig. 2.13 The dry-jet wet spinning process of producing Kevlar fiber.

jet and wet spinning, hence the name.

$$\begin{array}{llll} \text{PPTA} & \longrightarrow \text{Transfer line} \longrightarrow & \text{Spinneret (porous leakage plate)} & \longrightarrow \text{Air gap} \\ H_2SO_4 \text{ solution} & & \text{Heating to } 100^\circ \text{C} & T\downarrow \to \eta\uparrow \end{array}$$

$$\begin{array}{llll} \longrightarrow \text{Water (washing)} & \xrightarrow[\text{Under tension}]{\text{Drying}} \text{Kevlar-29} & \xrightarrow{\text{Heat treatment}} & \text{Kevlar-49} \\ \text{Concentration}\uparrow & \text{Crystallinity at } 94\ \% & & 96\%, T_m\ 570^\circ \text{C} \\ T\downarrow \to \eta\uparrow & & & \end{array}$$

4) Heat treatment

The dried Kevlar-29 becomes Kevlar-49 when we impose tension on it in nitrogen or inert atmosphere for subsection heat treatment in 150∼550°C, then we get Kevlar-49. Heat treatment is for the further orientation of molecular chain, improving the crystallization degree (96%), so that $\sigma \uparrow$, $E \uparrow$ but $\varepsilon_{fu} \downarrow$.

Preparation of Kevlar-49 fiber is shown: Using high-concentration and high-temperature PPTA solution to spin at a high speed into the low-temperature liquid coagulation bath through a spinning tube to form a tow. It is winded on spool and then washed and dried in hot rollers under tension. Kevlar-49 will be obtained after heat treatment in inert gas at high temperature.

2.4.4 The structure of kevlar fiber

1) Chemical structure

PPTA molecules has little entanglement and strong rigidity. Fig. 2.14 shows the planar molecular arrangement of Kevlar fiber. After appropriate heat treatment, Kevlar fiber can be made with a higher degree of orientation and crystallinity. Kevlar is a molecular chain composed of the benzene ring and amide groups in accordance with a certain rule. The amide group locates at the para position of benzene ring, so that the polymer has a good regularity, thus with a high

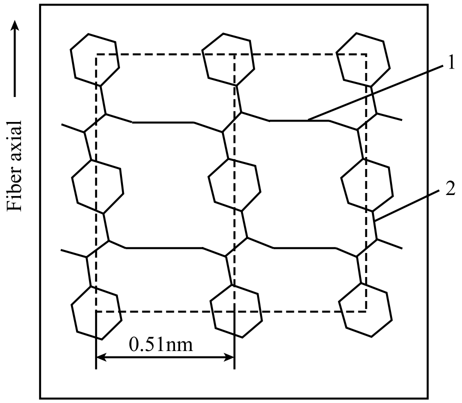


Fig. 2.14 Arrangement in molecular plane of kevlar fiber: 1-weak hydrogen bonds; 2-strong covalent bond.

crystallinity. This rigid linear chain is highly oriented at the fiber axial direction. The hydrogen atom in molecular chain combines with carbonyl in adjacent chain together to form hydrogen bond as the transverse link of polymer molecule.

Compared with other fibers, Polyester fibers (PET): flexible chain between benzene rings (ethylene glycol ester), the orientation degree is 84%; Nylon fibers (PA): flexible aliphatic molecular chain, has hydrogen bonds among molecules, the crystallization degree is 91%∼94%; Kevlar-49: its main chain is similar to polyester, but it is amide bond and there is hydrogen bond among molecules into a trapezoidal cross-linked polymer, and the crystallization degree is 96%; CF: microcrystalline graphite, more compact structure.

Three characteristics of Kevlar-49's chemical structure are shown: ① containing many benzene ring, difficult internal rotation, it is a rigid straight-chain crystal. ② Benzene ring and amide bond are arranges alternately, all at the para position, has good regularity, good symmetry and good crystallinity. ③ It has hydrogen bonds between the molecules to form a ladder compounds.

The impact of its structure on the performance: ① high modulus: molecular chain is rigid so that the molecular chain is difficult to rotate. Polymer molecules can not be folded and stretched into a rod-like structure and has very high crystallinity so that it has high modulus. ② High strength: polymer molecules arrange closely, and the number or molecular chain per unit area is great, so the fiber has high strength. ③ Anisotropic: along the fiber direction are strong covalent bond, and in the transverse are weak hydrogen bonds, which is the main reasons for anisotropy of the mechanical properties of fibers. ④ Toughness better than CF: the main chain still has flexible linkage. ⑤ Good heat resistance, good dimensional stability: because of the rigidity of benzene ring and the nature of crystal of the polymer, fiber is dimensionally stable at high temperature. For example, pyrolysis does not happen. There is no large change in its enthalpy, which makes fiber to have no plasticity at high temperature. ⑥ Good corrosion resistance: because of the conjugation of electron in benzene ring the fiber has chemical stability.

2) Microstructure

$$\text{Oval flake structure} \xrightarrow{\text{Composition}} \text{Fibril} \xrightarrow{\text{Composition}} \text{Fibril layer} \xrightarrow{\text{Composition}} \text{KF}$$

The structure of Kevlar fiber: stratification can be seen clearly from observation on SEM fractograph of Kevlar-49 monofilament tension, longitudinal splitting of monofilament became much thinner fibers, which is called fibril. From the scanning electron microscope of corrosion samples, we can see that a lot of fibrils parallel to the fiber axis orient and bend periodically to form the layers, which arrange parallelly to each other, and then Kevlar fiber will be obtained. Therefore fibril is the basic structural unit reflecting macro-mechanical properties of aramid fiber.

Fibril is 0.4μm in width, varies in length even up to dozens of μm. And fibril is composed of overlapping the smaller structure units - oval-shaped sheet structure (Fig. 2.15). Oval-shaped sheet structure is about 0.7μm in the long axis, 0.4μm in the short axis. Molecular chains impenetrate each other on the overlapping part. There still is periodic bending of fibril layers (cycles is about 2μm), but the overall direction coincides with fiber direction.

Oval-shaped sheet structure is ordered micro-region of liquid crystal. When using PPTA nematic liquid crystals solution for spinning under shear, the ordered micro-region orients and slides to form fibril structure overlapping each other.

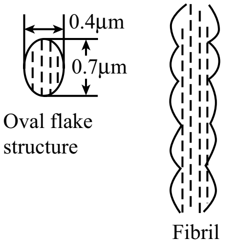


Fig. 2.15 Schematic of oval flake structure and fibril.

2.4.5 Properties of kevlar-49 fiber

1) Mechanical properties

(1) High elastic modulus. Tensile modulus of Kevlar-49 fiber E_f at 125GPa, is much higher than common organic fiber, about 2 times of GF, but is lower than CF. Kevlar fiber has so high tensile modulus and strength because it has complete straight chain crystal structure and high crystal degree.

(2) High strength. Tensile strength of Kevlar-49 fiber σ_{fu} is 3620MPa, which is equivalent to strength of S-GF or CF-II. It comes from the higher acumulating density of molecule chains and the more molecule chains in per unit area.

(3) σ-ε curve is straight line, and it has characteristics of brittle materials. Its break elongation ε_{fu} is at 2.5%, which is higher than CF but lower than GF. ε_{fu} of domestically produced aramid 1414 is 4%∼6%. It accounts for inadequate crystallization degree.

(4) The lowest density. Density of Kevlar-49 ρ_f is 1.45g/cm^3. It is lower than GF and CF, bringing about higher specific strength.

(5) Good toughness. There is still soft chain unit among benzene rings on the main molecular chains, fibrils are periodic bending, and molecules are linked by hydrogen bond. All these result in some toughness of fibers.

(6) Anisotropic. Molecular chains are straight in axial and linked by chemical bond, while molecular chains in transverse are only linked by hydrogen bond with lateral association, so the fiber has characteristic of anisotropic. Its lateral strength and modulus are much lower than longitudinal strength and modulus.

(7) Lower torsion and compression properties. These are the fatal weakness of aramid. Bad torsion and compression properties come from secondary bond among molecules and bending of molecular chains. It will easily delaminate under compression or torsion.

(8) High dispersed strength. There are still defects such as voids in fiber and on the surface of fiber. They also look like other brittle fibers which have high dispersity of strength. Strength is relevant to the standard test length.

(9) Good textile performance. The strength of weaved fibers can still retain over 90% because of their good toughness. But effect of twist (torsion) on the strength of Kevlar is greater than other fibers. The bigger the twist is, the bigger the strength lost.

(10) Good creeping resistance and fatigue resistance.

There is a specific manifestation in composites of characteristics of mechanical properties above all of Kevlar fibers.

Table 2.20 shows properties of untwisted yarn Kevlar-49 and Kevlar-149. From Table 2.20, we know that elastic modulus of Kevlar-149 is 40% higher than Kevlar-49, but its tensile strength and break elongation are lower than Kevlar-49. Table 2.21 shows tensile properties of epoxy resin impregnated yarns. From Table 2.21, we know that properties of Kevlar fiber are better than E-glass fiber, while specific tensile modulus of Kevlar-149 is approximately the same as high-strength carbon fiber. Its specific tensile strength and fracture strain are both higher than high-strength carbon fiber.

Table 2.20 Properties of untwisted Kevlar yarn

Properties	Kevlar-49	Kevlar-149
Density (g/cm^3)	1.44	1.47
Initial modulus (GPa)	129.6	163.2
Second modulus deform at 1% (GPa)	136.3	180.6
Tensile strength (MPa)	3312	2646
Fracture strain (%)	2.5	1.45
Equilibrium moisture content ,22°C,65%RH (%)	4.3	1.2

Table 2.21 Tensile properties of epoxy resin impregnated yarns

Properties	Kevlar-49	Kevlar-149	E-GF	HS-CF
Tensile modulus (GPa)	172-179	124-131	69	227
Specific tensile modulus (10^{6}m)	12.2	9.0	2.76	13.3
Tensile strength (MPa)	3447	3620	2410	3585
Specific tensile strength (10^{3}m)	240	256	99	203
Fracture strain (%)	1.8-1.9	2.9	3.5	1.5

2) Thermal properties

Kevlar-49 fiber has good thermal stability and low temperature resistance. It has fire resistance and nonflammable. It can not melt at high temperature while it will be carbonized rather than melt at 427°C (T_m is 570°C, $T_{carbonation}$ is 427°C). It will not deform until decomposition (T_d is 500°C). It still retains its properties and is not brittle at -196°C.

The T_g of Kevlar-49 is 327°C, but the temperature that the fiber used for a long time in air is lower than 160°C. When Kevlar-49 yarn in 1000 den is stored at 93°C in the air in long-term, its strength retention is 87% and elastic modulus retention at 89.7%. When thermal aging at 280°C for 1000h, retention of σ at 19.4%, retention of E at 26.2%. Fortunately, when it is exposed over 300°C for a short time, there is little influence on strength, so the used temperature for a short time can be 300°C.

The thermal expansion coefficient of Kevlar-49 is anisotropy. Thermal expansion coefficient in axial of Kevlar-49 is minus. It is -2×10^{-6}/°C from 0°C to 100°C and -4×10^{-6}/°C from 100°C to 200°C. Its thermal expansion coefficient in transverse is 59×10^{-6}/°C. This should be considered for producing Kevlar-49 fiber composites.

3) Chemical properties

Kevlar is almost free from the impact of organic solvents and oil except for strong acid and alkali. Kevlar-49 has the capability of erosion resistance to various organic solvents such as acetone, benzene, carbon tetrachloride, dimethylformamide, aviation fuel, and so on. The existence of amide bond is intolerance to strong acid (concentrated sulfuric acid, concentrated nitric acid) and strong base effects.

Due to the existence of a large number of benzene rings, aramid fiber is poor at UV-resistant. When it was exposed in the sun for a long time, loss of strength of aramid is great, so it should be in dark storage.

In saturated humidity, Kevlar-49 can absorb water by weight of 6% from the atmosphere, and its saturated absorption rate is high. After that, because water molecules penetrate in fibers, it destroys hydrogen bond, so that fiber strength decreases, compressive properties and bending properties of composites decrease. Saturated moisture absorption rate of Kevlar-149 decreases largely than Kevlar-49, so water resistance increases. Therefore, when using Kevlar-49 to produce composites, the fiber must be processed in a predry treatment at 80°C for 24h.

4) Other properties

(1) The poor interface bond between Kevlar and resin, which is even worse than CF.

(2) Dielectric properties of Kevlar are better than GF, so it can be used as radomes for wave-transparent materials.

We know that compared with carbon fiber, characteristics of Kevlar-49 are high tensile strength, but lower modulus than CF; good toughness, high impact strength; low density. But bad torsional resistance and compressive resistance, bad water resistance and UV resistance. The fatal defects of KFCM composites are low compressive strength and low interlaminar shear strength. Kevlar-49 fiber is suitable for combining with carbon fiber and preparing hybrid composites.

2.4.6 Varieties and specifications of kevlar fiber

It is the same as other fibers, Kevlar fiber can be made into a variety of continuous long-fiber rovings and yarns. Then they can be made into a variety of textile fabrics or unidirectional tape, or it can be directly used for filament winding and pultrusion moulding. Types of woven are the same with glass fiber, there are plain weave, twill, and satin; the size of yarn is usually expressed by den. There are also the products of aramid short fibers and aramid pulp.

Table 2.22 shows specifications of Kevlar-49 fabric products. It includes fabric types and models (light weight fabric, medium weight fabrics, unidirectional fabrics, roving fabric), weight of fabric (G_f, g/cm^2), structure of fabric (weave density, end/cm, 13×3), linear density (den), type of weave, thickness of fabric, etc. The organic fiber fabrics listed in Table 2.22 are similar to glass fiber fabric in structures and suitability of application. For example, thin cloth 120 with light weight uses on the surface layer of composites. Medium weight of clothes are mostly used in common, in which the plain and twill fabrics are suitable for forming parts with simple shapes, and the satin fabric for manufacturing parts with special shapes, cone and hyperboloid.

Table 2.22 Specifications of Kevlar-49 fabric

Types	Models	Fabric weight (g/m^2)	Weave density (end/cm)		Tensile breaking force (N)		Linear density (den)	Weaving types	Thickness of fabric (mm)
			warp	weft	warp	weft			
Light weight fabric	120	61	13	13	480	447	195	Tabby	0.114
	220	75	9	9	525	530	380	Tabby	0.114
Medium weight fabric	181	170	20	20	1190	1170	380	Satin	0.114
	281	170	7	7	1161	1161	1140	Tabby	0.254
	285	170	7	7	1110	1130	1140	Diagonal	0.254
	328	230	7	7	1125	1340	1420	Tabby	0.330
	335	230	7	7			1420	Diagonal	0.304
	500	170	5	5			1420	Tabby	0.279
Unidirectional fabric	143	190	39	8	2321	223	380/195	Diagonal	0.254
	243	190	15	7	2678	536	1140/380	Diagonal	0.330
Woven roving	1050	360	11	11			1420	4×4 basket	0.457
	1033	510	16	16			1420	8×8 basket	0.660
	1350	460	10	9			2130	4×4 basket	0.635

Table 2.23 shows the properties comparison of Kevlar-49 with other yarns. Table 2.24 shows the properties comparison of different types of Kevlar fibers.

Table 2.23 Properties comparison of Kevlar-49 with other yarns

Projects	Kevlar-49	Armos	PA728	Polyester 68	CF-II	E-GF	Stainless steel
σ_{fu} (MPa)	2760/without resin 3620/impregnated resin	4414	990	1120	2760	2410	2720
E_f (GPa)	124	124.4	5.5	13.8	221	69	200
ε_{fu}(%)	2.5	3.2	18.3	14.5	1.25	3.5	2.0
ρ_f (g/cm^3)	1.44		1.14	1.38	1.75	2.55	7.83

Table 2.24 Properties comparison of different types of Kevlar fibers

Projects	σ (MPa)	E_f(GPa)	ε_{fu}(%)	Moisture absorption rate (%)
Kevlar-29	2970	36.7	3.6	
Kevlar-129	3430	52.8	3.3	
Kevlar-49	3620	152/124-131	2.5	4.6
Kevlar-149	3433	165/172-179	1.8	1.1

2.4.7 Application of aramid

Composites reinforced by aramid fiber have low density, high special strength and specific modulus, good tensile fatigue properties, good toughness, but low compressive strength and interlaminar shear strength, and difficulty in cutting process. Applications of aramid and its composites are introduced in following.

(1) The aerospace field. In aviation, it is mainly used for a variety of fairing, front wings, flap, rudder, stabilizer tip, tail cone, emergency export system, window frame, ceiling, bulkhead, floor, door, luggage rack, and seating, etc. The use aramid composites can reduce the weight by 30% comparing with glass fiber composite materials. To reduce weight and improve economic efficiency, generally, aramid composites have been widely used in commercial aircraft and helicopters. For example, the total volume of aramid composites used on Samsung-style aircraft L-1011 is 1135kg, and the weight of aircraft reduces by 365kg. The volume of aramid composites on outer surface of commercial helicopters S-16 reaches 50%. The mixture of aramid with CF manufactured lightweight composites components of Boeing 767 and 777. Aramid laminated hybrid reinforced aluminum (ARALL) as a new type of aviation structural material has been successfully used in aircraft. In space, it mainly used for solid rocket motor casing and pressure vessel, spacecraft cockpit, container of oxygen, nitrogen and helium, and ventilation duct, etc.

(2) Electrical and electronic related fields. We use heat resistant epoxy resin to impregnate non-woven aramid fabric for preparing high-grade printed circuit board.

(3) Civil construction field. Because aramid has light weight, high strength, corrosion-resistant, non-magnetic, non-conductive properties and so on, it has been widely used in the field of civil engineering. Typical applications include

concrete reinforced by short fiber of aramid, materials of aramid reinforced resin to replace steel bar, curtain wall, reinforced bridge, etc.

(4) Aramid composites used in ship-building industry, the effect of lightweight is better than glass fiber reinforced plastic and aluminum, the hull can reduce weight by 28% to 40%. Fuel saves by 35% and navigation route can extend by 35%.

(5) In sports, it has been successfully used for many sport equipments, such as a mixture of aramid with wood in hockey stick, a mixture of aramid with carbon fiber in golf club, tennis racket, javelin, bow, fishing rod and skis. In mixed structure, aramid improves the tensile strength, impact and economic properties of composites.

(6) Making compressed natural gas tank and breathing apparatus for diving, etc.

(7) For protective material, such as tank, armored vehicle, aircraft, protective plate of boat, helmet and bullet-proof vests, etc.

(8) Aramid has these characteristics such as high strength, light weight, stability size and so on, thus it can also be used for coating fabric. It is especially suitable for the coating of structure building supported by air and inflatable coating fabric products such as rubber boat, life raft, inflatable bridge, blimp, balloon, special clothes and aircraft fuel bladder, etc.

2.5 Other reinforced fibers

2.5.1 Boron fiber (BF)

Advanced boron fiber (BF) was firstly developed by American (at the end of 1950s), which was mainly used for manufacturing resin matrix and metal matrix composite materials. It had a glorious moment for its successful application in aviation and space technology until carbon fiber appeared. The production process of CF is simpler and cheaper than BF and it offers equivalent performance. With the properties of carbon fiber being constantly improved, the occasions of using BF have been gradually replaced by CF. The United States and Europe still retain a certain amount of production of BF, which is mainly used in metal matrix composites, because some properties of BF are superior than carbon fiber and other fibers, such as modulus and longitudinal compressive properties.

1) Fabrication of BF

The melting point of boron is 2050°C, and it has the nature of brittleness and hardness (close to diamond), so the fiber cannot be made with melt drawing method, people usually use vapor deposition method to deposite the reverted boron vapor on the other fibers, such as W wire, CF and Al wire, then get composite system of boron-tungsten core fiber, boron-carbon core fiber and boron-aluminum core fiber.

From the source of boron vapor (raw materials), there are two methods for fabricating BF which are halogenation and organic metallization.

(1) Halogenation.

BCl_3 and H_2 are heated up to above 1000°C when B will be reverted on W wire or CF. It is a mature technology method, the obtained BF has high performance and high cost as well (because of high price of W wire and high deposition temperature).

① Preparation of BF with tungsten core by halogenation process.

W wire → Cleaning room → Deposition section → (Coating room) → BF
12.5μm H_2, 1200°C BCl_3+H_2, 1350°C Protective layer

Tungsten wire with diameter of 12.5μm for manufacturing boron - tungsten core fiber is heated by electric current, then through the cleaning room, tungsten wire is heated up to 1200°C in hydrogen to remove dirt and oxide on the surface, then it get into the reaction section with equal amount of mixed H_2 and BCl_3 and the maximum temperature of this region is 1350°C, then the reverted boron vapor will deposite on tungsten filament. Usually the diameter of this boron fiber is 100μm. Fig. 2.16 shows the entire production process, glass tube with inner diameter at about 1cm and length at about 2m is used as the reactor, and the inlet and exit are sealed with mercury to provide contact circuit, and cut off reactive gases from the outside. The output is 2 pounds per week. As the application of metal matrix composites, coating room should be added to form protective layer with thickness of 2μm to 4μm on the surface of boron fiber, such as B_4C_3.

The chemical reaction of boron deposition is expressed:

$$2\,BCl_3+3H_2 \longrightarrow 2B+6HCl$$

But actually only 2% weight of BCl_3 deposited on tungsten wire, and the unreacted BCl_3 is recycled under condensation temperature of 80°C, so the production cost is very high. In addition, the vapor deposition speed can not be too fast, otherwise there will form some crystal spots on tungsten, which become the weak point of boron fiber, making the tensile strength less than 1379MPa. Similarly, too slow speed will also decrease the tensile strength. Factors that affect the deposition rate are speed of reactants, flux, concentration of by-product chloride hydrogen, and temperature of coated substrate.

② Preparation of BF with C-core by halide process.

CF → Graphite pyrolysis section → Deposition section → (Coating room) → BF
H_2+CH_4 BCl_3+H_2, 1350°C Protective layer

Cleaning room is replaced by graphite pyrolysis section in manufacturing boron-carbon core fiber. Coal tar pitch carbon fiber with diameter of 33μm goes through the graphite pyrolysis section and a layer of pyrolytic graphite is painted on carbon fiber. Then it gets into boron deposition section and boron deposits on the surface of carbon fiber. See Fig. 2.16, for preparing boron fiber with carbon core, temperature of reaction chamber is higher than the temperature of preparing boron tungsten fiber, deposition rate increases by 40% which reduces the cost of carbon core BF.

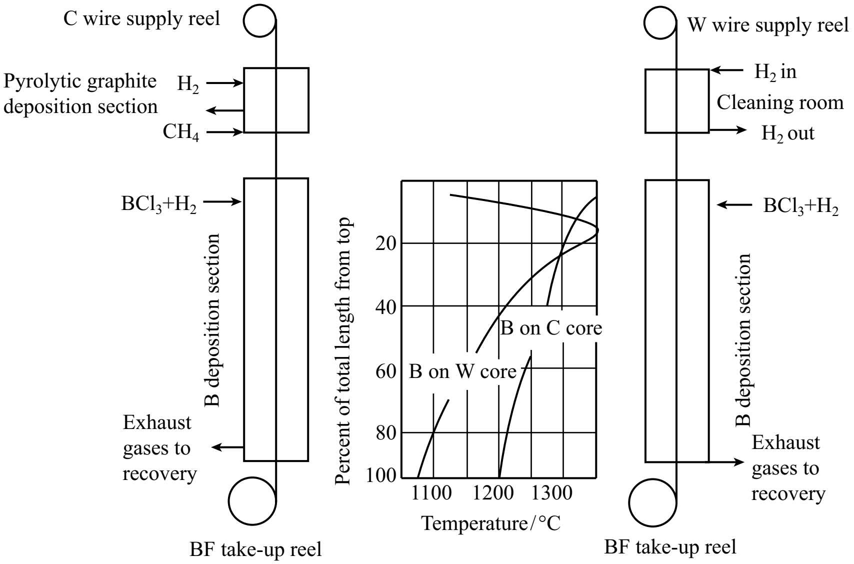


Fig. 2.16 Flow chart of boron deposition and temperature distribution of reactor.

(2) Organic metallization method. Organic metallization method is a way that boron sediment on the substrate wire by decomposing organic boron compounds at high temperature such as triethyl boron or borane compounds (B_2H_6 or B_5H_4). Because the deposition temperature is lower than 600°C, Al wire can be used as the core wire, so it greatly reduces the cost of boron fibers, but decreases the using temperature and properties as well.

2) Structure and form of BF

Boron fiber belongs to composite fiber: The core is W wire with diameter in a range of 12μm to 25μm. Then outside the W wire, there is the B-W area where the element B diffuses to the surface of W, reacts and forms WB, W_2B_5 and WB_4, etc. Further outside, the surface of the fiber is covered with amorphous boron. With corn-on-the-cob structure, the surface of BF with tungsten core is very rough, showing tumor-like form, so it gives good bonding strength with resin. The surface is smooth after coating B_4C_3. For Boron fiber with carbon core, since carbon core undergone the process by pyrolysis gas, the surface is relatively smooth, and it can maintain the smooth surface after boron deposition. Therefore the bonding strength with resin and transverse strength of composites are lower.

3) Properties of BF

Table 2.25 shows the mechanical properties of boron fiber with tungsten core and carbon core.

Table 2.25 Typical mechanical properties of boron fiber with tungsten core and carbon core

Projects	d_f (mm)	ρ (g/cm^3)	σ_b(MPa)	E (GPa)
BF-W core	0.1	2.59	3450	400~414
BF-W core	0.14	2.68	3520	400~414
BF-W core	0.11	2.1	3250	365
BF-W core	0.2	—	3650	—

In boron fiber with carbon core, the volume of carbon core is 10%, while tensile elastic modulus of this carbon fiber is only 34GPa. Thus if both boron fibers have a diameter of 100μm, the elastic modulus of boron fiber with tungsten core is 400GPa while the elastic modulus with carbon core is 358GPa, though the latter has advantages of low density and low cost. The density of boron fiber with carbon core is 2.22g/cm^3, while with tungsten core fiber is 2.59g/cm^3. The average tensile strength of boron fiber with carbon core which prepared by AVCO corporation in the United States is 3254MPa and the average tensile modulus is 362.6GPa.

When heat aging at less than 200°C in the air, the performance of boron fiber does not change; when aging at 330°C for 1000h, the strength decreases by 70%; it almost has no strength at 650°C. Its heat resistance is good for resin-based composites but not as metal matrix composites. BF is inert at room temperature, but it can react with metal at 650°C. The bonding of epoxy and polyimide resin matrix with BF is better than with CF.

The main characteristics of properties of boron fiber are high elastic modulus and big diameter, and its longitudinal compressive strength of composite materials is higher than any other fiber composites. However, because of its high cost, high density, as well as big fiber diameter, hard quality and poor woven performance which results in poor molding, it has been replaced by carbon fiber now and it is seldomly used in preparing resin matrix composites. Nonethelss, it is still used for metal matrix composites such as boron/aluminum and boron/titanium composites.

2.5.2 Silicon carbide fiber (SiC)

There are two methods for fabricating silicon carbide fiber. One method is similar to vapor deposition way of boron fiber, which deposits silicon carbide on the substrate wire; another method is to utilize organic compounds of silicon carbide. By adding catalyst and heating (optical radiation) polycondensation, a silicon carbide polymer with silicon-carbon main chain can be formed. Then we dissolve and draw it, pre-oxidate and carbonize the polymer to obtain silicon carbide fiber. This method can produce continuous silicon carbide fiber, and it is a major breakthrough in manufacturing technology of silicon carbide fiber.

1) Chemical vapor deposition of SiC fiber

SiC fiber with chemical vapor deposition (CVD) is a composite structure fiber (similar to BF, replace $BCl_3$with alkyl silane, the vapor deposition of silicon carbide on W or C wire). In 1961, Gareis et al first applied for patents this method of preparing SiC fiber with W core using ultra-fine tungsten wire as the deposition carrier. In the 1970s, Germany Gruler prepared continuous fiber SiC with W core and commercialized it. Its tensile strength is 3.7GPa and Young's modulus is 410GPa. Mehemy et al had reported that carbon filament for core, organic silicide (chloromethyl silane) as raw materials, which reacted on the hot surface of core wire with flow hydrogen, and pyrolyzed to form SiC and deposited on the surface of core wire.

Currently, British company BP and French company SVPE adopts CVD method for production of continuous SiC fiber with W Core. The brand products have series of SM1040, SM1140 and SM1240. Fibers are coated with different surface coatings suitable for production of polymer-based, aluminum, titanium and intermetallic compounds as well as ceramic matrix composite materials, respectively. Specialty fiber company Textron USA produces SiC fiber with C-core, such as SCS-6, in which carbon fiber lies in cross-section center, pyrolytic graphite, two layers of β-SiC and its surface toward outside, respectively. Two layers of SiC are formed by heat deposition in the two deposition areas. The grain size of inner layer ranges from 40nm to 50nm and outer layer ranges from 90nm to 100nm. The surface is designed to decrease the fiber's brittleness and sensitivity to the environment. Its tensile strength is 4.48GPa.

Monofilament diameter of SiC fiber by CVD is from 100μm to150μm. Its density is 3.1g/cm^3, tensile strength is 3.40GPa and the initial modulus is 400GPa. Table 2.26 shows the typical characteristics of SiC fiber by CVD method. According to the different metal matrices to be reinforced, silicon carbide fiber has different surface coatings. This type of fiber has high strength, high modulus, heat-resistant properties and in addition, antioxidant properties. They have been widely used as reinforcements for metal-based composites such as alloys of aluminum and titanium, etc.

Table 2.26 Typical characteristics of SiC fiber by CVD method

Properties	SiC(W core)		SiC(C core)		Chinese products
	1	2	1	2	
d_f (μm)	102	142	102	142	100±3
σ_{fu}(MPa)	3350	3300∼4460	2410	3400	>3700
E_f (GPa)	434∼448	422∼448	351∼365	400	400
σ_f(g/cm^3)	3.46	3.46	3.10	3.0	3.4
Surface coating	Rich carbon	C+TiB$_x$	—	Si/C	Rich carbon

Good chemical stability. SiC fiber has excellent corrosion resistance properties. When putting it in the solutions of 6 mol/L HCl, 9mol/L H_2SO_4, 7mol/L HNO_3 or 30% NaOH at 80°C for 24h, the loss weight of fiber is less than 1% and the mechanical properties remain almost unchanged.

Good compatibility with metal, it is easy to compound with metal matrix. At below 1000°C, silicon carbide fiber hardly reacts with any metals. It can form composites with a variety of metals and has good compatibility with metal, so it is commonly used in metal matrix and ceramic matrix composites.

2) SiC fiber by precursor method

The precursor way is that firstly, organic fiber is spun from polymerization of alkyl silane. It becomes continuous β-SiC fiber after handling at high temperature, and its basic component is ultrafine particles of silicon carbide. In 1981, Japan Carbon company launched the commercial silicon carbide fiber Nicalon prepared by this precursor way. Dimethyldichlorosilane, dechlorinated by metal sodium in solvent, produces polydimethyl silane with silicon carbon-based main chains. The polysilane becomes polycarbonsilane with three-dimensional structure at temperature of 400°C to 500°C and pressure from 0.1MPa to 3MPa and then we can obtain the brittle polycarbosilane fiber by dissolving or melting spinning. The fiber is pre-oxidized in the air under 200°C when silicon oxide film is made on its surface, then it is further carbonized in vacuum under 1300°C, after which we finally obtain silicon carbide fiber with good flexibility, high strength and high modulus. The process is shown in the following.

$$\text{Dimethyldichlorosilane+Metal sodium} \xrightarrow{\text{Dechlorination condensation}} \text{Polysilane}$$

$$\xrightarrow{\text{Pyrolysis rearrangement (autoclave)}} \text{Polycarbonsilane(PCS)} \xrightarrow{\text{Spinning}} \text{Polycarbonsilane fiber}$$

$$\xrightarrow{\text{Infusible treatment}} \text{Infusible polycarbonsilane} \xrightarrow{N_2 \text{ at high temperature}} \text{SiC fiber}$$

For SiC fibers made by precursor way, the main component is β-SiC ceramics, the grain is smaller than 10nm and contains SiO_2 fiber and free carbon (about SiC: C: SiO_2=1:0.57:0.31). It has 500 threads per bundle, and the diameter of monofilament is 10~15μm, the density is 2.55g/cm^3, the tensile strength is 2.45~2.94 GPa, the modulus is 176~196GPa, break elongation is 1.5%, thermal expansion coefficient (axial) is 3×10^{-6}/°C. The properties of Nicalon fiber are: fiber diameter is 8~12μm; density is 2.8g/cm^3; the tensile strength of monofilament is 2.5~4.5GPa; the tensile modulus of monofilament is 180~300GPa.

We can get Hi-Nicalon with low oxygen content with treatment for reducing oxygen content of Nicalon fiber (improve thermal stability). Then by increasing crystallinity and handling close to the theoretical chemical composition, S style, i.e., Hi-Nicalon-S is obtained (increase modulus, anti-oxidation and creep resistance). Table 2.27 lists heat-resistant properties of SiC fiber which obtained from polycarbonsilane.

Table 2.27 Typical heat-resistant properties of SiC fiber obtained from polycarbosilane

Properties	Nicalon NL-200	Hi-Nicalon	Hi-Nicalon-S
Filament diameter(μm)	14	14	12
Number of filaments (thread/bundle)	500	500	500
Linear density (g/1000m)	210	200	180
Tensile strength (MPa)	3000	2800	2600
Tensile modulus (GPa)	220	270	420
Elongation at break (%)	1.4	1.0	0.6
Density (g/cm^3)	2.55	2.74	3.10

The same with boron fiber and carbon fiber, silicon carbide fiber has characteristics of high strength, and high modulus, its tensile strength can reach to 4.5GPa. Like other reinforcing fibers, silicon carbide fiber has the peculiarity of strength increasing with the decease of the fiber diameter.

SiC fiber has good high temperature stability. Strength and modulus of silicon carbide fiber are almost unchanged at 1300°C; under the condition of loading, mechanical properties remain unchanged in oxidation atmosphere for long heating at 1000°C.

Silicon carbide fiber composite with ceramic, glass and other materials can improve impact resistance. Metal matrix (Ti-based) composites and ceramic matrix composites reinforced by SiC fiber, have been used for the manufacture of space shuttle components, high temperature structure materials such as high performance motors. It has become a new material in the field of high technology and aerospace in the 21st century.

Silicon carbide fiber can compound with adhesive matrix to make composite materials, such as silicon carbide/epoxy composites. Its tensile strength and modulus are similar to carbon fiber/epoxy composite material, but its high compressive strength is about twice as much as carbon fiber/epoxy composites and its interlaminar shear strength is also higher (up to 100MPa).

2.5.3 High silica and quartz fiber

Special kind of glass fiber includes glass fiber with high strength, high modulus, low-dielectric, alkali resistance, radiation resistance, hollow and special shaped cross-section, high silicon oxide content and quartz fiber and so on. Here is a brief introduction of fiber of high silicon oxide content (also known as silica fiber) and quartz fiber (also known as fused silica fiber).

High silicon oxide often refers to high-purity silica glass, but as a reinforcing material of silica fiber, the purity of SiO_2 is 95%. It is made of glass fiber with 65% silica content by hot acid treatment and removement of other components.

High silica is a glass fiber product with high temperature resistance which is developed in the study on the mechanism of glass phase separation. Many heat-treated glass forms discrete phase of rich SiO_2 and other phase of enrichment of other components, some of which drop into a spherical shape in isolation or like earthworms' interlinking in the overall glass. The size of the phase separation particle is in a range of 5nm to 20nm. After the phase separation glass being treated with acid, a great majority of non-skeletal components of glass are leached out, producing porous skeleton of SiO_2. Then we dry it and shrink it to glass or fiber with high content of silicon oxide whose content of SiO_2 is 94% to 99%. The production process of high silica glass is shown in the following.

Glass melting → Glass filament drawing → Weaving for a variety specifications of clothes and yarns products → Fiber leaching with HCl or H_2SO_4 → Porous glass fiber with high silica content

Glass with ternary composition of SiO_2, $B_2O_3$and Na_2O is most commonly used for producing glass fiber with high silicon oxide content. By melting the glass with 60% to 70% of SiO_2, 20% to 25% of B_2O_3, 5% to 10% of Na_2O at 1450°C, drawing it into a continuous fiber at 1150°C, then further dipping it in 5% of sulfuric acid, hydrochloric acid or nitric acid at certain temperature to remove other components except for SiO_2, we may finally sinter it at from 700°C to 900°C, so as to close the pore and form fiber with high silicon oxide content (over 96%). This ternary glass has advantages of easy phase separation and easily forming high silica glass fiber, but has the fatal shortcomings of high cost of glass raw material and low strength of fiber. At present, most developed countries have abandoned this production method, and have taken the method of using SiO_2-R_2O binary glass to produce high silica products. The glass has the advantages of low cost of raw materials, fusible, stable drawing operation and high yield. Furthermore when the fiber is leached by acid, the soluble matter is less and the ultimate fiber has high strength and soft properties. The result of the study shows that the strength of SiO_2-R_2O yarn is 40%∼50% higher than ternary glass of SiO_2, B_2O_3, Na_2O.

In order to increase the heat resistance of fiber, surface treatment can be carried out on high silica fiber by using Cr compounds usually. In N_2, N can also be infiltrated into porous fiber to form a stronger structure Si-N bond for improving the heat resistance. The long-term use temperature of high silica products can promote from 1000°C to 1200°C after this treatment.

Quartz is also a kind of high-purity silica glass, the fiber is made of high purity natural quartz crystal (SiO_2 content is 99.95%). Its process is generally to get bar of high purity quartz (diameter is 4.4mm) at first, then stretch it into fiber with diameter at about 10μm at high temperature between 2000°C and 2100°C. SiO_2 content of quartz fiber is more than 99%, heat resistance at 1700°C. However, the complexity of production processes, low output and high price have limited its application.

Texture of quartz fiber and high silica fiber are both soft, they can be made into a variety of yarns, rovings, tape, chopped fibers, felt, and braiding product in the same as glass fibers.

High silica and quartz fiber products, their specific strength are higher than most high temperature materials, and tensile strength of quartz fiber is 896MPa at 20°C and 682MPa at 204°C, which is almost five times of high silica fiber. High silica and quartz fiber are both completely elastic, and quartz fiber has higher density than high silica fiber, the former is 2.2g/cm^3 and the later is 1.74g/cm^3. Tensile strength of quartz fiber is 1500MPa, and elastic modulus is about 73GPa. It has small loss of high temperature strength, good dimensional stability, thermal shock resistance, chemical stability, transparency and electrical insulation, and the maximum temperature of safe usage is from 1100°C to 1200°C. Quartz fiber-reinforced composite materials can be used for ablation resistance parts of rocket and space shuttle and aircraft structural components.

High silica fiber and quartz fiber have similar chemical properties, and they can resist variety of halide, acid and weak base except for hydrofluoric acid and hot phosphoric acid.

High silica and quartz fiber both have exceptional heat resistance properties and they do not melt and evaporate at 1649°C. When the temperature rises to 982°C, they begin to transit from glass into quartz crystal, and become rigid, but the physical properties and electrical insulation properties remain unchanged. In addition they have good thermal shock resistance. If they are heated to 1093°C and immediately quenching in water, the properties will not change much.

High silica and quartz fibers have similar characteristics in high temperature resistance and low thermal expansion coefficient (7×10^{-7}/K), high resistance and high durability. But strength of the high silica fiber is lower, which is mainly used for thermal shielding system.

The dielectric coefficient and dielectric loss of high silica and quartz fibers are both lower than glass fiber at high-frequency electric field, so composite materials prepared by them have good high-frequency dielectric properties and can be used for advanced radome products.

2.5.4 Ultra-high molecular weight polyethylene fiber

Polyethylene fiber is the latest high performance organic fiber internationally with ultra-light, high specific strength, high specific modulus and low cost. In 1975, the Netherlands company DSM (Dutch State Mines) first invented the way which adopted the gel spinning-ultra-drawing technology to make UHMWPE (ultra-high molecular weight polyethylene, abbreviated as UHMWPE) fiber with excellent tensile properties, and thus broke the traditional situation of preparation of high-strength, high modulus fibers only with rigid polymer. The first patent was applied in 1979, and the first small-scale production line was built in 1990, the trade name of product was “Dyneema”. After the company Toyobo in Japan with DSM (the Netherlands DSM-Toyobo joint) set up a company Dyneema VOF, mass production of high-strength polyethylene fiber called "Dyneema" came. At that time the strength of fiber was only 6.4cN/dtex. Toyobo in Japan promoted the strength of fiber to 35.2cN/dtex in 1996. Properties of Dyneema SK76 are listed: σ_{fu} is 3.6GPa, E_f is 116GPa, ε_{fu} is 3.8%, ρ_f is 0.97 g/cm^3; in 1985, Allied Signal Company in the United States purchased DSM's patent, and improved the manufacturing technology to produce the high strength polyethylene fiber products called "Spectra". The strength and modulus of fiber both exceed DuPont's Kevlar fiber. Properties of spectra 1000 are listed: σ_{fu} is 3.09GPa, E_f is 172GPa, ε_{fu} is 3.0%, ρ_f is 0.97g/cm^3; in 1999, Mitsui Petrochemical Corporation in Japan also developed "semi-melt-spinning" technology which adopt its own development of paraffin as the solvent, and completed production line of 300 t/a, the trade name was "Tekmilon", the strength and modulus of the fiber are 1.5$\sim$3.5GPa and 60$\sim$100GPa separately. Properties of Tekmilon: σ_{fu} is 3.43GPa, E_f is 98GPa, ε_{fu} is 4.0%, ρ_f is 0.96g/cm^3; In 2000, Ningbo Dacheng Chemical Fiber Company in China built a test production line of 400t/a , the fiber size 8.3 dtex, strength is 31$\sim$32cN/dtex.

1) The manufacturing technology of ultra-high molecular weight polyethylene fiber

The conditions of polymer fiber with high-performance (high strength) are: very high molecular orientation (crystallinity); orderly side arrangement; very low content of axial defects; together with the high or ultra-high molecular weight ($M_w > 2\times10^6$). For high molecular weight polymers such as PE, PP, PAN, PVAL and so on, by hot drawing on its directionally solidified coiling network or gel at the controlled process conditions, we can satisfy the above conditions and make it become high-performance fiber. For PE with the narrow molecular weight distribution (MWD), such as $M_w = 5.5 \times 10^6$, $M_w/M_n = 3$, the strength of fiber can reach 7.26GPa.

UHMWPE fiber manufacturing technology is shown: firstly we use the general Zieglar Nata catalyst to polymerize ethylene to more than one million molecular weights. The average molecular weight of products is about 3 million for industry use, 10$\sim$60 times of ordinary polyethylene, so it known as ultra-high molecular weight polyethylene. Because of the high molecular weight, melt viscosity of fiber is high and very hard for fibrillation, so a variety of methods for fibrillation has been studied since the 1970s.

(1) High pressure solid state extrusion method. Use high pressure to extrude the pre-crystallization UHMWPE under melting point through capillary, induce crystallization orientation by high shear stress to get fiber. This method can be used to obtain fiber with high modulus of 720cN/dtex.

(2) Induce crystallization by solution flow. It relies on pressure gradient or

border movement to make UHMWPE solution to flow and then obtains crystal at the end of and around the crystallization seed. When the speed of crystal grain or spinning fiber coiling equals to the growth rate of crystallization, we obtain continuous and even UHMWPE fiber. As a result of crystal nucleation and growth being random, thickness of the crystallite structure is uneven, presenting "kebab" morphology. The best fibers produced with this method has strength at 41cN/dtex, modulus at about 1026cN/dtex, break elongation is 5.2%.

(3) Gel spinning of diluted solution by ultra-times hot stretching is the most suitable fibrillation method of industrialization. The solvent can be decalin, mineral oil, paraffin oil or kerosene, and with proper antioxidant added. Under the protection of N_2, it is mixed at high-speed. It dissolves and is heated up to about 50°C and maintain for about 2 days till polymer gel occur under slowly cooling. With twin-screw melt spinning at 90°C, we extract the solvent using n-hexane or kerosene distillate and then dry it in vacuum and thermally draw to more than 100 times. The strength of the high-performance fiber reaches 71cN/dtex and the modulus reaches 2700cN/dtex, which is made in the laboratory in this way. The only shortage is its low spinning speed. Later Pennings and others developed the high-speed gel-spinning technology. It means to be completed at the spinning speed about 4000m/min with gel directly spinning into high-performance fiber, and the hot stretching to get the fiber with strength of 24cN/dtex, modulus of 470cN/dtex and break elongation of 0.5%.

Toray selected similar spinning technology as the DSM and the difference is lower polymer concentration. UHMWPE is dry-jetted and wet-spun, and then cooled and solidified in the coagulation bath with two layers structure. For example, the direct chain UHMWPE with 3,000,000 molecular weight is dissolved in decalin into 3.0% solution at 160°C, and then use spinneret with 0.5mm diameter orfices to dry-jet wet spinning, height of air layer is 8mm; then go through the coagulation bath with two layers structure, in which the upper layer is water, lower layer is chloroform, bath temperature is 10°C and the height of water layer is 20mm, the distance of the passage in the lower chloroform is 800mm (in which the walking distance of monofilament separation is 300mm). The winding rate of solidified filaments is 7.5m/min. Then, the tow passes through the extraction bath of chloroform at 10°C, the remaining decalin in the filament is removed, and then it goes through to heat roller at 60°C for drying and coiling; at last we stretch the dry filament on hot plate with surface temperature at 140°C and with length at 120cm, the feeding filament speed is 20cm/min. According to different draw-ratio, the physical properties significantly change, and we can obtain fibers with the high strength and high modulus when the draw-ratio reaches more than 8 times.

The process of gel spinning and ultra drawing for preparation UHMWPE fiber is shown in following: ① UHMWPE ($1\times10^6 \sim 5 \times 10^6$) is dissolved in xylene, paraffin oil, then by gel spinning from no tangled molecular chain to the melt processing stage; ② rapid quenching of the extrusion fiber and solvent extraction; ③ heat drawing of the fiber at or after the solvent extraction process.

UHMWPE crystal belonges tablets and kebab structure (fibrous polycrystalline), structures and properties of the fiber depend on the spinning process conditions: spining speed, spining temperature, hot stretching, draw-ratio, polymer concentration, and relative molecular mass distribution.

2) Surface treatment of ultra-high molecular weight polyethylene fiber

The surface energy of UHMWPE is lower and it does not adhere easily with the resin matrix. The surface treatment is to improve its interface adhesion with the matrix and is conducive to stress transfer through the interface from the matrix to the fiber. The fiber surface treatment can increase surface area, improve the content of polar groups of fiber surface or introduce reactive groups on the fiber surface. Methods of surface treatment are shown in follows.

(1) The method of surface plasma reaction. Plasma processing in N_2, O_2, H_2, NH_3, Ar atmosphere, the partial activity H on the fiber surface has been deprived off and formed active points and reacted with the O_2, H_2O in the air to form polar groups. Different gases have different effects on improving the interface strength, treated with O_2 plasma treatment, the interface bond strength with epoxy resin increases more than 4 times, and with NH_3 plasma treatment the fiber strength does not decrease.

(2) The method surface plasma polymerization. The coating is formed on fiber in surface by plasma polymerization and the properties of the surface changes, that is, use organic gas or vapor plasma to form polymer. For example, when choosing the plasma acrylamide to treat UHMWPE fiber, a large number of amines, a small number of secondary and tertiary amine and imine, cyano functional groups, as well as C═O and C═N functional groups are generated on the resulting polymer surface coatings. After contact with air they will produce a small amount of carbonyl, amide, carboxyl and ethers, so as to improve the interface adhesion, and only lead a slight decrease in fiber strength. When choosing the polymerization system, we should pay attention to match the composite resin as much as possible. The common matrix resin for application is epoxy resin, polyester and unsaturated polyester and so on.

3) The applications of ultra-high molecular weight polyethylene fiber

Characteristics of UHMWPE fiber are very high specific strength (σ/ρ, 31×10^6cm), very low moisture absorption, resistant to UV, chemical stability, wear resistance and excellent electrical properties (used for radome). The biggest drawback is its limiting use temperature only from 100°C to 130°C (the melting point is150°C), LOI is only 16.5, high creep (which can be improved by chemical or radiation crosslink), and poor interface bonding; and thus restricts its usage in many fields. In addition, among the high strength fibers its fatigue resistance and wear resistance are the highest and impact resistance and chemical resistance are excellent. As reinforcements for composite materials, unidirectional (UD) prepreg made of UHMWPE fiber has been used for light military or racing car helmets, and a variety of protective board, sporting goods, superconducting coil tubes, automobile parts, etc. such as all kinds of absorbing energy parts resistant to impact and a variety of the vibration board for the speakers. Dyneema UD bullet proof plate has been applied to anti-rifle inserted plate of the human chest, light armor materials, bullet-proof sports car, senior police cars, tanks, light armored vehicles and personnel carriers, etc. It can be an effective missile defense, such as the shooting of steel bullet, compared with bullet-proof steel it can reduce the weight for almost 50%.

Allied Signal Company in the United States had produced a non-woven fabric made of UHMWPE which cross-stacked in 0° and 90° direction. Among the commodities, called "Gold Shield-PRC" and "Spectra Shield-PVR", are applicable for hard armor, chest protector plates, vehicles armor and barrier board for explosives. The helmet that the company designed in 2001 is made of composite materials with the highest performance and the lightest volume and there are many additional properties. Soldiers with the helmet can interfere with the surveillance of satellite.

Recently, Toyobo utilizes UHMWPE fiber composites having ultra-low temperature property which can be resistant from -269°C to -196°C, negative thermal expansion coefficient, low friction coefficient and high insulation properties, and has prepared superconducting coil which has been applied in practical.

Exercises

1. How to prepare glass fiber? During the process of preparation which technological factors need to be controlled? What effects on the structure and properties of glass do they have?

2. Why do bulk glass and glass fiber have different properties? What efffect on the strength does the thickness of glass fiber have? Why?

3. Describe the composition and the categories of glass fibers, what is the difference among the performances of varieties of glass fibers?

4. Why should we use the sizing in preparing glass fiber? What are mainly three types of sizing, what are differences of them?

5. What indicators are used to characterize the mechanical properties of fiber? Why is it said that the fracture elongation of fiber is particularly important?

6. What are the main characteristics of the performance of glass fiber?

7. When we measure the tensile strength of glass fiber and its composite materials, why should the distance between clamping chucks be limited? What effects on the test results will the gauge length have brought?

8. What is the strand, monofilament, number of turns, plied number, count, Tex, and Denier?

9. What indicators can be used to judge the thickness of the yarn according to? How to judge? What is meaning of the numbers in the yarn 6-80/2? Between two specifications Alkali-free yarn 6-80/2 and 6-160/4 which one is thicker? Compared to strand with linar density of 15 Tex and 80 count, which one is thicker?

10. Why is the strength of glass cloth much lower than monofilament strength?

11. Which issues should be taken into consideration when choosing glass cloth? What indicators should be put forward? Why?

12. For the situation of weaving, the thickness and weaving density etc., what influences do they have on the use property of glass cloth?

13. When the environmental humidity is high, what differences between performance of S-glass and that of E-glass fiber?

14. There are two types of glass clothes, the specifications are shown in follows. Try to calculate the conversion fracture strength of these two clothes.

Thickness (mm)	Test direction	Density of yarns (thread/cm)	Count of strand/N	Fracture force (kg) (width is 25mm, gauge length is 100mm)
0.1	Longitudinal	18	80/2	73.7
	Latitudinal	16	40/1	54.0
0.2	Longitudinal	20	80/4	132.4
	Latitudinal	14.4	80/6	147.3

15. During the preparation process of PAN carbon fiber, why should it have the three processes of the pre-oxidation, carbonization and graphitization? What effects do the three processes have on the performance of carbon fiber?

16. What are the major requirements on the quality of PAN precursor in CF production?

17. Briefly describe the structure of carbon fiber and what effects do the structure of carbon fiber have on the performance?

18. What's the difference between carbon fiber type I and type II in the structure and performance?

19. Compare the difference of CF and GF in the performance?

20. What impacts do the properties of carbon fiber have on its composite material?

21. What effects do the temperature and the tension in the process of heat treatment have on the structure and properties of the carbon fiber?

22. What are the major factors to impact the strength of carbon fiber?

23. What is the medium modulus and high-strength carbon fiber? Talk about its significance in the development of structure composite materials in aviation.

24. Please give examples to talk about the types of high modulus organic fiber and their main performance?

25. What is the difference of Nomex fiber and Kevlar-49 fiber about the chemical structure?

26. Briefly introduce the production process of Kevlar fiber?

27. What are the main features of Dupont's new aramid fiber Kevlar-149 in the performance?

28. If the measured tensile strength of organic fiber is 22g/den, how many kg/cm^2 would be equivalent for the tensile strength?

29. What is effect about the chemical structure of Kevlar fiber on the properties of fiber?

30. What is the structure of Kevlar? How does it affect the performance of fiber?

31. Why are the strength, modulus, chemical stability and thermal stability of Kevlar fiber higher than other common organic fibers?

32. Why is Kevlar fiber suitable for mixing with carbon fiber?

33. What are the main disadvantages of Kevlar fiber?

34. Compare the main advantages and disadvantages of GF, CF, and KF.

35. How to manufacture boron fiber?

36. What are the main performance characteristics of BF?

37. What are the main causes of stagnation in development of BF?

38. Please indicate the types, preparation and performance characteristics of SiC fiber.

39. What is UHMWPE fiber? How to make it? Describe its structure, performance and applications.

40. What is PBO fiber? What are the differences in molecular structure between it and aramid?

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3

Matrix materials

3.1 Overview

Composite materials are made up of reinforcing material and matrix, and during the composite molding process, the matrix material undergoes a series of the complex processes of physical, chemical and physicochemical changes, compounds with the reinforced material to form a whole body with certain shape. Therefore, the matrix properties directly affect the properties of composite materials, and the choice of process parameters and the forming method of composite materials are mainly determined by the process of matrix. The mechanical properties of the composites, especially the longitudinal tensile properties, undoubtedly depend mainly on the reinforcing material, but the role of the matrix cannot be ignored. Polymer matrix bonds the reinforcing material into a whole and transfers load among the fibers so that the load is uniformly distributed. Moreover, the transverse tensile properties of the composite materials, compressive properties, shear properties, heat resistance and resistance to environmental media, are all more closely related to the matrix.

The processability of composite materials mainly depends on the matrix material. The viscosity and the pot life of the matrix resin directly affect the impregnation on the reinforced materials, lay-up of the composites and the storage of prepregs. More importantly, the molding methods and process parameters of composite are mainly determined by the matrix resin.

Therefore, it is very important to study and understand the composition, the role and performance of matrix materials.

3.1.1 The basic components and the role of matrix materials

1) Polymer matrix resin

Components of the polymer matrix resin, their role and relationship are very complex. In general, matrix is rarely a single polymer. It often includes other auxiliaries.

Polymer is the main component of matrix, and it has a direct impact on the technical performance, molding technology and product price of composite material.

A synthetic resin used as composite materials must have high mechanical properties, dielectric properties, heat resistance and anti-aging performance, and also can be easily fabricated, i.e., have good processability.

Phenolic resin is one of the first resins in industrial production, its characteristics are: it can solidify at the heating conditions without adding curing agent; acid or alkali can promote the curing reaction; small molecules separated out during the process of resin curing, so the curing of resin should be carried out under high pressure, and the curing volume shrinkage is large; resin adhesion on the fiber is not good enough; curing resin has good compression performance, good water resistance, chemical resistance, and ablation resistance properties, but the fracture elongation is low and the resin is brittle. Therefore a large number of phenolic resins are used in molding powder and short fiber molding compound, and a small amount is used for glass fiber composite materials, resistance-ablative materials. It is rarely used in carbon fiber and organic fiber composite material.

Unsaturated polyester resin (UP) is an important resin to manufacture the glass fiber composite materials. UP accounts for more than 80% of the total resin for glass fiber composites at abroad. UP has the characteristics of good technology, i.e., it can cure at room temperature, mold at atmospheric pressure, and has simple tooling. This is also the most prominent advantage comparing with epoxy and phenolic resin. The performance of cured UP resin is common and not as good as the mechanical properties compared to phenolic resin or epoxy resin, and its price is much lower than the epoxy resin and only slightly more expensive than phenolic resin. The disadvantage of the unsaturated polyester resin is the larger curing volumetric shrinkage and poor heat resistance, so it is rarely used as matrix of carbon fiber composite materials and mainly used in civilian industry and living goods.

Synthesis of epoxy resin started in the 1930s, and it went to industrial production in the 1940s. Epoxy resin has strong bonding with the enhanced materials, high mechanical strength, excellent dielectric properties, and good chemical corrosion resistance. In recent years the species of epoxy resin and curing agent are greatly developed, it gets wide applications, especially in the carbon fiber and boron fiber composite materials.

In addition to the above commonly used thermosetting resin, there are melamine and silicone resin. A number of new thermosetting resins have been developed in recent years, and they all have their own unique high performance. For example, diallyl phthalate resin (DAP) has a high heat resistance and excellent electrical properties; polydiphenyl ether resin has excellent electrical properties and corrosion resistance; polyimide resins have outstanding long-term high temperature performance. Recently thermoplastic matrix resins, such as polyethersulfone (PES), polyphenylene sulfide (PPS) and polyarylether ketone (PAEK), etc., also have been studied and developed.

2) Auxiliaries

In order to improve the process performance of resin and the performance of cured products, or to reduce costs, it is needed to add the appropriate auxiliary agents to the formulations of matrix. Commonly used auxiliary agents are shown in follows:

(1) Curing agent, initiator and promoter.

Epoxy resin has a thermoplastic linear structure, so it must be cross-linked by curing agent into a macromolecular network structure and becomes insoluble and not-melting cured product. Curing of unsaturated polyester resin can be carried out by using initiator in heating conditions, or using initiator and promoter under the conditions of room temperature.

(2) Diluent.

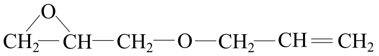
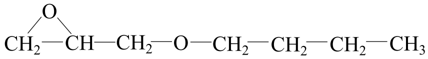
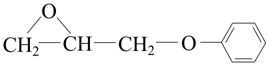
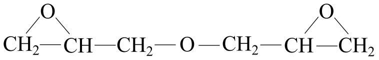
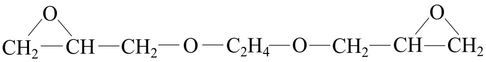
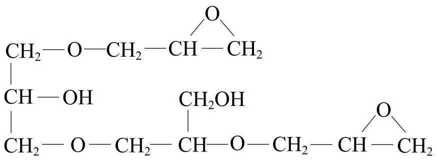
Viscosity of matrix resin at room temperature is an important process parameter. In order to reduce the resin viscosity to meet the technological requirements, it is usually needed to add a certain amount of diluents into the resin. Diluents can generally be divided into two broad categories: non-reactive and reactive.

Non-reactive diluents do not participate in resin curing reaction. Usually they go through the drying process after dipping to remove most of diluents. Commonly used non-reactive diluents are common solvents such as acetone, alcohol, toluene, benzene and so on, and the usage amount is generally $10\% \sim 60\%$ of resin by weight. Viscosity of most phenolic resins and epoxy resins are often very high and usually need the non-reactive diluents.

When the matrix resin is not allowed to add volatile substances, in order to reduce the viscosity, reactive diluent is needed. It participates in the resin curing reaction and become the part of network structure. The choice and usage amount depend on the structure of diluents and the type of resins. Amount of cross-linking agent of unsaturated polyester resin (such as styrene, ethylene derivatives, etc.) can adjust the viscosity of resin, therefore, this type of resin cross-linking agent can play the role of reactive diluents, and there is generally no need to add in additional diluents.

Mono-epoxy or multi-epoxy compounds with low viscosity can be added into epoxy resin systems as reactive diluents. Reactive diluents of epoxy resin are listed in Table 3.1. The usage amount of mono-epoxy compound is generally $5\% \sim 10\%$ of resin by weight. Excessive amount will have an adverse impact to the cured resin. The amount of multi-epoxy compound can be greater than 10%. Epoxy resin reactive diluent is generally toxic, and long term exposure can cause skin allergies and even ulceration when it gets serious. Proper protection is crucial for users of such diluents.

Table 3.1 Common epoxy reactive diluent

Diluent	Brand	Structural formula	Molecular weight	Viscosity (mPa·s)
Allyl ether of propylene oxide	500		114	1~2
Butyl ether propylene oxide	501		130	2
Phenyl ether of propylene oxide	690		150	7
Glycol diglycidyl ether	600		131	6
Ethylene glycol diglycidyl ether	512		174	100
Glycerol epoxy	662		300	160

(3) Toughening agent and plasticizer.

In order to reduce the brittleness of the cured resin and to improve the impact strength the joined component we can use is called toughening agent or plasticizer. The commonly used plasticizers are phthalate (eg dibutyl ester, dioctyl ester), phosphate and so on. They do not participate in the curing reaction, but only play a role of lowering crosslinking density, which results in the declined rigidity and at the same time decrease strength and heat resistance. On the other hand, toughening agents are often linear polymers with active groups, and are directly involved in the curing reaction. For example, polyamide, polysulfide rubber, carboxyl-terminated butadiene-acrylonitrile rubber (CTBN) and polyester are added to the epoxy resin, and nitrile rubber is added to the phenolic resin. Toughening agents improve the toughness without lowering the strength of cured resin, and sometimes not reducing the heat resistance.

(4) Thixotropic agent.

In the hand lay-up process for large products, especially on the vertical face, the downword flow of resin often takes place, affecting the quality of products. In order to eliminate the defects, we often add a certain amount of thixotropic agent to the resin. It can increase the viscosity of the resin in the static state, and under the external force such as mixing the resin would become the flow liquid, and thus it is applicable to brush large-scale parts, especially useful on the vertical face. Common thixotropic agent are active silica (white carbon black), the usage amount is generally 1%∼3%. In the gel coat resin (i.e. the surface resin) used in the hand lay-up process, thixotropic agent is often added.

(5) Filler.

Adding a certain amount of fillers to resin can improve its performance and reduce the cost. For example, a certain amount of fillers can increase the resin viscosity, change its flow characteristics, reduce shrinkage of cured resin and increase the surface hardness. Fillers commonly used are clay, quartz powder, mica, etc, and the wet fillers should be dried before using. Some filler will affect the curing rate and the gel of resin, and it should be aware. Sometimes, some special filler for certain special purpose, e.g., molybdenum disulfide (MoS_2) can improve the wear resistance, and metal powders can improve conductive properties of the resin.

(6) Pigment.

To create colorful products of composite materials, a certain amount of pigments or dyes must be added to resins. The amount of pigment used for the resin is from 0.5 % to 5%. The pigment should meet the following requirements: ① color, and heat resistance and light resistance; ② good dispersion in resin, without disturbance to curing resin; ③ no effects on the performance of products; ④ convenient source and low prices. Very few pigments can meet these requirements at the same time, so we must select according to specific circumstances.

3.1.2 The role of matrix in composite materials

Matrix material is a continuous phase and it bond fibers together. Single fibers can therefore join forces and make the most of the reinforced material. In the composite material, the force is transmited from the matrix to the fiber, namely the matrix plays the roles of balancing load and transferring load. A rope can bear pull, but can not bear compression, and even can not stand up. Fibers can only bear compression under circumstance of the matrix support, and at the same time matrix can prevent fibers from buckling. In addition, in the production and applications of composite materials, matrix plays the role of shielding the fiber and preventing the fiber from wearing.

Many properties of composite materials, such as heat-resistance, corrosion resistance, flame retardance, anti-radiation, solvent resistance and low moisture absorption, composite materials technology and the forming methods of parts are all determined by the matrix.

3.1.3 Matching principle of matrix resin system

Matrix material should be coordinately considered and selected from the three aspects of usage performance, processing property and economic efficiency.

1) Usage performance

Usage is the first factor to be considered. Each product has a corresponding designed performance, for example, the products are structural or non-structural parts, military or commercial, the size and direction of load, whether the environment condition is harsh, whether there is heat resistance or not, chemical corrosion, whether there are special requirements of the electrical performance and optical properties, and whether there are limits for toxic.

2) Processing property

The operational processes of the matrix resin should be considered, for example, whether curing at room temperature or heating for curing, whether requiring pressure or not, viscosity of resin, work life and its toxicity, etc.

3) Economic efficiency

For example, whether the source of raw material is rich or not, the cost is high and has the potential competition to enter market or not.

The important order of three aspects mentioned above is the use of performance, technology and economy. If the usage property cannot meet the performance requirements, the advantage of easy forming and low cost would be in vain. Only on the basis fully meeting the first two, the third can have great significance, because the price often determines whether the product has ability to promote and use, and is competitive or not. For example, for the waveform tiles that can be seen everywhere in our life, because of no special requirements for its performance, we can select inexpensive polyester resin with good processability. However, for manufacturing the corrosion-resistant tank for chemical storage, we should select excellent corrosion-resistant resin such as epoxy resin. If manufacturing rocket motor casing or missile nose cone, we would not only select special fibers but also select the ablation resistant and high-strength phenolic-epoxy or polyimide resin. Although the resin is expensive, difficultly forming, it is the only choice that can meet the rigorous requirements. For another example, the commonly used FRP waveform tiles use the generic UP resin, but is used for agricultural greenhouse or factory skylights, we should choose the UP resin which should has good weatherability and translucent property. However, if the transparent plate is used in aquaculture or food industry, we should select UP with low toxicity. If the products will be used in the occasion of contact with the fire, we should select flame-retardant UP, e.g., for the skylights of the steel rolling workshop we should choose the heat-resistant UP.

From the molding process, hand lay-up usually adopts UP and epoxy resin, and laminating, compression molding and filament winding process often use the epoxy resin and phenolic resin. Injection and extrusion process often used thermoplastic resin.

Considering cost, phenolic $<$ polyester $<$ epoxy.

In short, specific products should be analyzed in specific ways. We should grasp the principal contradiction, and synthetically consider the three aspects of performance, process and cost so as to obtain the best choice.

3.2 Basic properties of matrix materials

3.2.1 Mechanical properties

1) Strength and modulus

When considering the mechanical properties of matrix, we must know the using time, temperature, surrounding, etc. And the influences of "temperature-time-environment" are considered simultaneously, so the performance index of materials can be truly reflected. Mechanical properties of composites have close relationship with mechanical properties of polymer matrix, but the cured thermosetting resin which is used in general composites does not have good mechanical properties.

The strength of polymer depends on the intramolecular and intermolecular force. Destruction of polymer materials is caused by the rupture of chemical bond on the main chain or the breakage of the interaction force among polymer molecular chains. The actual strength of polymer is lower than the theoretical strength because of technology and internal stress, the internal stress is partly caused by impurity, or caused by defects. Hence, before the average stress of material reaches its theoretical value, the stress in the part of defect has already crossed the limit, and then breakage initiates from there, which will soon propagate and cause the fracture of whole material.

The relationship between the strength of matrix resin and mechanical properties of composites is a complicated issue. One of the most important roles of matrix in composites is to transmit stress among fibers. In the process, bond strength and modulus are two dominating factors in stress transfer of matrix, and the combination of both factors can affect the damage mode when composites undergo tension. If the matrix has low elastic modulus, fiber will be loaded in tension separately, and the damage mode is an incessant development of fiber breakage. Because this mode does not have the role of superposition, the average strength is very low. Conversely, if the matrix has enough adhesion force and elastic modulus under tension, fibers in composites will be a whole body, and high strength will be expected. Actually, materials have a moderate strength under normal circumstances, and therefore, if a variety of epoxy resins have no significant difference on performances, they have a very small impact on the properties of composite materials. Another example is bending properties of the three commonly used cast resin, which of epoxy resin is 130MPa, of unsaturated polyester is 60MPa and of phenolic resin is 78$\sim$120MPa. The flexural strength of the corresponding glass fiber reinforced composites is shown, which of epoxy resin-based composite materials is 410MPa, of unsaturated polyester-based composites is 340MPa, of phenolic resin matrix composites is 377MPa, the difference is not obvious.

2) The relationship between resin cohesive strength and structure

The uncured resin is linear structure, and relative molecular weight is not high and belonges viscous flow state, so the cohesive strength is very low. With the development of the curing reaction, the molecular weight increases, intermolecular force increases, so the strength increases, but it is still quantitative stage of curing process. In further curing, quantitative change will cause a qualitative change. Cross-linking among resin molecules generates gel, and at this time, resin molecular weight increases sharply, mechanical strength also enhances rapidly. If the curing continues, the cross-linked bond increases, resin strength will gradually increase to a very stable value. If crosslinking density continues to increase significantly, deformation capacity of resin lowers and it becomes brittle.

3) The relationship between fracture elongation and structure

The relationship between the elongation at break and structure of resin, in essence, is the deformation capacity of resin under external force. Three types of deformation of polymers are general elastic deformation, high elastic deformation and viscous flow deformation, etc. For the cured thermosetting resin viscous flow deformation is not existed. The cause of general elastic deformation is due to the change of bond length and bond angle of organic molecules, while high elastic deformation is due to the segmental motion of macromolecular chain. Because the general elastic deformation causes small deformation (about 1%), the high elastic deformation causes considerable deformation, the relationship between resin's break elongation and structure, in essence, is the relationship between resin structure and high elastic deformation.

In general, high elastic deformation will appear above the glass transition temperature, but because polymer chain has relaxation characteristics, if stress is large enough and time is long enough, forced high elastic deformation may appear below the glass transition temperature. Whether the forced high elastic deformation occurs or not, is mainly determined by two factors of cured resin: Firstly, the flexibility of macromolecular chain; Secondly, cross-linking density among macromolecular chain. Aliphatic chain composed by C—C is the representative of flexible chain, resin matrix with flexible chain structure has a big elongation; conversely, molecular chain composed by aromatic ring or aliphatic ring has considerable rigidity, this kind of resin has a relatively small elongation, and it is brittle. From the point of crosslinking density among molecular chains, the higher crosslinking density, the lower the elongation, and the more brittle the resin is.

4) The relationship between the volume shrinkage and the structure of resin

Thermosetting resin curing has volume contraction. It is the volume contraction that often causes a bad adhesion between resin and reinforced fibers, as well as resin crack, which often have an adverse effect on the quality of composite products.

Curing shrinkage rate of several resins is shown in follows:

epoxy resin	1%∼2%
polyester resin	4%∼6%
phenolic resin	8%∼10%

The factors which influence the volume shrinkage rate are density of resin system (including resin, curing agent, etc) before curing, close degree of network structure of the resin after curing, whether release of small molecules or not in curing process, etc. Curing shrinkage of epoxy resin is the lowest, because the epoxy resin before curing has a high density. The cured network structure is not close, and there is no release of small molecules during the curing process.

The main principle to reduce the curing shrinkage of resin is to adjust polymer chain segment to fully extended chain, to make the cured system have close space network. If add polymethylmethacrylate, polystyrene or polydiallyl phthalate,etc. into the uncured unsaturated polyester resin system, due to dissolving or heating, its macromolecule chain can be fully elongated in the uncured system, thus form close space network structure in the cured polyester resin, make the curing shrinkage only at 1%. This approach in use of thermoplastic polymers improving the unsaturated polyester's shrinkage, not only enables the shrinkage of products to reduce, but also enhances dimensional accuracy and thus improves the surface's smoothy, which has been widely used in the production of compression molding of large composite materials.

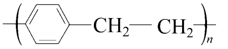
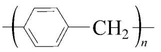
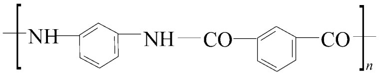
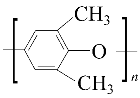
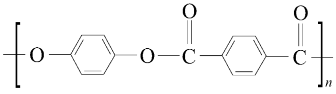
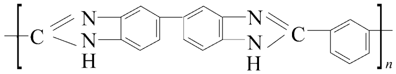
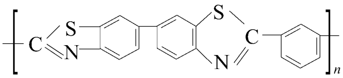
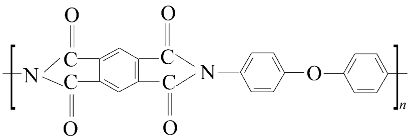
3.2.2 Heat resistance

Heat resistance of composite materials can be shown in different perspectives, but fundamentally, that is, the property change of composite materials at elevated temperature, including the physical and chemical properties. Physical properties include modulus, strength, deformation, etc. and chemical properties include weight loss, decomposition, oxidation, etc.

One expression of heat resistance means that under certain conditions resin retains its strength as the matrix material, this is called physical heat resistance; the other means the temperature range when heat aging happens in resin, this is called chemical heat resistance.

Physical and chemical changes will happen when polymer is heated. Physical changes refer to physical deformation, softening, flow and melting of the resin. Chemical changes include breakage of molecular chain, cross linking, oxidation, gas release, weight changes, etc.

Table 3.2 Impact on T_m by introducing conjugated double bonds, triple bonds or ring structure on polymer main chain

Polymer structure	T_m (°C)
$-\!\left(CH_2-CH_2\right)\!-_n$	137
$-\!\left(CH=CH\right)\!-_n$	> 800
$-\!\left(C=C\right)\!-_n$	>2300 transfer into graphite
	400
	> 400
$-\!\left[NH(CH_2)_6NH-CO(CH_2)_4CO\right]\!-_n$	235
	450
	> 300
	500
	> 500
	> 600
	> 500

Three ways for improving heat resistance of resin are shown:

1) Enhance rigidity of polymer chain

Glass transition temperature is the macro-manifestation of polymer chain's flexibility. If increasing rigidity of the polymer chain, the glass transition temperature of polymer will be increased too. We should decrease the single bonds in the polymer main chain, and introduce conjugated double bonds, triple bond or ring structure (including alicyclic, aromatic ring or heterocyclic), to enhance the heat-resistant of polymers. These are particularly effective. In recent years, a series of high temperature resistant synthetic polymers have the characteristics of such structures (Table 3.2). For example, aromatic polyester, aromatic polyamides, polyphenylene ether, polybenzimidazole, polybenzothiazole and polyimide have excellent heat-resistance.

2) Crystallize

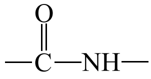
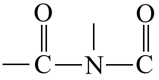
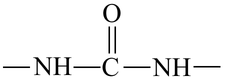
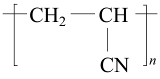
Introducing—C—O—C— (ether bond),  $—\overset{\overset{\displaystyle O}{\|}}{C}—NH—$ (amide bond),  $—\overset{\overset{\displaystyle O}{\|}}{C}—\overset{|}{N}—\overset{\overset{\displaystyle O}{\|}}{C}$ (imide bond),  $—NH—\overset{\overset{\displaystyle O}{\|}}{C}—NH—$ (urea bond) on the main chain or —OH, —NH_2, —CN, —NO_2, —CF_3 on the side group can improve the melting temperature of crystalline polymer (Table 3.3).

Table 3.3 T_m of polymers whose main chain or side group has polar groups or polymers which can form hydrogen bond

Polymer	T_m(°C)
$\left[CH_2O \right]_n$	175
$\left[NH(CH_2)_5CO \right]_n$	215~223
 $\left[CH_2—\underset{\underset{\displaystyle CN}{\vert}}{CH} \right]_n$	317
$\left[CF_2—CF_2 \right]_n$	327

3) Crosslink

Strong chemical bond in cross-linking instead of secondary valent bond among molecules, therefore, with the increase of cross-linking degree, heat resistance becomes high. When resin transforms into the fully cross-linked polymer, the heat-resistant temperature is T_{ox} (oxidation) or T_d (degradation).

3.2.3 Corrosion resistance

Among all the matrices and reinforcing fibers which constitute composites, glass fiber is poor at resisting water, acid, or alkali, but it is almost free from erosion of organic solvents.

Corrosion resistance of matrix against water, acid, or alkaline is better than glass fiber, but the erosion of organic solvents is worse than glass fiber. Chemical resistance of resin has significant differences with its different chemical structures. At the same time, the resin content of composites, especially the resin content of surface layer has close relation to its chemical corrosion resistance.

The interaction between resin and media causes corrosion, which includes the physical effect and chemical effect. Physical effect means resin adsorbs medium, then swells or dissolves, which causes resin structure damage and performance decrease; chemical effect means breakage of chemical bond of resin molecules in the media, or creates new chemical bond which again cause structure damage and performance to decrease. Therefore the fundamental effect of resin resisting solvent medium is determined by chemical structure of the component system, and their polarity, negative electricity and solvation ability all affect chemical corrosion resistance.

In general, the higher cross-linking degree of resin, the better corrosion-resistant to medium , so during the curing process of thermosetting resin, we must control a certain curing degree, too low curing degree will seriously affect the corrosion resistance.

Resistance of cured resin against water, acid and alkali medium is related to hydrolysis activation energy of the hydrolysis groups in acid or alkali medium. Table 3.4 shows some hydrolysis groups' activation energy; high active energy has good hydrolysis resistance. Introducing halogen into bisphenol A can not only retain its hydrolysis resistance, but also greatly improve its oxidation resistance.

Table 3.4 Hydrolysis active energy of some groups

Group types		Amide bond	Imide bond	Ester bond	Ether bond	Si—O bond
Active energy (kJ/mol)	Acidic medium	~ 83.6	~ 83.5	~ 75.2	~ 100.2	~ 50.1
	Alkaline medium	66.9	66.9	58.4	—	—

Corrosion resistance of epoxy resin might be different because of using different curing agents. Ester bond formed by acid anhydride curing agent is not alkali-resistant. The —O—, —C—N of amine-cured epoxy resin can hydrolyze in the strong acid, weak acid and organic acids, and with different amine curing agents, type of crosslinking bond is different, curing resin corrosion resistance is also different. For aromatic diamine curing resin, because of its volume shielding effect, the acid resistance and alkali resistance are both better than fatty amine cured. Benzoic anhydride cured epoxy resin has much better acid resistance. Table 3.5 shows relationship of corrosion resistance and functional groups.

3.2.4 Electric properties

Resin molecule is composed of covalent bond, so it is a good electric insulating material. There are two factors affecting the electric insulation properties of resin: one is the polarity of macromolecular chain of resin, and the other is the existence of impurities. Generally speaking, the more polar groups and the greater the polarity in the macromolecular chain, the worse the performance of electric insulation is. On the contrary, if the resin molecules consist of non-polar molecules which have no polarized groups, such as thermosetting styrene-butadiene resin, 1,2-polybutadiene resin, then they will have very good electric insulation performance. In addition, the availability of plasticizers also affects electricity property. Table 3.6 shows the electrical properties of the commonly used thermosetting resin. Comparing with glass fibers, electrical properties of synthetic resin are generally superior. Therefore to obtain composite materials with good dielectric properties, we should select not only a reinforcement material with good electric insulation property, but also a resin with good electric insulation property.

Table 3.5 Relationship between polymer corrosion-resistant and functional groups contained

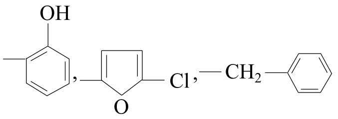
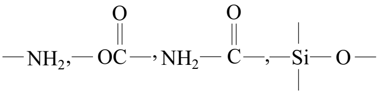
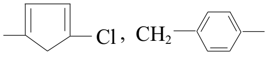
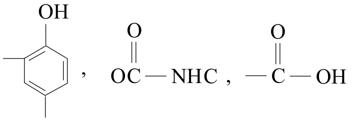
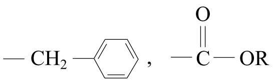
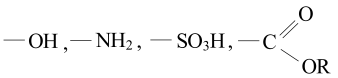
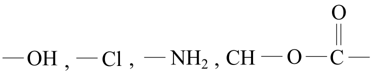
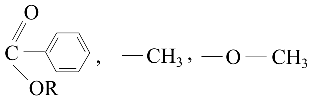
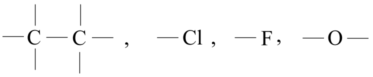
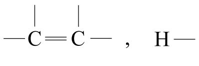
	Favorable group	Disadvantageous group
Acid resistance		 $-NH_2, -OC(=O)-, NH_2-C(=O)-, -Si-O-$
Alkali resistance		 $OC(=O)-NHC(=O), -C(=O)-OH$
Water resistance	 $-C(=O)-OR$	 $-OH, -NH_2, -SO_3H, -C(=O)OR$
Oil resistance	 $-OH, -Cl, -NH_2, CH-O-C(=O)-$	 $-CH_3, -O-CH_3$
Oxidation resistance	 $-C-C-, -Cl, -F, -O-$	 $-C=C-, H-$

Table 3.6 Electric properties of commonly used thermosetting resins

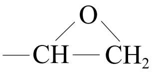
Properties	Phenolic resin	Polyester resin	Epoxy resin	Silicone resin
Density (g/cm^3)	1.30∼1.32	1.10∼1.46	1.11∼1.23	1.70∼1.90
Volume resistivity (Ω·cm)	10^{12} ∼10^{13}	10^{14}	10^{16} ∼10^{17}	10^{11} ∼10^{13}
Dielectric strength (kV/mm)	14∼16	15∼20	16∼20	7.3
Permittivity /60Hz	6.5∼7.5	3.0∼4.4	3.8	4.0∼5.0
Dielectric loss tangent /60Hz	0.10∼0.15	0.003	0.001	0.006
Arc resistance (s)	100∼125	125	50∼180	/

3.2.5 Other properties

1) Adhesion

From the thermodynamic viewpoint, under the condition of no chemical reactions on matrix and fiber surface, the size of adhesion force depends on the surface tension of matrix and surface wetting energy of resin to fiber, that is, good wetting is the prerequisite for good adhesion. In the fully wetted conditions, the wetting angle $\theta = 0°$, and adhesion force reaches the maximum, namely adhesion force between fibers and matrix equals the cohesion of the resins. If chemical bond between matrix and fiber comes into being through a chemical reaction, in this case even if there is no good wetting, good adhesion can also be obtained.

In addition, for evaluating cohesive property, besides the wetting and adhesion with fiber, it is also necessary to consider the curing volume shrinkage. Whether release of small molecule or not and whether break elongation of the matrix appropriate with the fiber or not affect the cohesion as well.

We can learn from the molecular structure of several commonly used thermosetting resins, epoxy resin containing polar groups such as —OH, —O— and  can cohere well with the polar fiber surface. Groups such as —COO— , —NH— are added to molecular structure after curing epoxy resin, and chemical bond may be formed by chemical reactions between resin's epoxy group and hydroxyl on fiber surface. Therefore, there is a great adhesion between epoxy resin and the fiber surface, epoxy resin has good adhesion.

Unsaturated polyester resin contains a number of ester, hydroxyl and carboxyl. Phenolic resin includes a lot of hydroxyl and ether bond, and should have good adhesion, but the big curing shrinkage seriously affects adhesion.

2) Curing shrinkage

Curing shrinkage rate includes volume shrinkage rate and linear shrinkage rate. Volume shrinkage rate is the ratio of the changed volume before and after curing and the volume before curing. Curing contraction includes physical shrinkage and chemical shrinkage.

The impact factors on shrinkage including: density of resin system before curing, close degree of matrix network structure after curing, whether release of small molecules or not in curing process. Epoxy resin has high density before curing, the cured network structure is not very close, and there's no release of small molecules, so it has small curing shrinkage.

Generally, the contractibility impacts products' performance, but sometimes suitable contraction is good for processing, such as the release from mold.

3.3 Technological properties of matrix materials

For polymer matrix composite parts, the basic molding process is shown: fiber is first impregnated with resin and then dried and cured for fixing shape, and at last post cure treatment is conducted for products to be cured entirely. Observing the process we may find that, the resin can flow at first. Through gel stage it gets into the hard solid state, and finally has a stable hardness. Therefore, resins' technological properties can be discussed in these four stages, which are wettability of resin, adhesion, flowing and curing properties. Among them, curing property is the most important characteristics, because it is the main basis of selecting molding method and determining processing parameters.

3.3.1 Wetting property

In preparation of fiber reinforcement composite material, it is always to impregnate or to brush synthetic resin evenly to the fiber or fabric, therefore, wetting ability of resin on fiber is an important factor whether resin is able to evenly distribute in fibers or not, and also an important factor to have good interface adhesion of resin and fiber.

We will discuss the representation of liquid wetting on the solid surface, the liquid wetting capacity on solid, the factors influencing liquid wetting angle, and so on in Chapter 4, but not here.

Besides the surface tension of fiber (or fabric), the wetting of resin on fiber mainly depends on resin surface tension and the interfacial tension between resin and fiber. The surface tension of resin depends on its molecular structure, i.e., the greater the attracting force among molecules, the greater the cohesive energy, the larger the surface tension. Interfacial tension between resin and fiber depends on the interaction force between resin molecule and fiber surface molecule, and the greater the force between them, the higher the interfacial tension.

From the process, if the resin has low viscosity, good fluidity, it will be good for the wetting of resin on fiber. For the fiber, if it is not twisted, it will be good for the infiltration of resin; on the contrary, the more twists of the fiber, the worse infiltration of the resin. For the fabric, satin weave and twill weave are better for infiltration of resin than plain weave.

3.3.2 Bonding property

Resin adhesion to the reinforcing fibers, as the adhesion of any liquid on the solid surface, the adhesion work can be calculated by the thermodynamic formula.

For glass fiber reinforced polymer composites, to evaluate the bonding property of resin, in addition to the wetting property and adhesion work with glass fiber, it is also necessary to consider the curing volume shrinkage, whether release small molecule or not, and whether break elongation of the matrix appropriate with the fiber or not .

3.3.3 Fluidity performance

The molecular weight of commonly used thermosetting resins is not too large (usually from 200 to 400), so they have a lower softening temperature and viscosity, and good fluidity like other low molecular weight compounds.

With the curing reaction of resin, molecular weight increases, also crosslinking appears, viscosity of resin enhances, and liquidity falls. For most polymer compound, relation between velocity of flow and shear stress is shown in follow:

$$D = A(\sigma - \sigma_1)^n \tag{3.1}$$

where D is the flow rate;

σ is the shear stress;

σ_1 is the limit of shear stress(that is, only when the shear stress is added to this value, fluid begins to flow. The higher the σ_1, the harder the object is, and the more obvious difference of the object with liquid is. σ_1 is related to the time of stress acting, the longer time, the smaller the σ_1; conversely, the higher the σ_1);

n is larger than 1;

A is the characteristic value which is related with temperature (when temperature rises, A increases, and A is inverse to viscosity).

We see that the flow rate of resin not only depends on the chemical structure of macromolecule, relative molecular weight, geometry, but also is affected by the temperature and the size of the shear stress. In addition, the existence of plasticizer significantly affects resin fluidity, since it can reduce the resin softening temperature and viscosity.

When the resin transformed into three-dimensional network, it lost their fluidity. At this point, there is only ordinary elastic deformation and high elastic deformation (or forced high elastic deformation) under the external force, so it is impossible for further processing this time.

3.3.4 Curing characteristic

Curing is a process that linear resin under curing agent or heating conditions through chemical reaction changes into solid resin with insoluble, non-melting, and three-dimensional conformation. In the curing process, resin transforms from the viscous flow state into solid state with certain hardness, so it is also called hardening. Therefore curing means not only the transformation of the physical state of resin in the process, but also the occurrence of chemical change in the course.

There are three stages in the curing process. For a variety of thermosetting resin, structure change from the linear molecule to three-dimensional network by cross-linking reaction is a common feature. In the molding process, it behaves the change of technique property from the viscous flow state soluble and fusible into the solid state insoluble and non-melting. However, on the chemical mechanism of curing reaction, the chemical changes of the various kinds of thermosetting resins in the curing process behave differently. Here, we only briefly discuss the common technical properties (the nature of curing stage) among various types of resins in the curing process. It must be pointed out that because various types of resins have particularity in the curing reaction, they also have their own characteristics which are reflected on the curing stage.

1) Phenolic resin curing process

Phenolic resin is used in dry method process, and there are three stages in its curing process.

(1) A-stage of phenolic resin. Thermosetting phenolic resin in its initial state, soluble and fusible, is called it A-stage of phenolic resin. It has low average molecular weight, lots of polar groups, and is soluble in alcohol and easily impregnated.

(2) B-stage of phenolic resin. Resin changes into the insoluble and infusible state under conditions of heating step by step, and at middle stages of change it is called B-stage. In dry method process, after the fiber impregnation of resin, we not only remove solvent, but also pre-cure at the same time to control the crosslinking degree of resin, which makes sure that resin transform from A into B.

(3) C-stage of phenolic resin. B-stage phenolic resin by further heating, due to further reaction, will loss liquidity and change into the insoluble and infusible solid state , and is known as the C-stage of phenolic resin i.e. the cured phenolic resin.

Polycondensation reaction is step by step, so the three stages of phenolic resin curing have clear boundaries. In the dry method process, it is often to separate impregnation and the curing in a different section in accordance with the stage property of resin curing. Therefore, the mastery of curing characteristics of resin stage is the key to grasp the curing process.

2) Curing stages of unsaturated polyester resin

In the wet process of unsaturated polyester, the curing process includes three stages, gel, setting and ripening. During gel stage the resin is from the viscous motion state to the semi-solid gel where mobility is lost; setting stage is from the gel to the stage having a certain hardness and a fixed shape, being able to remove from the mold; ripening stage is a stage in which resin becomes rigid in appearance, gains a certain mechanical properties, and gets stable physical and chemical properties after post heat treatment for using.

Since the curing reaction of unsaturated polyester resin has the characteristics of chain reaction, once reaction initiates, the molecular chain will grow rapidly. Therefore, it is not as obvious as the curing of phenolic resin in the three stages, especially from the gel to the setting, which often accomplish in a very short time.

Because B-stage of unsaturated polyester resins is not clear and short, and there is a sudden gel phenomenon from A to B, we generally use one step technique to cure and mold the viscous resin directly. And it can cure under the contact pressure at room temperature, especially for hand lay-up process to manufacture large size parts. In the hand lay-up process of unsaturated polyester resins, the mastery of gelation time is a key issue. If gelation time is too short, resin cannot fully impregnate fibers, and even the risk might happen that resin becomes gel before brushing on fiber; and if gelation time is too long, resin flows in the long term, which leads to easy loss of resin, influencing the resin content of the part.

3) Curing stages of epoxy resin

Three stages are gel, setting and ripening in the curing process of epoxy resin. The curing is caused by the ring-opening addition reaction between epoxy groups and curing agent, and has a nature of step by step, so the three stages are more obvious than that of polyester resin. At the same time, curing conditions (temperature, pressure, time, etc.) of epoxy resin have large changes in the scope with different curing agents. All these make epoxy resin to have better technology adaptability than polyester resin, and may adapt almost all molding processes. For example, epoxy resin with amine for curing agent has been widely used in hand lay-up process, while epoxy resin with the type of acid anhydride and phenolic resin for curing agent is commonly used in laminates, compression molding and filament winding process.

From the technology viewpoint, it is very important for controlling the gelation time accurately, which is equally applicable to epoxy resin.

From the using viewpoint, accurately controlling the resin to C-stage is necessary for ensuring good performance of product, which is the control problem of curing degree in cure cycle. The degree of curing generally refers to the degree of completely curing. In fact, it is very difficult to achieve the complete curing degree, and this is because at the later stage of curing reaction, viscosity of system increases so dramatically that molecular diffusion is hampered. Therefore, it is generally believed that the curing process has been accomplished according to material properties getting stabilized.

3.3.5 Toxicity and allergic

The matrix resin, curing agent, diluent, etc which are used in composite materials all have toxicity in a varying degree, and some also have a strong volatility. In the process of forming parts inbreathing or directly contacting with these by the operator would give rise to different cases of poisoning and allergic reactions.

1) Toxicity

The classification of toxic substances is generally in accordance with the size of LD_{50} the oral lethal dosage of lab rats (see Table 3.7). LD_{50} is meant that the minimum oral dosage of medicine at which with a weight of 1 kg white rats dosed and died half, the unit is mg/kg, and the lower the LD_{50}, the more poisonous is. The toxicity of common harmful substances used in hand lay-up process is shown in Table 3.8.

Table 3.7 Classification of oral toxicity

Serial number	Toxicity and classification	Rodent oral LD_{50} (mg / kg)
1	Extremely poisonous	$\leqslant 1$
2	Highly toxic	1~50
3	Moderately toxic	50~500
4	Slightly toxic	500~5000
5	Non-toxic	5000~15000
6	Relatively harmless	$\geqslant 15000$

Table 3.8 Toxicity of harmful materials

Name	Toxicity LD_{50} (mg/kg)	Name	Toxicity LD_{50} (mg/kg)
Triethanolamine	14	Diethylenetriamine	2330
Epoxy chloropropane	90	Triethylene-tetramine	4340
Triethylamine	460	β-hydroxyethylethylamine	4205
Ethylenediamine	620	Bisphenol A	4200
Maleic anhydride	400~800	Styrene	5000
Phthalic anhydride	800~1600	Glycol	5500
Imidazole	1000	Methyl methacrylate	3400
2 - ethyl -4 - methylimidazole	1180	Triethylene glycol	20700
2 - methylimidazole	1420	Polyamide 600	1750
Benzene dimethylamine	1750		

In accordance with the oral toxicity standards, except triethanolamine, the matrix material basically belongs to moderately toxic and slightly toxic, and raw material with a slight toxicity takes up majority. Despite this, the long-term exposure to these materials will affect the health in some certain extent. For example the use of unsaturated polyester resin will often contact with styrene, although it is of low toxicity, but the long-term exposure can cause neurasthenia, nausea, loss of appetite and symptoms of decreased white blood cell. Amines curing agent in the epoxy resin, or epoxy chloropropane, is greatly irritant to people, and long-term exposure can cause dermatitis, skin itching, chronic laryngitis, stomach discomfort, loss of appetite and dizziness, fatigue and other symptoms. Acid anhydride curing agent has minimal toxicity, but some acid anhydride inhaled by the human such as benzoic dimethyl acid anhydride, can damage the liver and strongly interfere with gastrointestinal function.

2) Allergic reactions

There are two kinds of allergic reactions which are contact and inhaled allergens generally. The allergic reaction after direct contact of hands or other exposed part with the object is called contact allergy; allergic reaction due to inhalation of toxic gas or steam is called allergens allergic. For example, in a factory for the use of phenolic resin curing agent for epoxy resins, some staff have the occurrence of allergic dermatitis and eczema situation. This is because phenol and formaldehyde containing in phenolic resin and their evaporation cause allergic reaction. In general the degree of allergic reactions is not only related to the toxicity of glue itself, but also to the using condition of glue and personal physical conditions. For example, at high temperature harmful substance volatilizes in the large amount, allergy situation becomes more serious; the experience has shown that the allergy situation is more serious in younger people than the elder, and more serious in women than men. Determination of allergy degree is conducted by confecting a matter to a solution of some concentration, droping a drop on the inner forearm of tester, affixing medical adhesive plaster and opening it after 24 hours to check the allergic situation.

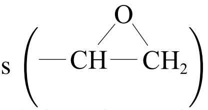
3.4 Matrix resin of composites

Polymers are the main components of polymer matrix composites, two main types are thermoplastic resin and thermosetting resin. Thermosetting resins include epoxy resin, unsaturated polyester resin, phenolic resin, and thermoplastic resins include polyamide, polysulfone, polyimide, polyester, etc.

3.4.1 Epoxy resin

1) Introduction

Epoxy resin is a type of synthetic resin including a wide variety, and with continuous development; it can be used as adhesives, coatings, fluxes, casting plastics and the matrix resin of fiber reinforced composites, and is widely used in mechanical, electrical, chemical, aerospace, automotive, building and other industrial sectors.

Epoxy resin is the type of organic prepolymer that refers to molecules containing two or more epoxy groups  $\left(-\overset{\;\;O}{\overset{/\;\backslash}{CH-CH_2}}\right)$. Epoxy groups can be located at the end, middle of molecular chain or into a ring structure. Because of the active epoxy group of molecular structure, they can crosslink with many curing agents and form insoluble, non-melting three-dimensional network structure polymer.

(1) Properties and characteristics of epoxy resin:

① A large number of varieties. A variety of resins, curing agent, modifying agent system can adapt to a wide range of applications on the request form, which can range from very low viscosity liquid to high melting point solid.

② Facility of curing. By selecting a variety of curing agents, epoxy resin system may almost cure at the range of 0°C to 180°C.

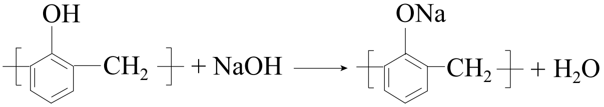
③ Strong adhesion. Inherent polarity hydroxyl and ether bond of epoxy resin make it to have a high adhesion with various substances. Low curing shrinkage of epoxy resin will also help to form a tough adhesion bonding with little inner stress. Because there is no release of volatile by-products in curing reaction, so no need for molding at high pressure or time to remove volatile by-products, which further enhances the bond strength of epoxy resin system.

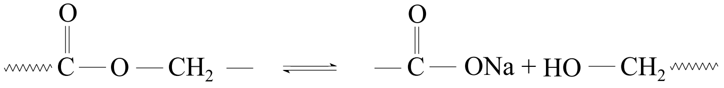
④ Low shrinkage. Epoxy is different from other thermosetting polymer resins, it does not produce by-products in curing process, and there is a high degree of association in liquid. Curing is carried out by direct addition reaction, so it has small contraction. For a non-modified system, its shrinkage rate is less than 2%, while the curing of general phenolic resin and polyester resin has considerable contraction.

⑤ Mechanical properties. The cured epoxy resin system has excellent mechanical properties.

⑥ Electric properties. The cured epoxy resin system has good electric performance in a wide frequency and temperature range, which is a good insulating material with high dielectric, surface leakage resistant and good arc resistant.

⑦ Chemical stability. The cured epoxy resin has a strong chemical stability. In the curing epoxy system, benzene ring and fatty hydroxyl are basically less susceptible to base erosion, and they are extremely acid resistant. We can make a comparison of stability to NaOH among epoxy resin and phenolic resin with weak acidity or ester bond of polyester resin.





$$\sim\!\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2- \rightleftharpoons -\overset{\overset{\displaystyle O}{\|}}{C}-ONa+HO-CH_2\!\sim$$

Reaction of phenolic resin with sodium hydroxide, phenolic sodium generated is easily dissolved, breaking the chains eventually. For polyester resin, ester hydrolysis becomes original alcohol and acid sodium salt.

Chemical stability of curing epoxy system has been increased because of the closed block in a pile of dense structure especially for solvent resistance.

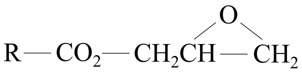
⑧ Dimensional stability. Colligating above performances, curing epoxy resin system has outstanding dimensional stability and durability.

⑨ Fungal resistance. Curing epoxy resin system can resist most fungal, and can be used under harsh tropical conditions.

(2) Types of epoxy resin. There are many kinds of epoxy resin. According to their molecular structure, they have five main categories.

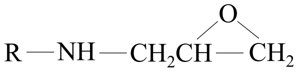
① Glycidyl ether:

② Glycidyl ester:



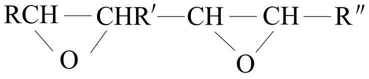
$$R{-}CO_2{-}CH_2\overset{\overset{O}{\diagup\ \diagdown}}{CH{-}CH_2}$$

③ Glycidyl amine:



$$R{-}NH{-}CH_2\overset{\overset{O}{\diagup\ \diagdown}}{CH{-}CH_2}$$

④ Type of linear aliphatic:



$$\underset{\underset{O}{\diagdown\ \diagup}}{RCH{-}CHR'}{-}\underset{\underset{O}{\diagdown\ \diagup}}{CH{-}CH}{-}R''$$

⑤ Alicyclic category:

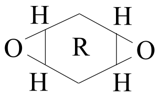


Table 3.9 Codes and types of epoxy resin

Code	Type of epoxy resin	Code	Type of epoxy resin
E	Bis(4-hydroxylphenyl)propane epoxy resin	N	Phenolphthalein epoxy resin
ET	Organic titanium modified diphenol-propane epoxy resin	S	Tetra-phenolic epoxy resin
EG	Organosilicon modified diphenol-propane epoxy resin	J	Resorcinol epoxy resin
EX	Bromine modified diphenol-propane epoxy resin	A	Tricyanic epoxy resin
EL	Chlorine modified diphenol-propane epoxy resin	R	Bicyclopentadiene dioxide epoxy resin
Ei	Diphenol propane side chain epoxy resin	Y	Dioxide vinyl cyclohexene epoxy resin
F	Phenolic multi-epoxy resin	YJ	Dimethyl replaced dioxide vinyl cyclohexene epoxy resin
B	Glycerol epoxy resin	D	Epoxidized polybutadiene epoxy resin
L	Organic phosphorus epoxy resin	W	Dioxide bis-cyclopentenyl ether resin
H	3,4-epoxy group-6-methyl cyclohexane carboxylic acids 3',4'-epoxy group-6-methyl cyclohexane methyl ester	Zg	Fatty glyceride
G	Silicon epoxy resin	Ig	Naphthenic glycidyl ester

Types of ①, ② and ③ are condensation epoxy resin from epichlorohydrin and compounds containing active hydrogen atoms such as phenols, alcohols, organic acids and amines, etc. Types of ④ and ⑤ are made from epoxidizing olefin with double bonds $\left(\rangle C{=}C\langle\right)$ by peracetic acid or hydrogen peroxide at low temperature. The largestly-used one in composites is the first category, glycidyl ether epoxy, of which the main type is bis(4-hydroxylphenyl)propane type of epoxy resin (briefly called bisphenol A epoxy resin) which is from the polycondensation of 4,4’-dihydroxyldiphenylpropane (in short called bisphenol A) with epichlorohydrin.

Epoxy resin is classified according to its different major components, and Table 3.9 shows the codes and types.

(3) Principle of naming epoxy resin model.

① Epoxy resin uses one or two Chinese phonetic alphabet and two Arabic numerals as models to show types and varieties.

② First character of the models is usually from the name of the main substance components (choose the first letter of Chinese phonetic alphabet of it). In case of the first letter collision with other model, we add the second letter, and so on.

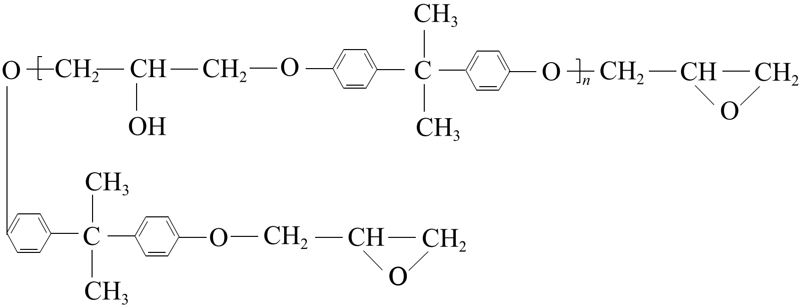
③ Second character of the model is the Chinese phonetic alphabet of modified substance if there is any, and we use mark “-” instead if the material is not modified.

④ Third and fourth characters are digits representing the value of main performance of the product, the arithmetic mean epoxy value.

For example, a grade of epoxy resin, using bisphenol A as the main component material, the epoxy value from 0.48 equivalent/100g to 0.54 equivalent/100g, while the arithmetic average is 0.51, the resin is called “E-51 epoxy resin”.

2) Diglycidyl ether of bisphenol A (DGEBA)

Bisphenol A epoxy resin is a polymer which comes from polycondensation with epichlorohydrin and 4,4’-dihydroxyldiphenylpropane, and it has the common performances of general polymers. Synthesis in different conditions can obtain resin with different molecular weights, the average molecular weight generally is from 300 to 2000, and its structural formula is shown in follows.



In the formular, $n = 0 \sim 19$, when $n = 0$, the low-molecular-weight epoxy resin is an amber or yellow liquid, and when $n \geqslant 2$, the high molecular weight resin is in solid state. In a wide range of epoxy resins, bisphenol A epoxy resin accounts for about 90% of the total output, and it has the broadest usage and has been widely used in casting, bonding, coatings, paints, composite materials and so on. Bisphenol A epoxy resin has lower using temperature, and it can mix with other resins to improve certain properties. Table 3.10 shows specifications and grades of homemade bisphenol A epoxy resin.

Table 3.10 Specifications of epoxy resin

Unified brand	E-51	E-44	E-42	E-20	E-12
The original brand	618	6101	634	601	604
Average molecular weight	350∼400	450	—	900∼1000	1400
Epoxy value (equivalent/100g)	0.48∼0.59	0.40∼0.47	0.38∼0.45	0.18∼0.22	0.09∼0.15
Epoxy equivalent	175∼210	225∼290	—	450∼525	870∼1025
Softening point(°C)	<2.5Pa·s1)	14∼22	21∼27	64∼76	85∼95

Note: Softening point of the liquid is lower than the normal temperature, and the data is the viscosity value at 25°C.

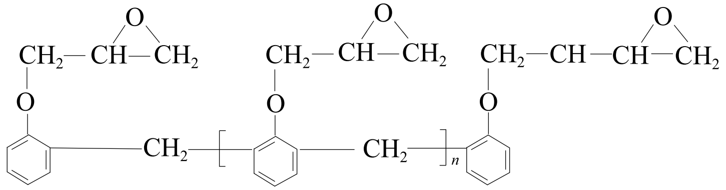
Table 3.11 shows physical and mechanical properties of cured bisphenol A epoxy resin and other thermosetting resin systems. See Table 3.11, the various properties of epoxy resin system are better than other resins, which is widely used as matrix resin usually at generic temperature, but not used at higher temperature.

A majority of bisphenol A epoxy resin curing system will degrade thermally at 200 °C for a long term using, so in order to improve thermal performance there appears phenolic epoxy resin.

Table 3.11 Physical and mechanical properties of commonly used thermosetting resin

Properties	PF	Polyester resin	Epoxy resin	Silicone resin
Density (g/cm^3)	1.30∼1.32	1.10∼1.46	1.11∼1.23	1.70∼1.90
Tensile strength (MPa)	42∼64	42∼71	∼ 85	21∼49
Elongation at break (%)	1.5∼2.0	5	5	1
Tensile elastic modulus (GPa)	∼ 3.2	2.1∼4.5	∼ 3.2	1
Compressive strength (MPa)	88∼110	92∼190	∼ 11	64∼130
Flexural strength (MPa)	78∼120	60∼120	∼ 130	∼ 69
Water absorption/24h (%)	0.12∼0.36	0.15∼0.60	0.14	Not good
Heat distortion temperature (°C)	78∼82	60∼100	120	
Linear expansion coefficient (10^{-6}/°C)	60∼80	80∼100	60	308
Rockwell hardness/6.35mm,100kg	120	115	100	45
Shrinkage rate (%)	8∼10	4∼6	1∼2	4∼8

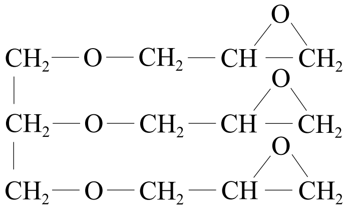
Phenolic epoxy resin includes epoxy resin of phenol formaldehyde type, o-cresol novolac type and three kinds of mixed cresol formaldehyde type. Compared to bisphenol A epoxy resin, there are two or more epoxy groups on the linear chain, so the cured product has high cross-linking density, and thus it has excellent thermal stability, mechanical strength, electric insulation, water resistance and corrosion resistance. It comes from the polycondensation with linear phenolic resin and epichlorohydrin, and its structural formula is shown in follows.



Homemade products models are F-51, F-44 (644), F-46 (648) and JF-46 (o-cresol novolac), etc., and these resin systems are selected as matrix systems of heat-resistant composites.

3) Fatty polyol glycidyl ether epoxy resin

Fatty polyol glycidyl ether epoxy resin molecules contain two or more epoxy groups. A majority of these resins have low viscosity, and are water-soluble. Also, most of them are long-chain linear molecules, so they have good flexibility. Glycerol epoxy resin (glycerin epoxy resin) is one of the most common types, and the structure is shown in follows.



Glycerol epoxy resin has strong bonding and can be used as a binder. Adding it into bisphenol A epoxy resin can decrease the operation viscosity of the resin and increase the toughness of the cured system. In addition, it is also used as treatment agent in wool fabric, cotton cloth and chemical fiber, the fabric after treatment has characteristics of wrinkle-free, shrink-proof and anti-moth-eaten and so on.

4) Glycidyl ester epoxy resin

Comparing with bisphenol A epoxy resin, glycidyl ester epoxy resin usually has low viscosity, good using processabilty, high reactivity, and higher adhesion force than other common epoxy resins. The cured has good physical properties, electric insulation, and in particular, traces of leakage-resistant. It also has good resistance to ultra-low temperature. Under ultra-low temperature from −196 to −253 °C it still has higher adhesive strength than other types of epoxy resin. Moreover, it has good surface gloss, transmittance, and good climate resistance. Table 3.12 shows the structure of several glycidyl esters.

Using acetyhydroperoxide to oxidize the double bond of four hydrogen phthalic acid epoxy resin, we may obtain TDE-85 epoxy resin, and its molecular structure is shown in follow.

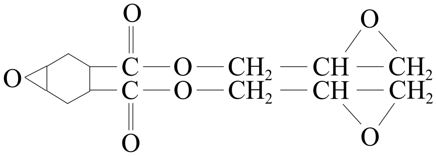
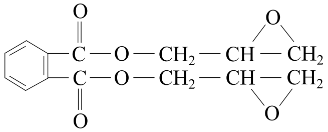
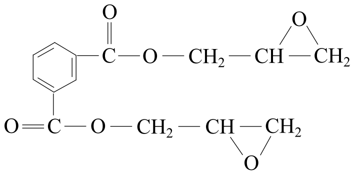
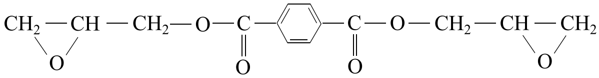
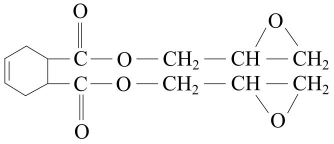
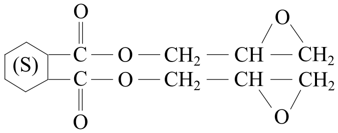
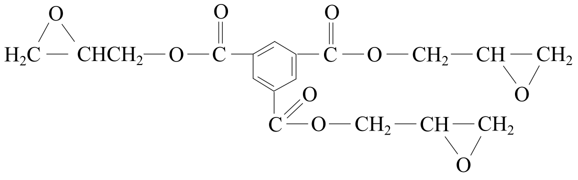
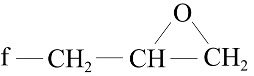
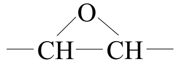


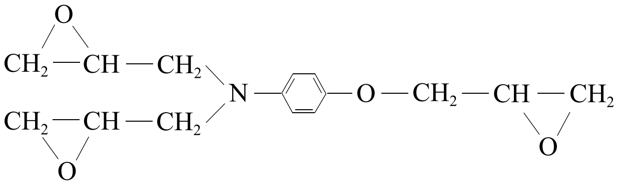
Table 3.12 Structure of glycidyl esters

Glycidyl ester	Structure
o-phthalic acid diglycidyl ester	
m-phthalic acid diglycidyl ester	
Terephthalic acid diglycidyl ester	
Tetrahydrophthalic acid diglycidyl ester	
Hexahydrophthalic diglycidyl ester	
Trimellitic acid triglycidyl ester	

It is a light yellow transparent viscous liquid, with a viscosity (25°C) from 1.6Pa·s to 2.0Pa·s, epoxy value $\geqslant$ 0.85 equivalent/100g. Calculation result of its epoxy value according to the molecular structure is 0.97equivalent/100g, so there is a certain gap between calculation and the measured value. Therefore, the average number of epoxy groups in TDE-85 resin is more than 2 and less than 3. TDE-85 molecule contains two different types of epoxy groups which have different activity. In general, the activity of  $-CH_2-\overset{O}{CH-CH_2}$ is high,the activity of alicyclic epoxy group  $-\overset{O}{CH-CH}-$ is low.

5) Glycidyl amine resin

Glycidyl amine resin can be synthesized with aliphatic or aromatic primary amine or secondary amine and epichlorohydrin. The characteristic of this kind of resin is multi-functional, high epoxy value, high crosslinking density, significantly improvement of heat resistance. The main disadvantage is brittleness. The most important resin in this category is AFG-90 epoxy resin, name (1- glycidyl ether 4-diglycidyl amine). Its structure is shown in follow.



The resin is brown-black liquid at ambient temperature, with low viscosity from 1.6Pa·s to 2.3Pa·s at 25°C, epoxy value from 0.85 equivalent/100g to 0.9 equivalent/100g, odorless, short curing cycle, and it has high heat resistance and mechanical strength. See Table 3.13.

Table 3.13 Mechanical properties of glass fiber reinforced plastics AFG-90

Formulations (parts in weight)	Resin content (%)	Flexural strength (MPa)					Bending modulus (GPa)
		Room temperature	100°C	150°C	200°C	250°C	
AFG-90 100 BF_3/MEA 3	40	487	423	420	283	178	16.9

6) Alicyclic epoxy resin

Alicyclic epoxy resin is fabricated by epoxidation of double bonds of alicyclic olefins, and their molecular structure is very different from bisphenol A epoxy resin and other epoxy resin. In the former, epoxy group directly connects on alicyclic, while the glycidyl ether groups in the latter connect on benzene nuclear or aliphatic hydrocarbon.

Characteristic of alicyclic epoxy resin is shown in follows: ① high compression and tensile strength; ② retain good mechanical properties and electric properties when exposed at high temperature for long term; ③ good arc resistance; ④ good UV resistance aging properties and climate resistant.

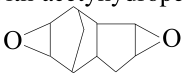
Dicyclopentadiene dioxide is an important species, and the homemade brand is R-122 (6207), which is fabricated with acetyhydroperoxide oxidation on dicyclopentadiene. Its structure is given: . Its molecular weight is at 164.2, appearing white crystalline powder, with a specific density of 1.33. Its melting point is higher than 185°C and epoxy equivalent is 82. Comparing with bisphenol A epoxy resin, its epoxy group directly connects on alicyclic, so it can obtain close rigid alicyclic polymer structure after curing, and have high heat resistance, the heat distortion temperature is higher than 300°C. From Table 3.14, the glass fiber reinforced plastic still has high strength at high temperature of 260°C. In addition, as the resin does not contain benzene ring, effect free from ultraviolet, it has excellent climate resistance. At the same time, because they do not contain other polarity groups, they have excellent dielectric properties, the drawback is the high brittleness of the cured matter, and the adhesion force of resin is not high enough.

Table 3.14 Bending strength of cured FRP $6207^{\#}$ with maleic anhydride

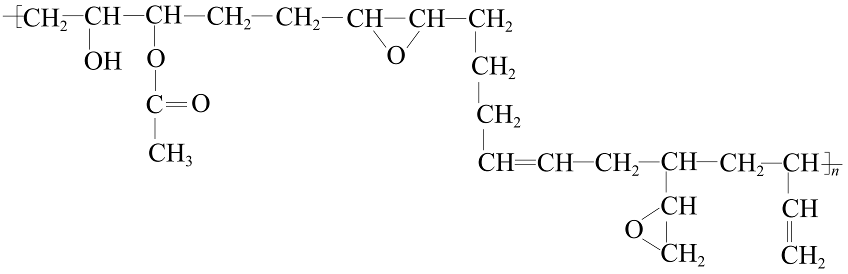
Test Conditions (°C)	Room temperature	150	200	260
Flexural strength (MPa)	525	467	477	331

Usually, this type of resin is difficult to cure with amine as the curing agent, and mostly we use acid anhydride. Due to the nonexistence of hydroxyl, we must add a small amount of polyol for initiation. For example, when we use maleic anhydride or 647 anhydride as curing agent, a small amount of glycerol should be required to add as initiator.

$6207^{\#}$ epoxy resin, although it is solid powder with a high melting point, when it is mixed with curing agent and heated to higher than 61°C, the viscosity is only 0.1 Pa·s at liquid, it not only has long using time and is easy to operate, but also has good wettability on fillers. As a result of these processing characteristics and excellent performance, it has a wide range of applications such as casting materials, adhesives, and glass fiber reinforced plastics at high temperature.

7) Aliphatic epoxy resin

This type of resin is different from bisphenol A epoxy resin and alicyclic epoxy resin, there is no benzene nor alicyclic in its molecular structure. It only has fatty chain and epoxy groups are linked with fatty chain. The structure formula is shown in follow.



In such resins, polybutadiene epoxy resin is representative (grade $2000^{\#}$). It dissolves in benzene, toluene, ethanol, butanol, acetone and other solvents, and reacts with curing agent such as amine and acid anhydride for curing. The product has a high heat resistance and impact properties.Table 3.15 shows the physical and mechanical properties of casting materials. With unsaturated double bond in the molecular structure, we can increase crosslinking density of the cured product and improve heat-resistant of the resin by using peroxide for crosslinking. The disadvantage is its large shrinkage. In some cases, it can mix with other types of resin to improve toughness of composite materials.

Table 3.15 Physical mechanical properties of epoxidized polybutadiene resin casting material

Properties	Indicators
Tensile strength (MPa)	38
Flexural strength (MPa)	97
Compressive strength (MPa)	187
Impact toughness (kJ/m^2)	19.5
Brinell hardness (kg/mm^2)	7.5
Martin resistant temperature (°C)	60

3.4.2 Curing of epoxy resin and curing agent

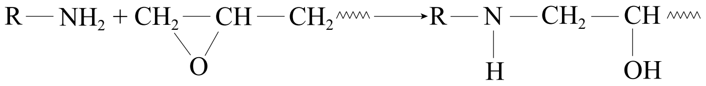
Epoxy resin is thermoplastic resin with linear structure, hence cannot be used directly. We must add curing agent in the resin, so that it changes into cross-linked network structure at certain temperature and become useable. Epoxy resin curing agent is classified into two types. The first type of curing agent can carry out the addition with epoxy resin, transforming the epoxy resin into the cross-linked network structure through a gradual process of polymerization, such curing agent is called addition reactive curing agent. Usually it has reactive hydrogen atoms and the reaction includes the transfer of hydrogen atoms. Chemicals like multi-primary amine, polycarboxylic acid, multi-mercaptan, polyphenol, etc belong to this type. The other is catalytic curing agent. It can lead epoxy group of resin to cure according to polymerization of cationic or anionic. Such curing agents include tertiary amines and boron trifluoride complexes. Both types of curing agents carry out the curing process with hydroxyl and epoxy group within molecular structure of the resin.

1) The curing process of epoxy resin by step polymerization

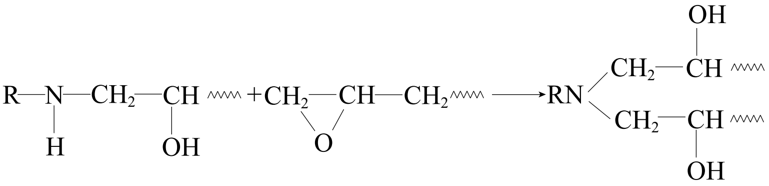
(1) Multi-aliphatic primary amine.

Primary amine reacts with epoxy resin is the reaction of hydrogen atom connected to the primary amine nitrogen atom with epoxy group, the primary amine changes into secondary amine and then converts into tertiary amine. Reaction principle is shown in follows.

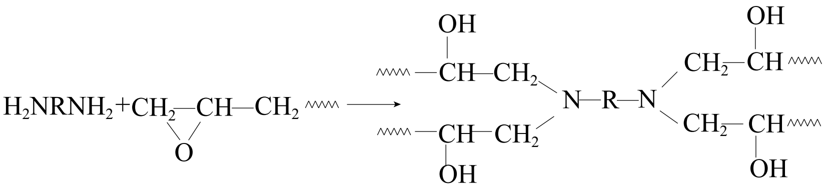
① Reaction with epoxy to get secondary amine:



② Then reaction with another epoxy group to get tertiary amine:



③ For diamine, curing reaction is:



Primary amine and epoxy resin crosslink into a complex network polymer by progressive polymerization.

The reaction of multi-aliphatic primary amine with epoxy resins does not need catalyst, but different additives have different effects on the reaction. A series of proton donor materials accelerate the curing reaction, for example, alcohol, phenol, carboxylic acid, sulfonic acid and water all have hydroxyl. On the contrary, the proton acceptor of the substances can inhibit the curing reaction, such as ester, ether, ketone and nitrile, etc., and aromatics also have the effect of inhibition.

The reaction of aliphatic polyamine and epoxy resin is by active amino hydrogen, and theoretically each active hydrogen atom on amino nitrogen atoms can open one epoxy group, so it has the following stoichiometric relationship.

$$\text{The amount of amine (phr)} = \text{Amine equivalent} \times \text{Epoxy value} \tag{3.2}$$

Where

$$\text{Amine equivalent} = \frac{\text{Molecular weight of amine}}{\text{The number of active hydrogen in amine}} \tag{3.3}$$

Here phr is the required mass of curing agent for each 100 shares of epoxy resin.

For example, for the bishydroxylphenyl propane epoxy resin with epoxy value at 0.51 equivalent/100g, we use triethylene tetramine as curing agent. The dosage is shown in follows.

$$\text{Amine equivalent} = 146 \div 6 = 24.3$$

$$\text{The amount of TETA(phr)} = 24.3 \times 0.51 = 12.4$$

Table 3.16 shows the properties of the commonly used aliphatic amine of curing agent.

Table 3.16 Properties of the commonly used aliphatic amines curing agents

Amine	Molecular weight	Appearance	Active hydrogen	Calculation dosage[1] (phr[2])	Density at 25°C (g/cm^3)	Pot life of 50g at 20°C(min)
Diethylenetriamine	103	Liquid	5	11	0.95	25
Imino bispropanamine	131	Liquid	5	14	0.93	35
Triethylene-tetramine	146	Liquid	6	13	0.98	26
Tetraethylene-pentamine	189	Liquid	7	14	0.99	27
Diethylamino propylamine	130	Liquid	2	7	0.82	120 (454g)
p-menthane diamine	170	Liquid	4	22	0.91	480 (1135g)
N-aminoethyl piperazine	129	Liquid	3	23	0.98	17

Note: 1) Calculation according to bishydroxylphenyl propane epoxy resin (epoxy equivalent in a range of 185 to 192).

2) phr is the required mass of curing agent for each 100 shares of epoxy resin.

(2) Multi-aromatic primary amine.

The reaction mechanism of aromatic polyamine curing epoxy resin is basically similar with aliphatic polyamine. Since electron cloud density on nitrogen atom is lower, multi-aromatic amines are less alkaline, and have the three-dimensional steric effects of the aromatic ring, the corresponding reaction with epoxy group is slower than that of aliphatic amines. Alcohols, phenols, boron trifluoride complexes and stannous octoate can accelerate the curing reaction of aromatic polyamine and epoxy resin, and stannous octoate has particular effect on speeding up alicyclic epoxy curing. Table 3.17 shows the typical aromatic polyamine curing agents.

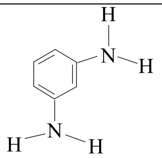
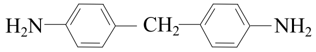
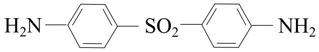
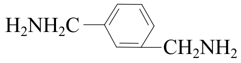
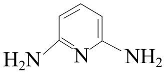
(3) Polyamide.

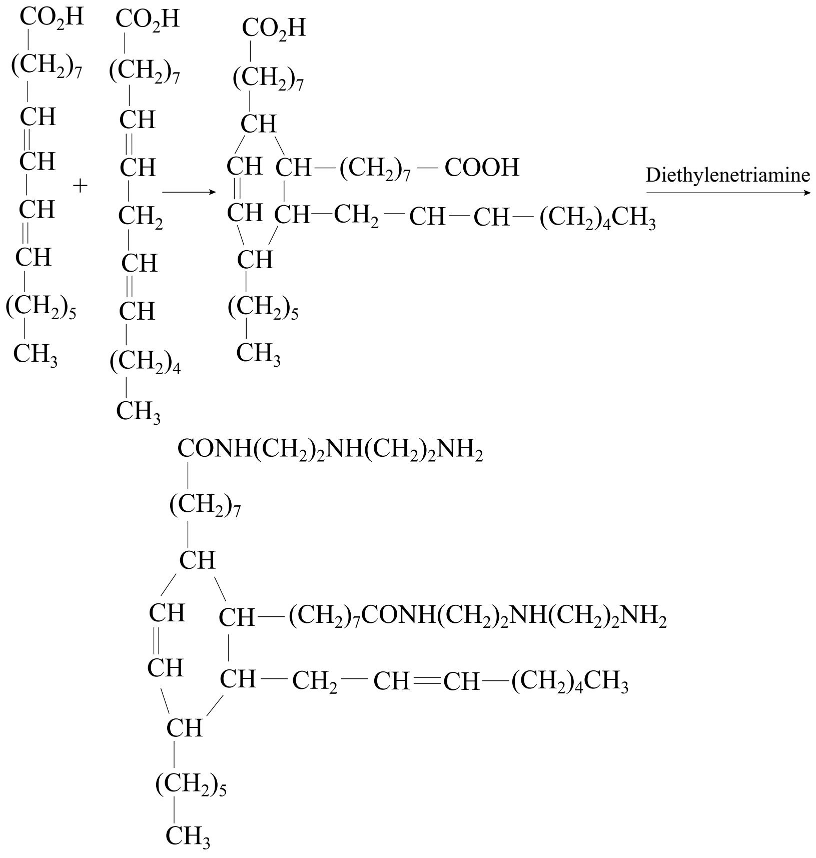
Because the hydrogen of amide group is not active, usually amide isn't only used as curing agent but as curing accelerator of anhydride.

Amino-polyamide is widely used in the curing of epoxy resin, which is reaction product of the dimerized or trimerized vegetable oil fatty acids and aliphatic polyamine.

For example, 9,12- and 9,11-linoleic acid firstly dimerize, then it reacts with two molecules of diethylenetriamine and thus obtain amino-polyamide with amide group. There are primary amine group and secondary amine group in the molecular structure simultaneously. The curing reaction of epoxy resin is usually caused by the primary amine group and the secondary amine group, therefore,

Table 3.17 Typical aromatic amine curing agents

Chemical name	Abr. name	Melting point(°C)	Molecular Structure
m-Phenylene diamine	MPD	63	
Diamino diphenyl methane	DDM (MDA)	89	
Diamino diphenyl sulfone	DDS	175	
m-xylenediamine	MXDA	Liquid	
Diamino pyridine	DAPO	121	



mechanism of the curing reaction is similar to that of aliphatic polyamine. Table 3.18 shows all kinds of polyamide curing agents which all belong to the category of this product.

Table 3.18 Properties of polyamide resin

Grade	Appearance	Viscosity at 40°C (Pa·s)	Active hydrogen equivalence, Amine value (mg/g)	Reference amount (phr)
Polyamide200	Viscous liquid	20~80	215±15	40~100
Polyamide300	Brown-red liquid	6~20	305±15	40~100
Polyamide400	Reddish brown viscous liquid	15~50	200±20	40~100
Polyamide203	Brown liquid	1~5	200±20	40~100
Polyamide500	Brown liquid	2~7	400±20	40~100
Polyamide600	Brown liquid	0.1~0.3	600±20	20~30
Polyamide650	Light yellow liquid		200±20	80~100
Polyamide651	Light yellow liquid		400±20	45~65

Amino-polyamide is widely used as curing agent in curing process of epoxy resin, its main advantages are shown: ① little volatility and toxicity; ② good compatibility with resin; ③ no strict requirement of chemometrics (for liquid bisphenol A epoxy resin, the usage amount can vary from 40 phr to 100 phr), and curing operation is simple; ④ it has toughening effect on cured material, which help to improve the impact strength; ⑤ small exothermic effect and long pot life. The disadvantage is the reduction in heat resistance of cured product, the heat distortion temperature of the reactant is about 60°C.

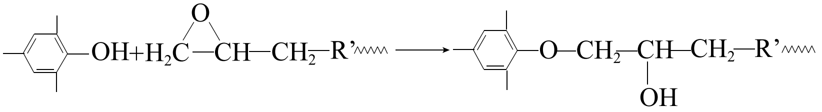
2, 4, 6-tri-(dimethylamino methyl) phenol (DMP-30), boron trifluoride complex etc. can accelerate the curing reaction of amino-polyamide.

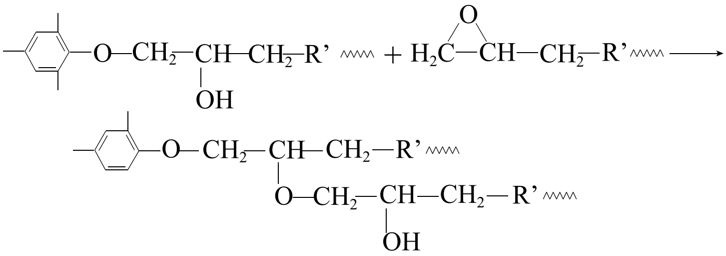
(4) Phenolic resin.

The system of epoxy resin and first-stage phenolic resin is usually used in coating industry. The system of epoxy resin and second-stage phenolic resin with accelerator is widely used as adhesive. The system of epoxy resin and second-stage phenolic resin without accelerator is widely used in reeling pipe, laminating, compression molding, and filament winding process of glass fiber reinforced composites industry.

The reaction of first-stage or second-stage phenolic resin and epoxy resin is mainly the reaction by phenolic hydroxyl group, alcohol hydroxyl group in phenolic resin with epoxy group, secondary hydroxyl group in epoxy resin.

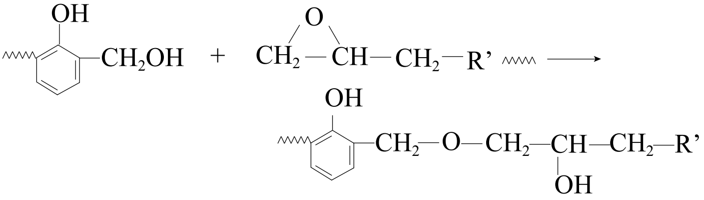
① The reaction between phenolic hydroxyl group in the first-stage or the second-stage phenolic resin and epoxy group in epoxy resin is given by

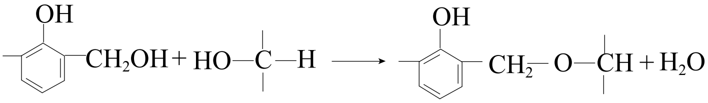




Phenolic hydroxyl group itself has a catalytic effect on further etherification between the secondary hydroxy of product and epoxy group.

② The reaction between alcohol hydroxyl group in the first-stage phenolic resin and epoxy group and secondary hydroxyl group in epoxy resin.





Inorganic alkalis(such as potassium hydroxide, benzyl dimethylamine and benzyl hydroxide trimethylamine)all can promote the above curing reaction, the effect of benzyl dimethylamine is much greater than potassium hydroxide, but benzyl hydroxide trimethylamine is the best.

(5) Anhydride.

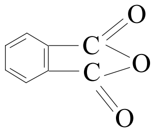
Anhydride-type curing agent is mainly used in cast and composite materials. The anhydride curing agent makes the cured materials to have excellent physical, electrical and chemical properties. Although the volatile gas is irritating vapor, generally speaking, it is not a skin-sensitive agent, and the cured product with such substance has a medium or high heat distortion temperature.

The characteristic of anhydride is the low exothermic peak, so it needs higher temperature and longer time in the curing reaction. We may add amine accelerator to lower the curing temperature and shorten the curing time. In order to induce crosslinking of epoxy resin, it must make use of the esterificationan between hydride and hydroxyl to open the anhydride ring, so some formulations would include a small amount of compounds containing hydroxyl to accelerate the reaction. Commonly used accelerators are benzyl dimethylamine, 2- methylbenzyl dimethylamine, 2, 4, 6-tri- (dimethylamino) phenol and its salts, pyridine, triethanolamine, thiols, phenols, glycol and polyol. Amine accelerator can be used to accelerate the gelation and shorten the curing time, and the amount of it is

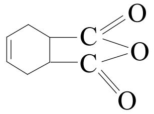
0.5%~3%. Nevertheless, the amount of amine must be controlled strictly, bigger or smaller amount will significantly decrease the heat resistance.

The commonly used anhydrides include aromatic and aliphatic, and the representative types are shown in follows.

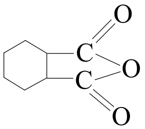
Phthalic anhydride (PA):



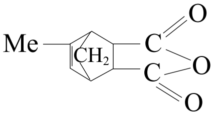
Tetrahydro phthalic andydride (THPA):



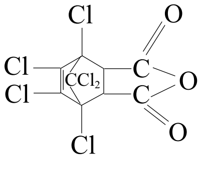
Hexahydro phthalic andydride (HHPA):



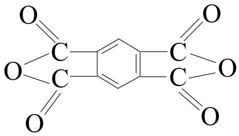
Methyl Nadic anhydride (MNA):



Hexachloro endoethylene tetrahydrophthalic anhydride (HET):



Pyromellitic dianhydride (PMDA):



In actual usage, we can determine the stoichiometric relations between anhydride and epoxy resin.

$$\text{The amount of anhydride curing agent (phr)} = C \times \frac{\text{Anhydride equivalent}}{\text{Epoxy equivalent}} \times 100$$

or

$$C \times \text{Anhydride equivalent} \times \text{Eqoxy value} \tag{3.4}$$

Here, C is constant, which is different for different types of anhydride varying. For common anhydride C is 0.85; anhydride containing halogen C is 0.60; if having tertiary amine catalyst $C = 1.0$.

$$\text{Anhydride equivalent} = \frac{\text{The relative molecular weight of anhydride}}{\text{The number of anhydride groups}} \tag{3.5}$$

2) The curing of epoxy resin by ionic polymerization and types of curing agent

The curing agent of epoxy resin by ionic polymerization belongs to catalytic type of curing agent, since the catalytic role in curing reaction leads the epoxy group opening ring polymerization of resin, and thus obtain the polymer with cross-linking structure. The cured polymer basically has a polyether structure. The amount of curing agent is based on experiment, and it can be used as curing agent individually or accelerator of amine or anhydride curing agent.

This type of curing agent can make resin molecules to cure by anionic polymerization process (using Lewis base) or cationic polymerization process (using Lewis acid).

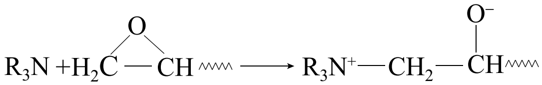
(1) Anionic curing agent.

Anionic curing agent belongs to Lewis base. It has a pair of not shared electrons at the outer layer of nitrogen atom, and thus has the nature of nucleophilic and it is electron donors. Tertiary amines are the commonly used types, for example, benzyl dimethylamine, DMP-10 or DMP-30, etc. The secondary amine with single functional group (for example, imidazole compounds) also has the same effect as Lewis base catalytic after the reaction between the active hydrogen and epoxy group.

The promoting effect of tertiary amine in the curing reaction is related to electron density of the nitrogen atom and molecular chain length. The higher the electron density and shorter the chain length, the greater the promoting effect.

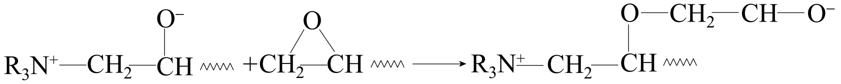
Its curing principle is shown in follows.

The tertiary amine firstly causes the epoxy ring-opening, and forms alkoxide ion.

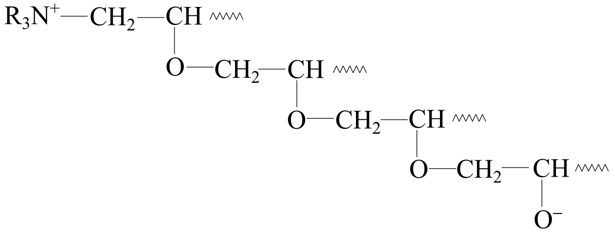


$$R_3N + H_2\overset{O}{C-CH}\text{~~~} \longrightarrow R_3N^+-CH_2-\overset{O^-}{\overset{|}{CH}}\text{~~~}$$

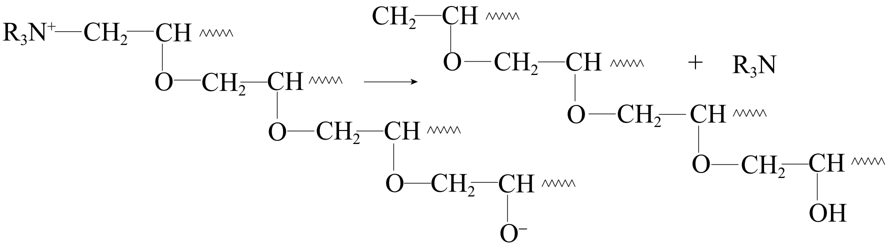
The alkoxide ion reacts with epoxy group of another epoxy molecule, the length of molecular chain increases.



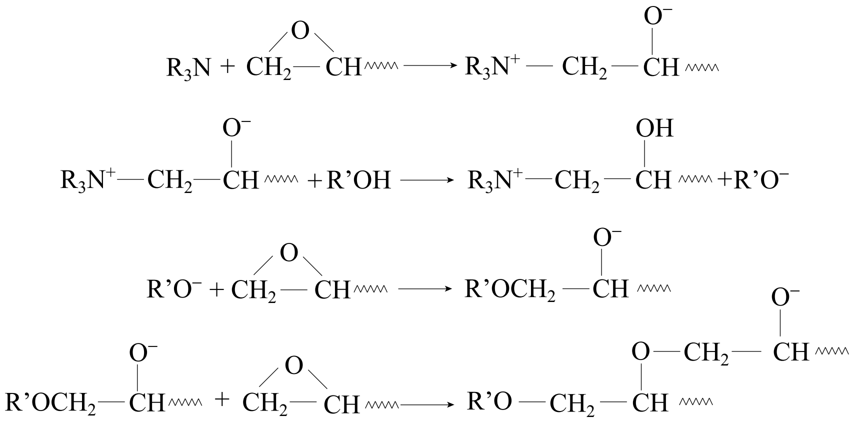
The reaction continued, and so many resin molecules cross-linked together formig three-dimensional polymer.



Chain termination process may be due to the elimination of tertiary amine end-group, and form unsaturated double bond-end group.

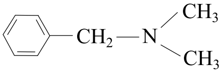
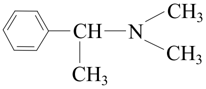
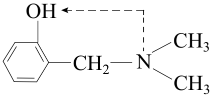
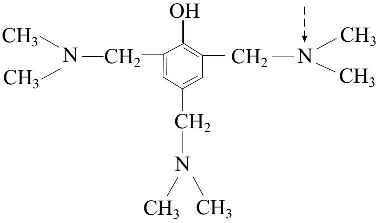


The molecules containing hydroxyl (alcohols and phenols) can accelerate the above reactions, and the catalysis may be caused by the faster initiation of further generation of alkoxy ion.



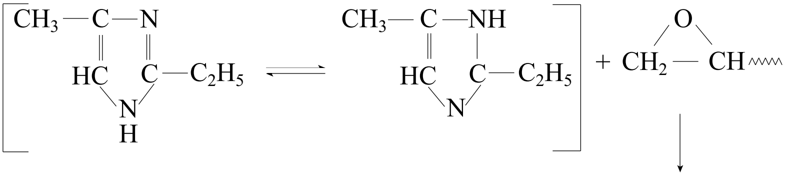
Aromatic substitutes of trimethylamine are the commonly used anionic curing agents. See Table 3.19.

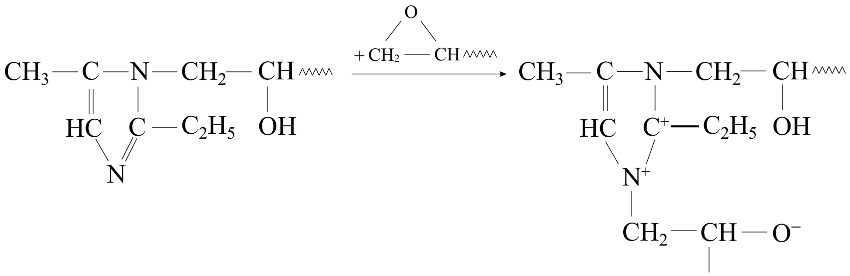
Table 3.19 Aromatic substitutes of trimethylamine

Name	Structure	Abbreviation
Benzyl dimethylamine		BDMA
α-methyl benzyl dimethylamine		
o-hydroxy benzyl dimethylamine		DMP-10
2 ,4, 6-tri- (dimethylamino-methyl) phenol		DMP-30

2-methylimidazole and 2-ethyl-4-methylimidazole are another important type of anionic curing agents. The advantage is small toxicity, easy mixing ingredients, and low viscosity of curing system, long pot life, simply curing, good electrical properties and mechanical properties of the cured materials. When they are used in the liquid bisphenol A type epoxy resin, the amount is from 3phr to 4phr, the pot life is from 8h to 10h at 25°C (material by weight of 500g). The melting point of 2-ethyl-4-methylimidazole is 45°C, so it can be melted by slightly heating, and can be easily miscible with epoxy resin. The melting point of 2-methylimidazole is from 143°C to 145°C, so it is difficult to be miscible with epoxy resin directly and must be dissolved by solvent (like diglycol) firstly, and then mix with epoxy resin.

The initiated process of imidazole curing agent is shown in follows.

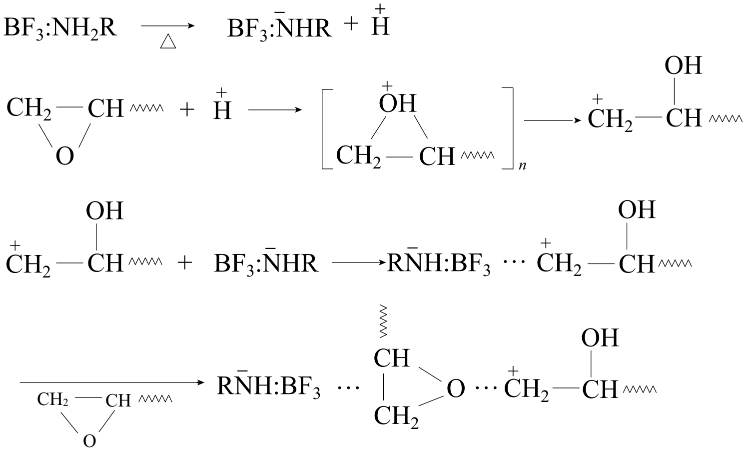




(2) Cationic curing agent.

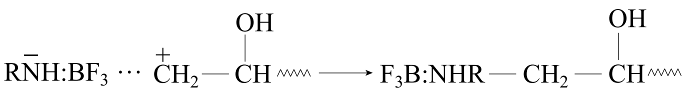
Lewis acid is an eletron-acceptor, which belongs to cationic curing agent. The complex composed of boron trifluoride with amines or ethers is the main species. Boron trifluoride-triethylamine complex is commonly used in industry, which is also called BF_3:400. The melting point is 87°C; the dissociation temperature is about 90°C. BF_3.400 is highly hydrophilic, in the wet air it can hydrolyze into viscous liquid which is not used as curing agent any more. In actual usage, it can be directly mixed with hot resins, or alternatively, it can dissolve in carriers with hydroxyl (such as binary alcohol, furfuryl alcohol, etc.), and then we can use the solution as curing agent. We must avoid contacting such agents with asbestos, mica and other certaining alkaline fillers in using.

Curing bisphenol A epoxy resin with boron trifluoride-amine is complex, firstly BF_3-amine complex released H^+at a certain temperature conditions, then the H^+ attacked epoxy group to trigger initiating polymerization.



$$BF_3{:}NH_2R \xrightarrow[\triangle]{} BF_3{:}\overset{-}{N}HR + \overset{+}{H}$$

Chain termination reaction might be the composition of ion-pairs.



$$R\overset{-}{N}H{:}BF_3 \cdots \overset{+}{C}H_2-\overset{\overset{OH}{|}}{C}H\sim\sim \longrightarrow F_3B{:}NHR-CH_2-\overset{\overset{OH}{|}}{C}H\sim\sim$$

It is mainly used in laminating and compression molding process.

3) Practical formulations examples of epoxy resin for composite materials

(1) Table 3.20 shows epoxy adhesive formulation of 618$^{\#}$(E-51)+300$\sim$400$^{\#}$ (W-95).

Table 3.20 Epoxy adhesive formulation of 618$^{\#}$+300$\sim$400$^{\#}$

Components	Epoxy- m-xylenediamine	Epoxy-polyamide
Epoxy 618$^{\#}$	100	100
Epoxy 300$\sim$400$^{\#}$	15	30
2-ethyl-4-methylimidazole	4	4
m-xylenediamine	9	
Polyamide		15

The adhesive has low viscosity and can be cured at room temperature, and then post cured at 120°C for 3h, which is suitable for hand lay-up.

(2) Polyester-epoxy adhesive formulation is shown in follow.

Liquid A	By weight of shares	Liquid B	By weight of shares
Epoxy resin 634$^{\#}$	28	Styrene	30
Polyester193$^{\#}$	32	Benzoyl peroxide paste	2
Phthalic anhydride	8	Benzyl dimethylamine	0.035$\sim$0.05

Liquid A and B are firstly prepared, and mixed for using after cooling down below 60°C. It can lay for 24h at room temperature, and the curing is at 180°C for 4h. It is suitable for hand lay-up to manufacture large sized parts. Table 3.21 shows the properties data of the composites.

Table 3.21 Properties of polyester-epoxy adhesive

Items	Data	Items	Data
Tensile strength (MPa)	$\sim$200	Impact strength (kJ/m^2)	$\sim$255
Tensile modulus (GPa)	16.7	Density (g/cm^3)	1.66
Flexural strength (MPa)	$\sim$240	Water absorption (%)	0.27
Shear strength (MPa)	$\sim$76	Glue content (%)	55

(3) Formulation of epoxy adhesive 6207$^{\#}$(R122)is shown in follow.

	By weight of shares
Epoxy 6207$^{\#}$	100
Maleic anhydride	54
Bisphenol A	14
Glycerol	4

We can use hand lay-up, stepped curing, such as at 60°C for 2h → at 90°C for 4h → at120°C for 3h → at 160°C for 6h → at 200°C for 6h. The heating interval is 0.5h, and it can be used at high temperature. Properties of FRP at 200°C are flexural strength: 450MPa, flexural elastic modulus: 20GPa and compressive strength: 160$\sim$240MPa.

(4) Formulation of phenolic resin-epoxy resin adhesive is shown in follow.

	By weight of shares
Epoxy resin	60
Phenolic resin(Ammonia catalyzed)	40
Toluene/ethanol	Appropriate amount

It is suitable for pre-dipping process, and mainly used for glass cloth laminated board.

(5) Formulation of Novalac epoxy resin 648$^{\#}$(F-46)and Boron trifluoride-monoethylamine

The formulation is 648$^{\#}$ epoxy resin by weight of 100 shares and complex of boron trifluoride-monotriethylamine by weight of 3 shares. Its shelf life is about 6 months and has a short curing cycle. Flexural strength of FRP at 200°C is 220MPa. It is suitable for pre-dipping process, such as impregnating the unidirectional prepreg of carbon fibers.

3.4.3 Toughening epoxy resin

The simple epoxy resin curing material is brittle and has low impact strength and the property of heat shock. In order to improve the properties, it needs toughening. The prevailing methods for toughening are shown in follows.

1) Elastomer toughening

Elastomeric molecule with active end-groups can access to the cross-linked epoxy network in block by the reaction of active end-group and epoxy group, so the toughening effect is better than generic rubber. The elastomers for toughening include liquid carboxyl-terminated butadiene-acrylonitrile (CTBN), random carboxylated butadiene-acrylonitrile rubber, liquid hydroxyl-terminated nitrile rubber, prepolymer of hydroxylated butadiene-acrylonitrile and isocyanate, hydroxyl-terminated polybutadiene, liquid hydroxyl-terminated silicone rubber, liquid thiokol, liquid polyether elastomers and so on. To achieve toughening, elastomers should be compatible with the resin before curing, and also dispersion phase with the main content of elastomers should be formed after cured. The toughening effects of elastomers on epoxy resin depend on the structures of dispersion phase (rubber) and continuous phase (matrix) as well as condition of interphase bonding.

Among the many tougheners, the most widely used is carboxyl-terminated butadiene-acrylonitrile (CTBN)). In the epoxy system with high crosslinking density and high rigidity of network chain, energy dissipation mainly occurs at the tensil tearing of rubber, whereas in the epoxy system with low crosslinking density, the main energy dissipation occurs in particle-induced matrix. Expansion of the plastic body cavity, which is caused by the degumming or breakage of CTBN particles, and shear yielding deformation, which is induced by particles or plastic body cavity, are the two main toughening mechanisms existed in the CTBN toughened epoxy resin system. The main factors affecting CTBN toughening are:

the contents of acrylonitrile in CTBN, the molecular weight of CTBN, the adding amount of CTBN, curing agent, curing temperature, the average length of network chain of epoxy matrix and the number of functional groups.

2) Thermoplastic resin toughening

Thermoplastic resin, which is of high-molecular-weight or in the form of oligomer with low-molecular-weight, is used to improve the toughness of epoxy resin system. Generally speaking, the toughening effect of thermoplastic resin is worse than rubber. But if we choose a suitable thermoplastic resin, it can play role in improving the toughness while not affecting modulus and glass transition temperature of the epoxy matrix.

The elastic modulus of thermoplastic resin used for toughening is similar to epoxy resin but the elongation at break is much larger than matrix, this makes the ductile thermoplastic particles bridged at the cracking surface of brittle epoxy matrix have a closure effect on the crack growth. Not only have the bridging particles a constraint role on the overall advancement of the crack front, but its distributed bridging power also have the effect of screw anchors to the crack at bridging point, making the crack front propagate wavily.

Generally, when the amount of thermoplastic resin is large in the epoxy resin system, it will form semi-interpenetrating polymer networks because thermoplastic resin consecutively penetrates in thermosetting resin network. As a result, both thermoplastic resin and thermosetting resin exist in the semi-IPN, so the cross-linked networks maintain not only the good toughness and low water absorption, but also good chemic stability, etc. For example, Petrarch system in US developed a product of S-IPN called Rimplast in commerce. This material is made up of thermosetting polysiloxane, thermoplastic polyamide and polyurethane, and has not only the lubrication, insulation, high temperature properties of silicone resin, but also the mechanical properties of thermoplastic resin.

Two conditions are required to form an effective S-IPN of thermoplastics modified thermosetting resin: ① the initial network must exist or can be formed in shear stress field during the preparation, and generally it is physical cross-linked network; ② polymer must have chemical reaction, so that there is sufficient liquidity to fill the gap in the initial network when the discrete melt forms unlimited crosslinking network. Only in this way can it form the better domain size and improve the toughness.

3) The thermotropic liquid crystalline toughening

Liquid crystal polymer (LCP) is a new type of polymer. LCP is a new kind of polymer terminated by the reactive groups which can crosslink and containing the mesogenic element with rigid rod-like and anisotropic shape. The mesogenic element can be in main-chain for main-chain LCP or in side chain for side-chain LCP, and in the side and main-chain. Toughening epoxy resin by thermotropic liquid crystalline polymer (TLCP) can improve the toughness of epoxy resin and can also ensure that it does not reduce the other mechanical properties and heat-resistance of epoxy resin. Attentions have been paid on this technology since the 1990s. If using thermotropic liquid crystalline polymer by weight of 2%, fracture toughness can be increased by 20%, and with the increase of TLCP content, there is a substantial increase in material toughness, and bending modulus is essentially the same, glass transition temperature is slightly higher. The cured system is two-phase structure, TLCP exists in the epoxy resin continuous phase in the form of fibril, and the morphology of liquid crystal depends on its way of mixing with epoxy resin. A small amount of TLCP fibril can prevent the cracks, improve the toughness of the brittle matrix, and not reduce the material's heat resistance and stiffness. Comparing with the thermoplastic resin, liquid crystal polymer will receive the same toughening effect under only the amount of 25% to 30% dosage of thermoplastic resin.

4) Core-shell latex polymer toughening

Core-shell latex polymer (CSLP) is defined as a kind of polymer composite particles which are obtained from emulsion polymerization of two or more monomers. Internal and external of the particle enrich different components showing the special two-tier or multi-storey structure, and core and shell have different functions. By controlling the particle size and changing composition of CSLP, the modified epoxy resin has obvious toughening effect.

Compared with the traditional methods of rubber toughening, mixing the incompatible CSLP with epoxy resin guarantees that good toughening effect can be obtained and at the same time glass transition temperature remains unchanged. We can get better results if using the compatible CSLP.

Epoxy resin adhesives modified with core-shell polymer can reduce the internal stress, and enhance the bonding strength and the impact resistance. Zhang Mingyao etc., studied the influence of Pn-BA/PMMA core-shell structure toughener on the mechanical properties of epoxy resin. The result of the impact test showed that after adding 30 parts of the toughener the impact strength of epoxy resin had a significant increase, and the fracture mode changes from brittle fracture to ductile fracture. For the anhydride curing system, the impact strength increased about 32 times, and it exceeds the impact strength of engineering plastics such as ABS.

According to some researches, the mechanism of CSLP toughened epoxy system is mainly the CSLP particle cavitation-plastic deformation. The main bases are the followings: stress white zone exists on the material surface and the toughness becomes larger with the increase in the length of stress white areas. Stress whitening is a phenomenon that the void formed from the CSLP particle cavitation scatters the visible light. Occurrence of such phenomena proved the existence of the particle cavitation. Besides, we can observe the voids and shear zones on the crack surface by TEM.

5) Rigid nano-particles toughening

There are more non-matching atoms on the nano-particles' surface, the possibility of physical or chemical combination of the nano-particles with the epoxy resin will become larger. By enhancing the combination of the particles with the surface of matrix, larger surface area interaction of particle with matrix and reducing the initiative of the polymer bond, it is possible to bear a certain load and have the possibility of enhancing and toughening. From the existed researches, its mechanism is shown in follows.

Lv Yan-mei thought that the raising level of impact toughness is mainly decided by the dispersion of nano-particles. As nano-particles uniformly disperse in the matrix, the micro-cracks (crazing) will be generated between the particle and the matrix when the matrix is under impact; at the same time, the matrix between the particles also begins plastic deformation to absorb impact energy. That is how the effect of toughening is achieved. The surface area of particles and the contact area existing between filler and matrix will become larger if the particles become slighter, and the more micro-cracks (crazing) will be generated between the particles and the matrix when the matrix is under impact, hence absorbing the more impact energy. However, if we use too much filler, it is easy to produce aggregate and micro-crack will easily develop into macro-crack, resulting in lower property of the system. Besides, the existence of rigid inorganic particles has an effect of stress concentration, lead to micro-cracks in the resin around particle, absorbing a certain degree of deformation work.

Xiong Chuan-xi and others believed that the impact toughness of composite materials is related to the thickness (L) of the polymer matrix layer among dispersed particles, and L is related to the volume fraction (V_f) and the radius (r) of the dispersed particles, its calculation formula is shown as follows.

$$L = 2r\left[\left(\frac{\pi}{6} \times V_f\right)^{1/3} - 1\right] \tag{3.6}$$

The critical thickness of nano-particles toughening (L_c) is 28nm. For composite materials of polymer / inorganic rigid particles, the impact toughness is related with two factors. The first is the dispersion capability of the resin matrix for the impact energy; and the second is the absorption capability of the surface of rigid inorganic particle for the impact energy. The impact energy taken by these two factors is not entirely alloted by their volume fraction, and is related to matrix layer thickness L. Toughening critical thickness L_c is the transition point where resin matrix and the surface of the rigid inorganic particle comtributes the same amount in the impact energy absorption. When $L > L_c$, impact energy allocated to the resin matrix and inorganic rigid particle by the volume fraction, so the impacted energy taken by the unit volume of the resin matrix will not change, that is to say the toughness will not change. When $L < L_c$, the capability that the rigid inorganic particles absorb impact energy will increase greatly, and resin matrix does little role or even not share the impact energy, therefore, the impact damage at this time is only the destruction of rigid particle interface, and the impact toughness is only related to the interfacial property, i.e, is related to the nature of the matrix and rigid particles, independent of L and V_f. Assume that the interfacial thickness of the polymer and the rigid inorganic particles is L_i, thus, when $2L_i < L < L_c$, composite interface is perfect, and it absorb the impact energy easily, so the impact toughness is good; when $L \leqslant 2L_i$, composites do not form a complete interface, at this time, impact toughness of the material will decrease obviously with the decrease of L and the increase of V_f. If the size of the rigid inorganic particle is very large (such as at 30μm), leading the small surface area, its absorption capability to the impact energy is poor, so the percentage of the impact energy taken by the resin matrix is higher than the volume fraction of the resin, the resin matrix is easy to damage, impact toughness of composite material will decrease with increasing V_f and decreasing L.

Improvement on the stiffness and the strength of nanocomposites is due to the small radius of nanoparticles and the large surface area. The unique properties of surface atoms and the physical and chemical defects on the surface, make it the easier for physical and chemical combination with polymer chains to happen. In this way, it increases the stiffness, improves the toughness, strength and heat resistance of the materials.

Through finely controlling the dispersion of the inorganic ultrafine particles in epoxy resin, advanced organic-inorganic nanometer epoxy composites can effectively improve the comprehensive performance of composite materials in a considerable range with only a small volume fraction of inorganic particles, enhancing, toughening, and anti-aging, while not affecting the processing performance of materials.

3.4.4 Unsaturated polyester

Usually polyester resin used for FRP is unsaturated polyester resin (UP). It is one type of polyester.

1) Synthesis of unsaturated polyester

In industry, we usually use dicarboxylic acid, such as, maleic acid (or anhydride), fumaric acid (or phthalic anhydride) and diols (eg ethylene glycol) or ternary alcohol (such as glycerol) etc., to form unsaturated polyester through the esterification reaction. The reaction is shown in follow.

$$n\mathrm{HOOCR\ COOH} + n\mathrm{HO{—}R'{—}OH}$$

$$\longrightarrow \mathrm{HO} \left[\mathrm{OCORCOOR'O} \right]_n \mathrm{H} + (2n-1)\mathrm{H_2O}$$

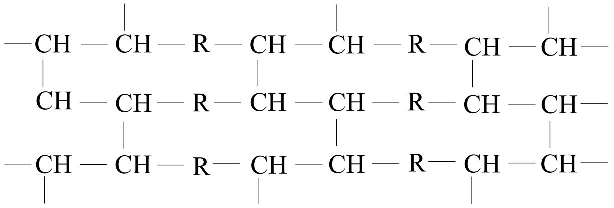
Here R and R′ represent alkyl or other groups.

The structure of alcohol and acid used in the synthesis mainly decides the performance of unsaturated polyester. If we adopt the saturated acid in place of the partial unsaturated dicarboxylic acid, we can increase the average distance between double bonds in the molecular chain and reduce the number of cross-linked bonds, and thus improve the flexibility of the unsaturated polyester. Introduce bisphenol A in the synthesis can get good properties of acid resistance, base resistance and heat resistance.

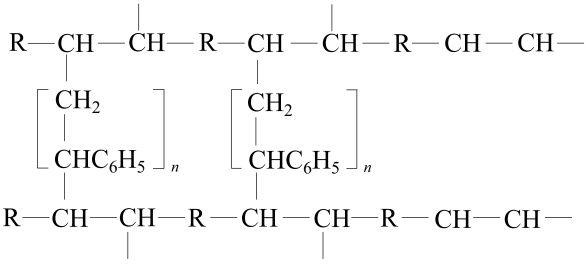
2) Curing of unsaturated polyester

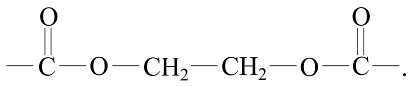
There are unsaturated double bonds in the unsaturated polyester molecular structure, so addition polymerization can happen with the other unsaturated compounds in the presence of initiator, and cure to form a three-dimensional structure. It can also cure by its own double bonds.

Curing by its own double bonds, the cured structure is shown in follow.



The cured structure by styrene cross-linking is shown in follow.



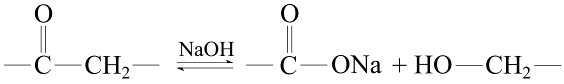
Here R = 

$$-\overset{\overset{\displaystyle O}{\|}}{C}-O-CH_2-CH_2-O-\overset{\overset{\displaystyle O}{\|}}{C}-.$$

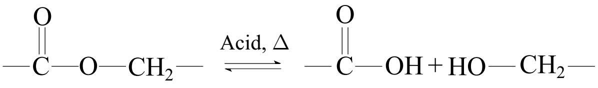
The curing reaction of the unsaturated polyester needs crosslinking agents, which are compounds containing double bonds, such as styrene, methyl methacrylate, etc. Besides, we should also add the initiator, promoter, inhibitor and thixotropic agent.

3) Properties of unsaturated polyester resin

Unsaturated polyester resin is intolerant to oxidizing mediums. For example, it is vulnerable to nitric acid, concentrated sulfuric acid, chromic acid and other oxidizing mediums. In these media, the resin tends to become aged. In particular, high temperature will accelerate the aging process, making it intolerant to acid corrosion. The performance of alkali and solvent resistance is low. This is because there are many ester bonds in molecular chains which will hydrolyze in hot acid or alkali.



$$-\overset{\overset{O}{\|}}{C}-CH_2- \overset{NaOH}{\rightleftharpoons} -\overset{\overset{O}{\|}}{C}-ONa + HO-CH_2-$$



$$-\overset{\overset{O}{\|}}{C}-O-CH_2- \overset{Acid,\ \Delta}{\rightleftharpoons} -\overset{\overset{O}{\|}}{C}-OH + HO-CH_2-$$

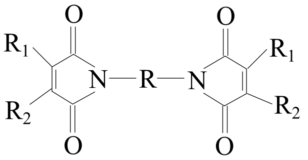
The nature of acid and alcohol in the synthesis determines the physical and mechanical properties of UP. Generally speaking, the longer the chain of diol is, the better the flexibility of polyesters is. The larger content of unsaturated acid can improve the heat resistance and hardness, and reduce the flexibility of resin; the larger content of saturated acid or the increase of the chain length of saturated acid will enhance the flexibility of resin.

Polyester resin has good technology, and can be processed at room temperature. In the curing process, there is no escape of volatile compounds, so the compact degree of product is higher.

3.5 High performance resin matrix

3.5.1 Bismaleimide resin matrix

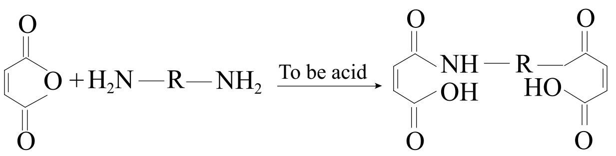
Bismaleimide (abbr. BMI) is a class of resin system which derives from polyimide resin system.The general formula can be written as:

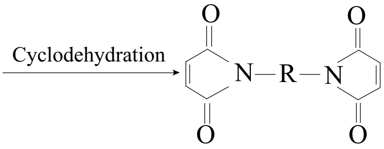


BMI is a bifunctional compound with the maleic imide (MI) for the active end-groups, which has the mobility and the molding property of typical thermosetting resins and can mold using the processing method similar to the epoxy resin.

1) Synthetic principle of BMI

The synthetic route is given by:





Firstly two molecules of maleic anhydride react with a molecule of the diamine to generate bismaleamidic acid. BMI is generated by dehydration of bismaleamidic acid. Different structures of diamine can generate different BMI.

2) Properties of BMI

Monomer of BMI is usually crystalline powder and they have different melting points for different structures. Generally speaking, aliphatic BMI monomers have lower melting point, and the melting point will decrease with the increase of n in methylene chain $(CH_2)_n$, since the density of polar groups in molecules reduces and the flexibility of molecular chains increases. The melting point of aromatic BMI is always higher. When the symmetry of the molecular structure is broken by introduction of asymmetry factors (such as the substituent group, chain extending), the crystallinity and the melting point will be lower.

In molecular structure of BMI, C═C will become a negative-electron bond because it is influenced by the attracting electron effect of two carbonyl groups. So it can actively have addition reaction with the compounds containing active hydrogen such as diamine, amide, hydrazide, mercaptan, cyanuric acid and polyphenol, etc. Also it can easily polymerize with compounds containing unsaturated double bonds, epoxy resin and BMI with other structure. Moreover, self-polymerization reaction can occur under catalyst or heating.

Cured material is with excellent heat resistance because BMI contain benzene ring, heterocyclic imide and the density of cross-linking is high. Usually T_g >250°C and the using temperature ranges from 177 °C to 232°C.

The curing reaction of BMI belongs to addition polymerization. The curing process has no release of by-products of low molecular weight. It is easy to control the reaction as well. Thereby, the cured material has compact structure and few defects, which naturally gives BMI high strength and modulus. Cured material is brittle, has poor impact strength, small fracture elongation and low fracture toughness. PBMI also have excellent electrical properties, chemical resistance, anti-environment and radiation-resistant properties.

3) Modifing methods for BMI

The modifing research of BMI developed rapidly in recent years, the main purpose is to reduce the melting point of monomer and viscosity of melt, improve dissolving capacity in acetone, toluene and other common organic solvents, reduce the polymerization temperature, increase the tack of prepreg and improve the toughness of cured materials, etc. At present the main modified methods are:

① aromatic diamine and the epoxy resin modified BMI; ② thermoplastic resin modified BMI; ③ rubber modified BMI; ④ sulfur compounds modified BMI; ⑤ allyl phenyl compounds modified BMI; ⑥ copolymerizing modification of BMIs containing different structure; ⑦ chain extension of BMI; ⑧ synthesis of new BMI.

4) The typical BMI matrix resin

(1) X4502 resin.

Resin X4502 developed by Northwestern Polytechnical University is a heat-resistant modified BMI resin, and the softening point of uncured resin is about 30°C. It can dissolve in acetone at any proportion, and the cured resin material and composite materials have outstanding toughness and high heat resistance and heat stability.

Cure cycle of the resin is 140°C for 2h, 160°C for 2h and 180°C for 2h, and the postcure treatment is 200°C for 2h and 240°C for 6h.

The forming process of composite materials: heat from room temperature to 120 °C at a rate of 2 °C/min, stay for 30min to 40min, keep pressure at 0.7MPa, and then continue to heat to 180 °C, hold the temperature and pressure for 4h, cool to room temperature naturally. Then the postcure treatment is the same as that of the cast resin.

Table 3.22 and Table 3.23 show the properties of X4502 cast resin and composite materials.

Table 3.22 Properties of cured X4502 cast resin

Properties	Test value	Properties	Test value
Density (g/cm^3)	1.25	HDT (°C)	250
Tensile strength (MPa)	71.8	$T_g$by DSC(°C)	265
Tensile modulus (GPa)	3.90	$T_g$by TMA(°C)	286
Break elongation (%)	2.4	T_{di} (°C)	389
Flexural strength (MPa)	136	T_{dp} (°C)	431
Bending modulus (GPa)	3.6	Y_c at 700°C (%)	32
Impact strength (kJ/m^2)	13.5	Water absorption in boiling water for 500h (%)	3.2
G_{Ic} (J/m^2)	203		

(2) Resin QY8911.

Resin QY8911 is a series of modified BMI resin which was manufactured by Beijing Institute of Aviation Technology, and it includes five varieties, QY8911-1, QY8911-2, QY8911-3, QY8911-4 and QY8911-5.

QY8911-1 is from the copolymerization of BMI resin with diallyl-bisphenol A. Its toughness and heat resistance harmonize with its processabilty. This system has been used for more than a variety of structural parts, which can work at 150°C for a long time. Resin QY8911-2 is a BMI resin modified by low-molecular-weight PES with active hydroxyl end, and can dissolve in acetone. The using temperature is up to 230°C and it has good toughness. Resin QY8911-3 mainly includes components of bismaleimide containing bisphenylether sulfone and bismaleimide containing isopropyl bisphenyl ether. Resin QY8911-4 is RTM resin matrix, whose viscosity is within the range from 0.9 Pa·s to 1.4 Pa·s at 105°C to 120°C. Resin QY8911-5 is a modified BMI resin with heat-resistance from 200 °C to 230 °C, and it has some advanced features such as low price, superior performance and easy operation, which can be evenly mixed with chopped fibers, graphite powder, alumina and other fillers, and can form composite material parts with different shapes in the press.

Table 3.23 Properties of X4502/T300 composites

Properties	Direction (°)	Test temperature (°C)	Test value
Fiber volume content (%)		RT	60
Tensile strength (MPa)	0	RT	1676
	90	RT	81.7
Tensile modulus (GPa)	0	RT	178
	90	RT	10.6
Break elongation (%)	0	RT	1.04
	90	RT	0.81
Flexural strength (MPa)	0	RT	1848
	0	150	1479
	0	200	1327
Bending modulus (GPa)	0	RT	130
	0	150	125
	0	200	120
Interlaminar shear strength (MPa)	0	RT	96.9
	0	150	68.1
	0	200	53.0

QY8911 resin can be easily comminuted, soluble in acetone and has good film-forming property. It is suitable to prepare prepregs using wet, hot-melt and electrostatic powder method, and has good operation processabilty.

Molding technique of composites is: keep 125°C to 130°C for 10 to15min, then apply pressure of 0.3MPa to 0.8MPa (vacuum exsisting), and heat up to 185°C, hold for 2h.

Postcure processing: QY8911-1 is 195°C for 2h to 3h, and QY8911-2 is 230°C for 4h to 5h.

Table 3.24 and Table 3.25 show mechanical properties of QY8911 and composites.

Table 3.24 Properties of cured resin QY8911-1

Properties	Test value	Performance	Test value
Tensile strength (MPa)	65.6	Density (g/cm^3)	1.24
Tensile modulus (GPa)	3.0	Saturated wet absorption (%)	2.9
Fracture elongation (%)	2.2		

3.5.2 Cyanate ester resin matrix

1) Synthesis of cyanate ester resin monomer

There is only one method to prepare high temperature thermosetting cyanate monomer in industry, that is, halogenated cyanide reacts with phenolic compounds to make cyanate monomer in the alkaline condition:

$$\mathrm{ArOH} + \mathrm{HalCN} \longrightarrow \mathrm{ArOCN}$$

Where "Hal" can be halogen such as Cl, Br or I, the usually used is cyanogen bromide; "ArOH" can be single-phenols, polyphenols, as well as aliphatic hydroxy compounds. The usually used alkali in reaction medium is organic alkali such as triethylamine, etc., which can accept protonic acid.

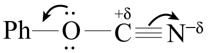
Table 3.25 Properties of composites QY8911/T300

Properties	Test temperature (°C)	QY8911-1	QY8911-2
Interlaminar shear strength (MPa)	25	118	108
	150	76	78.4
	200	/	59
	230	/	54.6
Flexural strength (MPa)	25	1922	2038
	150	1400	1667
	200	/	1467
	230	/	1261
Bending modulus (GPa)	25	136	142
	150	134	140
	230	/	139
	25	1482	/
Compressive strength (MPa)	150	1080	/
	230	835	/

Note: test direction at 0°.

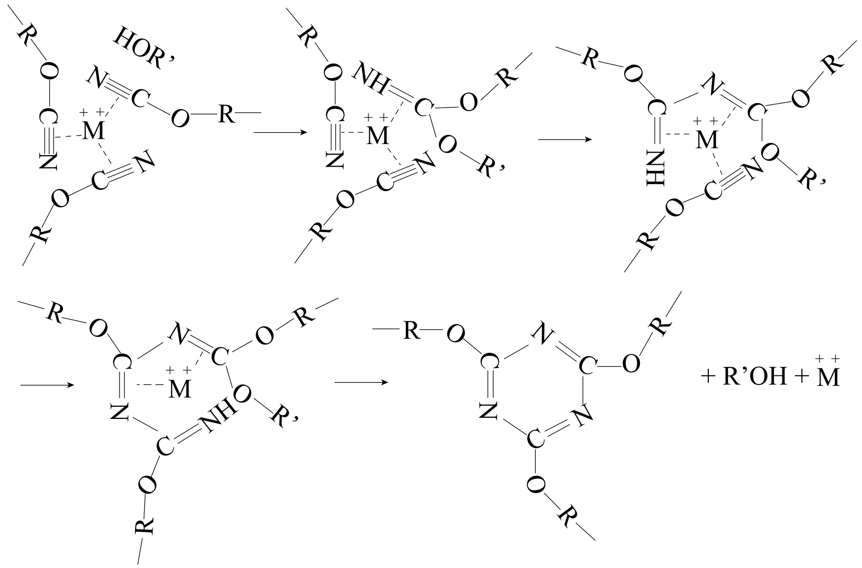
2) The curing reaction of cyanate ester resin

In cyanate ester functional group, because oxygen atom and nitrogen atom are electronegative, the adjacent carbon atom.shows strong electrophilic reactivity.



$$\mathrm{Ph}-\underset{\cdot\cdot}{\ddot{\mathrm{O}}}-\overset{+\delta}{\mathrm{C}}\equiv\mathrm{N}^{-\delta}$$

Therefore, under the effect of nucleophile, the cyanate ester functional group can react either by acid catalysis, or by alkali catalysis. The polymerization reaction mechanism of cyanate ester resin which is catalyzed by metal salts and phenol is shown in follows. In the process of reaction, when cyanate molecules have relatively high mobility, metal ions firstly gather cyanate molecules around, and then perform nucleophilic addition reaction of phenolic hydroxyl group with cyanate group around the metal ions so as to to generate imido-carbonate, which then continue addition with two cyanate groups and finally form a closed triazine ring with the drawing off a phenol molecule. In the process of reaction the metal salts is the main catalyst, and the phenol is a coordination catalyst, the effect of phenol is to accelerate the closed-loop reaction by proton transfer. The mechanism is shown in the following.



3) Properties of cyanate ester resin

Cyanate ester resin has plenty of ether bonds which connect benzene-ring and triazine ring, which makes it to have good impact resistance (compared with other thermosetting resins). This is because the C—O—C ether bond has a free rotation of σ bond by theory, and C—O bond length is longer, that make it easier to rotate freely. Table 3.26 shows a variety of mechanical properties of thermosetting resins. From the table, we know that cyanate ester resin, no matter how we look at it, (from the bending strain, impact strength, tensile strain and G_{Ic}, etc.), has excellent toughness. Flexural strain of cyanate ester resin of Arocy series is 2~3 times of AG80/DDS epoxy resin and BMI-MDA bismaleimide resin.

The triazine ring structure formed in the curing reaction of the cyanate ester resin by the cyclization reaction makes the macromolecular network to form a resonance system. Such resonance structure makes cyanate ester resin to have very low dielectric loss factor $\tan\delta$ and low and stable dielectric constant in the effect of electromagnetic field. When the frequency changes, this molecular structure is insensitive to polarization relaxation, therefore, cyanate ester resin has frequency stability. It can be applied in a large frequency bandwidth and in a wide temperature range, while the dielectric properties change very little.

The thermal decomposition temperature of cyanate ester resin is much higher than epoxy resin, and also higher than BMI resin.

Table 3.26 Mechanical properties of various thermosetting resins

Properties	Arocy					Xu-71787	RTX-366	AG-80/DDS	BMI-MDA
	B	M	T	F	L				
Flexural strength (MPa)	173.6	160.5	133.7	122.6	161.9	125.4	121	96.5	75.1
Flexural modulus (GPa)	3.1	2.89	2.96	3.31	2.89	3.38	2.82	3.79	3.45
Flexural strain (%)	7.7	6.6	5.4	4.6	8.0	4.1	5.1	2.5	2.2
Izod impact strength (J/m^2)	37.3	43.7	43.7	37.3	48	—	—	21.3	16
G_{Ic}(J/m^2)	138.9	173.6	156.3	138.9	191.0	60.8	—	69.4	69.4
Tensile strength (MPa)	88.2	73	78.5	74.4	86.8	68.2	—	—	—
Tensile modulus (GPa)	3.17	2.96	2.76	3.1	2.89	2.78	—	—	—
Break elongation (%)	3.2	2.5	3.6	2.8	3.8	—	—	—	—

Many excellent properties of the cyanate ester resin matrix are inherited by its composite materials. Many characteristics such as heat resistance, wet hot property, high impact resistance and good dielectric properties, etc., are preserved. Table 3.27 is the comparison of properties between BMI, cyanate ester and epoxy resin composite material. It can be seen that the compressive strength after impact of cyanate ester composite materials is as high as 236 $\sim$ 276MPa, and its heat resistance is one of its prominent advantages.

Table 3.27 Comparison of properties among BMI, cyanate ester and epoxy resin and their composites

Items	BMI	Cyanate ester	Epoxy resin
Curing temperature (°C)	180～200	177	177
Post-processing temperature (°C)	240	204	/
Curing time (h)	16～24	3～4	3～4
Saturated moisture absorption rate of bulk resin (%)	2.93	1.56	4.13
Glass transition temperature -dry(°C)	300	250～290	>250
Glass transition temperature -wet (°C)	200	214	
The reduction rate (%)	33	9	
Shear strength difference between dry and wet state 20°C	Hygroscopic <0.6%	Hygroscopic<0.6%	No effect
Shear strength difference between dry and wet state 100°C	Sharp decline	Influence	Linear decline
Compressive strength after impact (MPa)	214$^{1)}$	236～276$^{1)}$	
Work temperature (°C)	<250	<177	<177

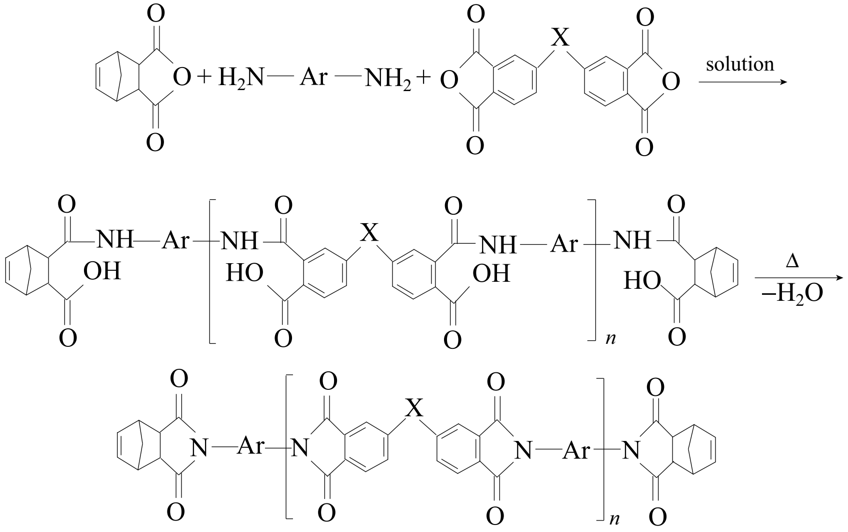
Note: 1) Impact energy: BMI at 4.45kJ/m, cyanate at 6.67kJ/m.

3.5.3 Thermosetting polyimide resin

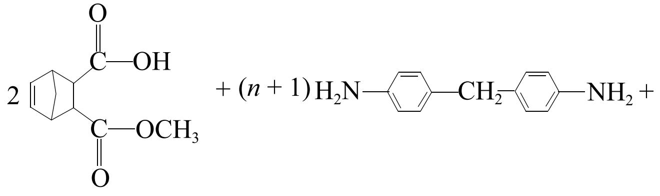
For thermosetting polyimide oligomers containing reactive end groups, there are three main types according to the terminated reactive groups which are PMR polyimide, acetylene terminated polyimide (ACTP) and bismaleimide. Here we mainly introduce PMR polyimide.

1) Synthesis of PMR polyimide

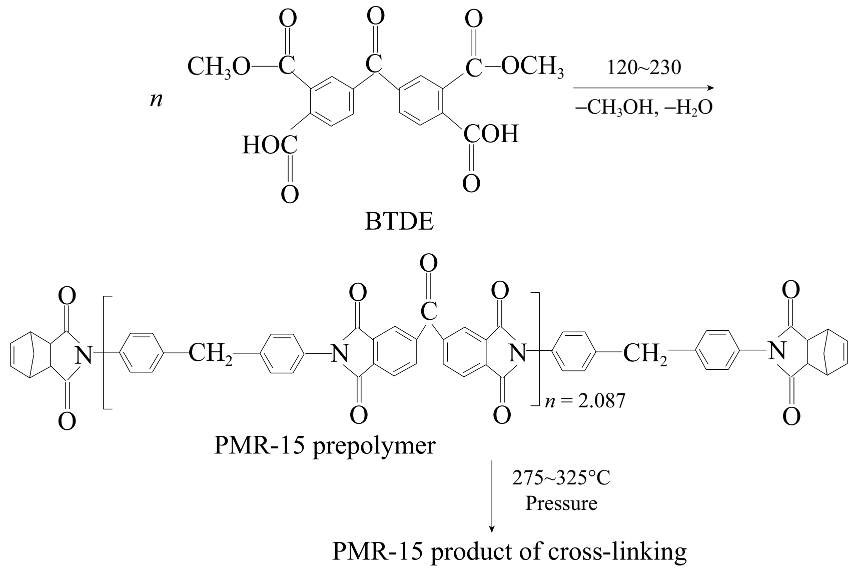
PMR is for in-situ polymerization of monomer reactants.The reaction monomers of polyimide PMR are aromatic diamine, aromatic dianhydride and Nadic anhydride. Synthesis process of PMR polyimide prepolymer is shown in the following. Different molar ratio of three monomers impacts on the molecular weight of intermediate amide acid and polyimide prepolymer.



PMR-15 is the most commonly used polyimide PMR, using Nadic acid monomethyl ester (NE), 4,4 ’- methyl dianiline (MDA) and 3,3’, 4,4’ -benzophenone tetracarboxylic dimethyl ester (BTDE) for reaction monomers. When molar ratio of reaction monomer is NE : MDA : BTDE = 2.000 : 3.087 : 2.087, we obtain the prepolymer with molecular weight at 1500. Changing various molar ratio of monomer could obtain PMR polyimide prepolymer with different molecular weight, and the synthesis reaction is given by:



NE MDA



2) Properties of PMR polyimide

PMR polyimide can form high crosslinking density thermoset polymer after cross-linking curing, which has a better comprehensive mechanical properties than BMI and epoxy resin.

Polyimide has high glass transition temperature, so that it maintains high strength at 300°C. Using different monomers, different synthetic routes can get different structure of polyimide resin, and the different resins have thermophysical properties, too. Polyimide has excellent heat aging resistance. It shows that thermal stability and thermal oxidative stability of polyimide increased with the increase of imino content in the polymer through thermogravimetric analysis, and thermal degradation rate in the air is faster than that in the vacuum. We can learn from the infrared analysis that the thermal loss of resin in the air is due to the destruction of imine bond. Molecular weight of polyimide resin impacts its elevated temperature properties, and with molecular weight increasing, the thermostability of composite materials reduces.

Acetylene terminated polyimide has excellent thermal oxidation stability and dielectric properties, good hot-wet properties, and behaviors in a long term under 288 °C changed little. Table 3.28 shows properties of polyimide Thermid 600.

3.5.4 High performance thermoplastic resin matrix

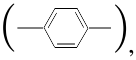
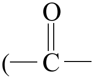
High-performance thermoplastic resin matrix overcome generic thermoplastic resin's weaknesses-low using temperature, poor rigidity and poor solvent resistance. Compared with the thermosetting resin, high-performance thermoplastic resin has excellent toughness, damage tolerance, good environment resistance, wet

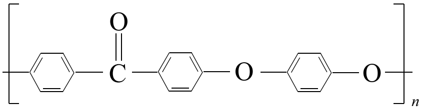
Table 3.28 Properties of polyimide Thermid 600

Properties	Test values
Flexural strength (MPa)	131
Flexural modulus (GPa)	4.49
Tensile strength (MPa)	82.8
Tensile modulus (GPa)	3.66
Elongation at break (%)	2
Compressive strength (MPa)	17.3
Water Absorption at 50°C, RH95% for 1000h (%)	2.1
Permittivity	3.38(10MHz),3.13(9GHz), 3.12(12GHz)
Dielectric loss angle tangent	0.0006(10MHz),0.0068(9GHz), 0.0048(12GHz)
Weight loss aged at 316°C for 500h (%)	2.89
Weight loss aged at 316°C for 1000h (%)	4.40
Bending strength maintaining rate after aging at 316°C for 1000h (%)	72(room temperature),62(316°C)

and heat resistance, low moisture absorption rate, low heat release rate and smoke density, short molding cycle, and of course, easy recyclability. High-performance thermoplastic resin matrices mainly include polyketone resin, polyarylene sulfide resin, thermoplastic polyimide, polyetherimide, polyamideimide, polysulfone, thermotropic liquid crystalline polymers and polybenzimidazole.

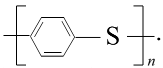
1) Polyketone resin

The major product of polyketone resin is PEEK that is linked by phenylene ring , the oxygen bridge (—O—ether) and carbonyl ( $-\overset{O}{\overset{\|}{\mathrm{C}}}-$ ketone) and the structure is written as



The resins have excellent mechanical properties, toughness, radiation-resistance and flame retardant properties. They have little volatility under the vacuum conditions, high performance retention in high temperature and harsh environment, etc. They can be applied to electronic instruments, military equipment, wires, cables, transportation, petrochemical and aviation industries, etc.

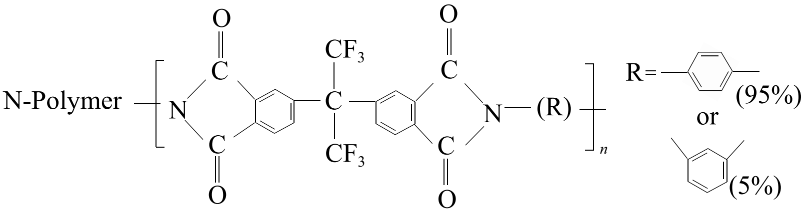
2) Polyarylene sulfide resin

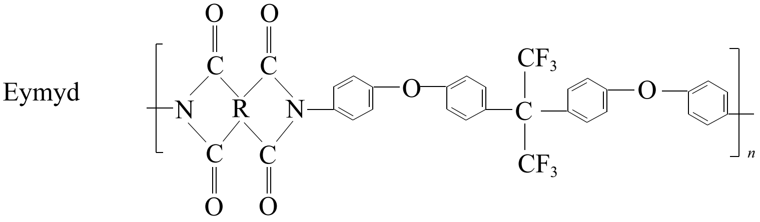
The most representative resin of polyarylene sulfide resin is the polyphenylene sulfide (PPS), and its structure is written as .

PPS is a semi-crystalline polymer which has good mechanical properties, excellent medium resistance. PPS is stable in inorganic acid, alkali, salt, organic acid, ester, ketone, alcohol, and so on. It is very difficult to dissolve below 200°C, but it can be oxidized by strong oxidizer. PPS has good flame retardant properties, and the class of flame retardant is V-O. As a result of poor toughness, PPS is rarely used in resin matrix of continuous fiber reinforced composites, but it is widely applied to the short fiber and other filler filled PPS.

3) Thermoplastic polyimide (PI)

The two most important species of thermoplastic polyimide are N-polymer made by Dupont Company and Eymyd made by Eythyl Company. Their structures are given by:

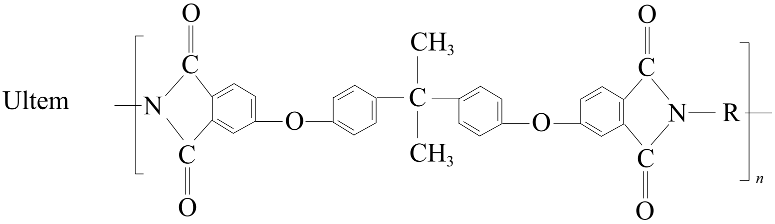




The resins are characterized by high T_g and high long-term using temperature, good thermal stability and thermal oxidative stability, excellent mechanical properties, good medium resistance and environmental resistance. The resin is able to be used in high-temperature and harsh environment. The disadvantage is long molding cycle because that small molecule formed in amidation process needs a long time to be removed in the molding process.

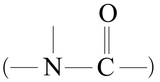
4) Polyether imide (PEI)

Ultem 6000 is the trade name of PEI and the structure of Ultem 6000 is given by:

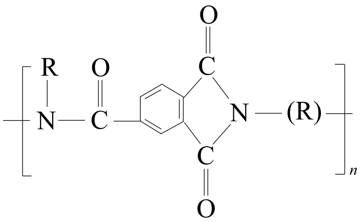


PEI has excellent mechanical properties, good heat resistance and processing performance, which can be used for preparation of mechanical parts with high temperature resistance and high strength. Compared with PEEK, PEI has high glass transition temperature, high using temperature and low molding temperature.

5) Polyamide imide (PAI)

Polyamide imide is the polymer that has both amide group  $(-\overset{|}{N}-\overset{\overset{O}{\|}}{C}-)$ and imide group in molecular chain. And its structure is shown in the following.

PAI

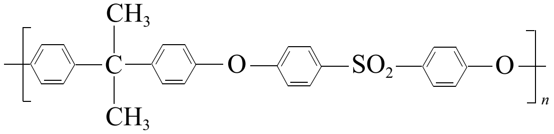


PAI resin has excellent toughness, good mechanical properties, high temperature performance and high heat distortion temperature, good chemical resistant properties. The disadvantage is that PAI is not used under conditions of wet and high temperature because the resin has high absorption rate, and its melt viscosity is so high that it becomes difficult to process.

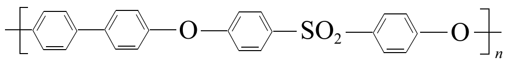
6) Polysulfone (PSU)

According to the molecular structure, PSU resins include three types: polysulfone (such as Udel), polyphenylsulfone or polyarylethersulfone (such as Radel R), polyethersulfone (such as Radel A, Vitrex PES). Their structures are given by

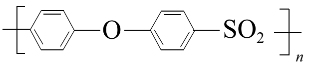
Udel



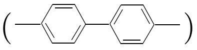
Radel R



Vitrex PES

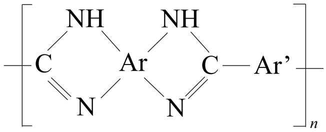


Polysulfone resin is bisphenol A polysulfone in general, which has good heat resistance, electrical performance, flexibility, anti-aging, flame-retardant properties and low smoke release, but has high notch sensitivity. Its mechanical properties (especially tensile, flexural modulus) are slightly lower than PEEK, etc.

Benzene nucleus will link sulfonyl and ether bond in the structure of polyarylethersulfone and there is no aliphatic chain, the general structure contains a certain amount of biphenyl structure , the heat distortion temperature and continuous using temperature of polyarylethersulfone is 100 °C higher than that of bisphenol A polysulfone. In polyethersulfone structure, ether bond and sulfone bond are mainly linked with phenyl and the heat-resistance is intermediate between bisphenol A polysulfone and polyarylethersulfone.

7) Polybenzimidazole(PBI)

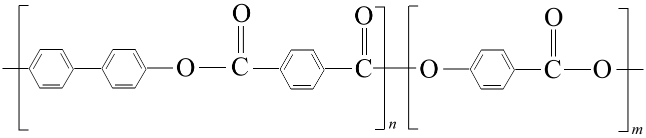
The general structure of polybenzimidazole is given by:



PBI belongs to ultra-heat-resistant polymer and has high compressive strength, surface strength and low thermal expansion coefficient. T_g is 430 °C and it reaches 500 °C after annealing. PBI has excellent chemical resistance properties, good flame-retardant in the air, and low gas release rate. PBI can replace asbestos for flame-retardant and thermal protection. The performance of the PBI is good enough to be used in spacecraft as the heat insulation layer upon entering the atmosphere or on the nuclear reactor as protective materials.

8) Thermotropic liquid crystalline polymer

Polyester polymer is the main type of resin. For example, the Xydar of Amoco Company, its structure is given by:



This is the liquid crystal polymers with high temperature resistance and good flame-retardant performance. Liquid crystal regions in molecules can enhance amorphous regions. It shows order in the molten state, oriented in the certain direction and it's easy to flow. Therefore, the melt viscosity and the shrinkage are much lower than the general polymer, mechanical properties are excellent and impact properties are good, too.

3.6 Resin matrix used for corrosion-resistant composites

The corrosion resistance of composites used in corrosion engineering is mainly determined by matrix resin. First of all, resin matrix in corrosion-resistant composites must be stable in the chemical medium. At the same time it has to prossess high heat resistance and good physical, mechanical properties. Moreover, it must be easy to construct and have good processability. Only a few resins are able to meet these requirements simultaneously. Currently, matrix resins used for corrosion-resistant composites are mainly phenolic resin, epoxy resin, furan resin and polyester resin.

3.6.1 Phenolic resin

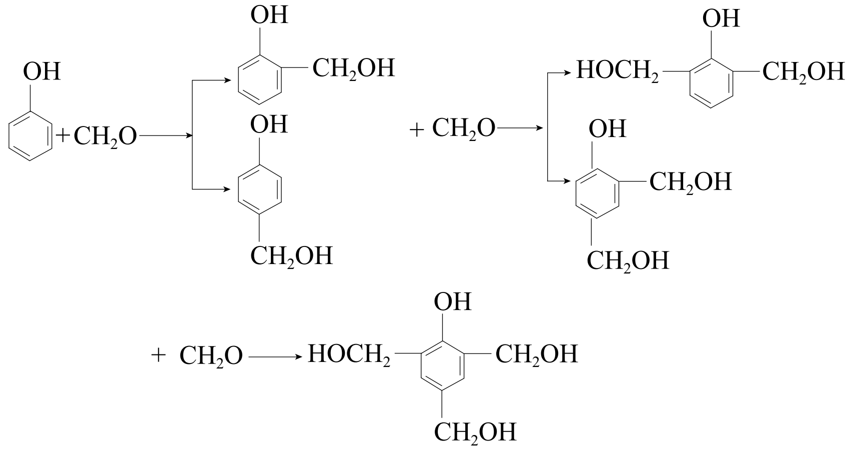
1) Condensation reaction and curing process of phenolic resin

Phenolic resin is the resin synthesized from the condensation reaction of phenol with formaldehyde in the presence of a catalyst.

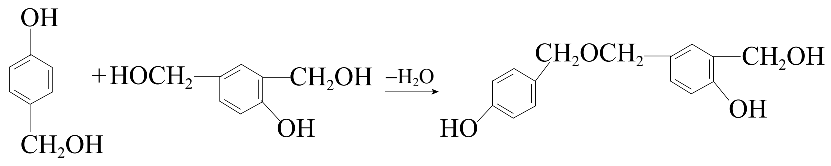
In the synthesis, because the proportion of phenol and formaldehyde is different and the catalyst used in the reaction is different (acidic or alkaline), the characteristics of phenolic resin generated are also very different. In the presence of acidic catalyst and excessive phenol, the generated polycondensate is thermoplastic phenolic resin. Thermosetting phenolic resin is generated with the increase of formaldehyde amount in the presence of alkaline catalyst. In the anti-corrosion engineering, thermosetting phenolic resins are mainly applied.

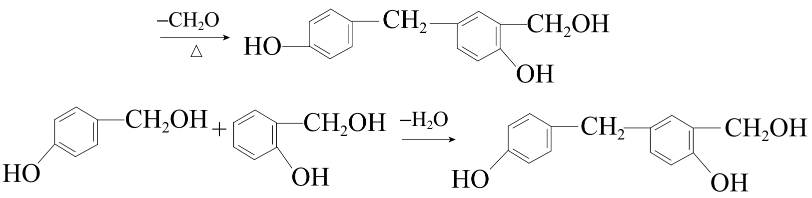
The synthetic reaction of thermosetting phenolic resin is carried out in the presence of alkaline catalysts and the common catalysts are sodium hydroxide, ammonia, barium hydroxide and so on. In general, the molar ratio of phenol and formaldehyde ranges from 1.1 to 1.5. The two steps of overall reaction process when using NaOH as catalyst are shown as follows.

In the first step, the hydrogen atom of benzene ring located on the ortho- or para-position of hydroxyl (—OH) in phenol molecule can carry out addition reaction with formaldehyde to form hydroxymethyl phenol.



In the second step, hydroxymethyl phenol can be condensed further and there are two possible condensation reactions.





Although the two above reactions can happen, the ether bond produced in the first reaction is unstable under the heating and alkaline catalytic conditions, so the second one is the main reaction. Under these conditions, the hydroxymethyl mainly reacts with active hydrogen located on the ortho- or para- position of phenol ring to form methylene (—CH_2—) bridge, rather than the dehydration of two hydroxymethyl.

The unitary, binary or ternary substituted complex is generated by the above reactions which can be further dehydrated to gradually form long chain polymer in the heating conditions. Since molecules contain active groups of hydroxymethyl (—CH_2OH), when the temperature rises or acid catalyst exists, condensation will go on to produce cross-linked generation with hard-infusible, non-melt-network structure. This process is known as "curing ".

There are three stages in the curing of phenolic resin. First phase (stage A) of thermosetting phenolic resin is the product controlling three-dimensional polycondensation to some extent and can continue three-dimensional polycondensation at the appropriate reaction conditions to cure into a three-dimensional polymer. The resin at this stage is linear, less branched-chain, low-molecular-weight mixture, average molecular weight of which ranges from 300 to 1000, and shows the solubility in ethanol (alcohol), acetone and other solvents. The resin has fluidity under ambient temperature and can be heated to B, C stage. The second phase resin, also known as stage B, is the product of further polycondensation of first stage resin by heat-treating or acid-catalyzing. The resin generated at this stage has a rubber-like elasticity. It will not stick on hand and can be pulled into a wire under the heating condition; it is not soluble in alcohol and acetone at ambient temperature and it will only swell, or partly dissolved if heated. The phase is the middle state of curing resin, which has the characteristics of softening when heated. In the third phase, also known as stage C, the resin of the second stage continues polycondensation by heat-treating or acid-catalyzing to form three-dimensional network resin, which belongs to solid material of insolublity and infusibility. The phase is the final state of heat-curing.

The curing reaction by heating thermosetting phenolic resin is very complex and depends on not only the temperature, but also the structure of raw materials used for resin preparation as well as the species of catalyst and so on. The study shows that below 170 °C the condensation of hydroxymethyl mainly produced methylene bond and ether bond between phenol nucleus and release low-molecular-weight water, and when the temperature rose from 170 °C to 200 °C or above 200 °C, resin would begin with the second phase reaction which is more complex, i.e., main reaction is further decomposition of dibenzyl ether and there is a small amount of formaldehyde releasing, and almost no water releases. Thermosetting phenolic resin must be under pressure in hot curing process (laminating pressure is 10MPa to 12MPa, and compression molding pressure is 30MPa to 50MPa). The purpose is to avoid the porosities generated by the volatiles (solvents, water, and water or active formaldehyde generated by cured products during the hot-curing) during the material curing and to increase the liquidity of materials.

We usually use acid as curing agent in thermosetting phenolic resin. Inorganic acid is not often used as catalyst because the poor affinity and insolublity with resin. The viscosity of resin gradually increases in the curing process, which makes H^+ difficult to diffuse, thus affecting the catalytic effect. Organic acids such as p-methyl benzene sulfonic chloride, ethyl sulfate and benzenesulfonyl chloride have good catalytic effect. The compatibility of organic acids and resin is good and organic acids are easy to spread into the resin. The reaction is characterized by the intensity and mass of heat discharged.

The curing rate of phenolic resin is related to the acidity and addition volume of curing agent and construction temperature. Generally, the curing rate of resin accelerates as the acidity of curing agent, the amount of curing agent and environment temperature increase, and slows as the temperature goes down. When the acidity of curing agent is different, the curing rate of curing agent with lower acidity decreases significantly as the temperature dropped. The curing rate of curing agent with higher acidity changes gently with temperature. Therefore, at the construction site, when the temperature is low, curing agent of high acidity is more appropriate.

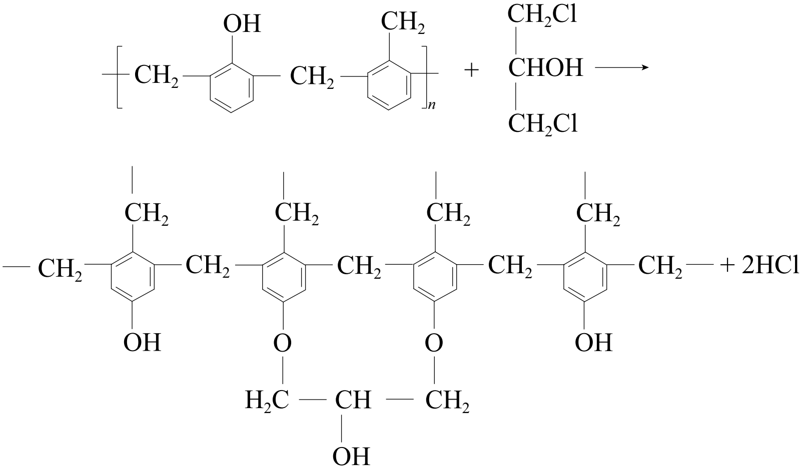
(1) Benzenesulfonyl chloride. The solidification point of benzenesulfonyl chloride is 14.5°C, and it becomes the oily liquid when the temperature is above 15°C. The acidity of the curing agent is moderate, and this leads to easily mix with the phenolic resin and the curing speed is suitable to meet the construction, the cured product has good performance. These advantages make it be used widely. Because the curing agent emits irritant gases, which stimulate people respiratory to tears, we should pay attention to ventilation and labor protection in using.

(2) Ethylsulfate. In fact, ethylsulfate is acid ethylsulfate, which can be prepared with different acidity by different weight ratio (usually 1 : 2, 1 : 2.5, 1 : 3) of sulfuric acid and alcohol in order to meet the requirements. The curing speed of ethylsulfate is fast, pot life is short, and so it is not easy to adjust. When the ambient temperature is high, the operating conditions need to be strictly controlled and curing products has high brittleness.

2) The corrosion resistance of phenolic resin

The molecular chain of phenolic resin consists of the C—C bonds and has a three-dimensional network. Phenolic resin is stable to various chemicals. Corrosion resistance of phenolic resin is better than the epoxy resin and polyester resin. Phenolic resin is very stable in non-oxidizing acid, especially for sulfuric acid with concentration below 50% and hydrochloric acid with any concentration. Phenolic resin does not have corrosion resistance in oxidative acid as the result of oxidation and degradation reaction, such as concentrated sulfuric acid and nitric acid.

Phenolic resin is intolerant to alkaline medium, because there are phenolic hydroxyl groups that show weak acidic in the phenolic resin. It can react with the alkali and produce soluble phenolic sodium. Adding α, γ-dichloro-propanol of 20% in the amount of resin can improve the alkali resistance of phenolic resin. The reason is that α, γ-dichloro-propanol, phenol hydroxyl and free phenol can etherify to form a more stable ether bond that increases the alkali-resistant of phenolic resin.

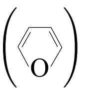


Generally, the added volume of α, γ-dichloropropanol is 20% of resin. Because α, γ-dichloropropanol can easily decompose the free hydrochloric acid when stored, it should be added before using and be used immediately. Otherwise the curing of phenolic resin will be accelerated. Modified phenolic resin can resist NaOH below 30% under 100 °C.

If resin contains excessive free phenol, the corrosion resistance of resin will become weak. In general, the content of free phenol is limited at 7%. Free formaldehyde will escape easily as the resin cures which will lead to an increase in resin porosity. Generally, the content of free formaldehyde is limited at 2% or less.

Phenolic resin contains a large number of rigid benzene rings which are linked by methylenes (—CH_2—) and have many polar hydroxyls. Therefore rigidity of the molecular chain is large, flexibility is bad, and molecular chain is difficult to rotate. That is why phenolic resin is hard and brittle. Phenolic resin has a three-dimensional network and good heat resistance. Its heat distortion temperature is about 120 °C.

3.6.2 Furan resin

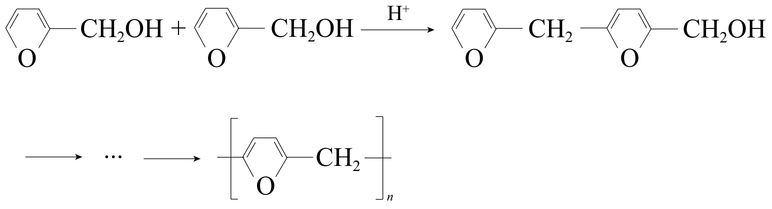
Furan resin is the general term of synthetic resin containing furan ring  in the molecular structure. Because their molecular structures all have furan ring, this group of resins share many common characteristics, such as prominent alkali, acid, solvent resistance and excellent heat-resistant properties.

1) The type and curing of furan resin

There are mainly three types of furan resin.

(1) Furfural alcohol resin.

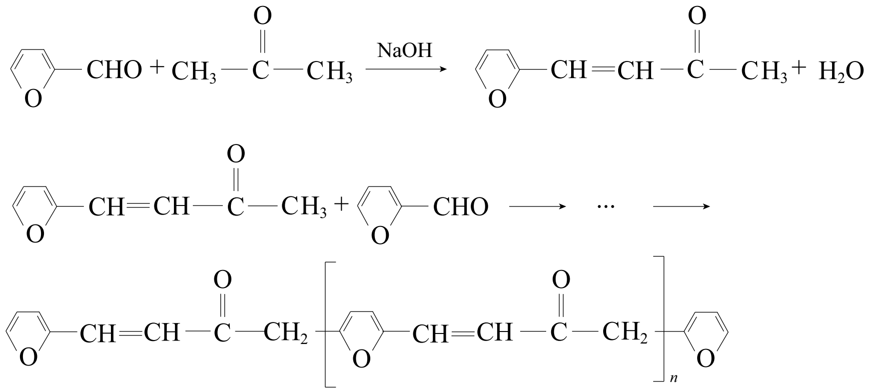
Furfuryl alcohol resin is produced by self polycondensation of furfuryl alcohol monomer which reacts with the active α-hydrogen of another furfuryl alcohol molecule in the presence of acid catalyst to from the polycondensation resin. Reaction formula is shown in follow.



The curing speed of furfural alcohol has much to do with the intensity of acid. Uncured furfural alcohol rapidly solidifies in the presence of strong acid curing catalyst, for example, it can solidify quickly in the presence of sulfonic acid at room temperature. On the other hand, it will not be able to solidify in the presence of the weak acid, such as anhydride, maleic anhydride, or phosphoric acid, etc, at the room temperature at all. Even at between 100 °C and 200 °C, it still takes dozens of hours to cure.

(2) Furfural-acetone resin.

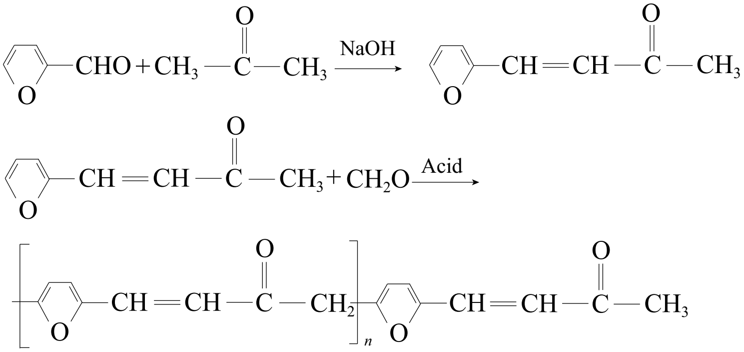
Furfural-acetone resin is produced by condensation polymerization of furfural and acetone in 1 : 1 or 1 : 2 (molar ratio) between 40 °C and 65 °C, and sodium hydroxide is used as catalyst. A series of condensation reaction can be prepared by changing the molar ratio; the products of different viscosity also can be prepared by controlling the level of polycondensation. Reaction formula is shown in follow.



Furfural-acetone resin can be cured into a non-melting resin in the presence of benzene sulfonic acid, *p*-chlorobenzenesulfonic acid. The cured resin has good acid, alkali and heat resistance, which is widely used for anti-corrosion. The tensile strength of glass fiber composite made of furfural-acetone resin is 208.8Mpa, compressive strength is 349MPa. The adhesion with metal is bad. Furfural-acetone resin is usually used in conjunction with the epoxy resin and maleic anhydride or *m*-phenylene diamine is used as curing agent in order to overcome this disadvantage and improve mechanical properties.

(3) Furfural-acetone-formaldehyde resin.

Using NaOH as catalyst, furfural-acetone monomer condensates to a certain extent to form initial condensation compound, which further condensates with formaldehyde to produce furfural-acetone-formaldehyde resin in the presence of sulfonic acid. Reaction formula is shown in follow.



The resin has good acid, alkali and heat resistance, but poor bonding and toughness. Thus it is usually modified by epoxy resin to improve impact strength and bond strength. Furfural-acetone-formaldehyde resin modified by epoxy resin is widely used for chemical corrosion protective engineering, and it has excellent solvent, acid and alkali resistance and can be used in 120 °C to 130 °C.

The above furan resins contain furan ring, double bond, carbonyl and active hydrogen on adjacent carbon atoms. So they can cross-link and form the insoluble, infusible network structure by either opening the double bond group or losing water under alkali and acid catalyst.

The curing agents for furan resin are the same as the curing agent for phenolic resin, such as benzenesulfonyl chloride and ethylsulfate. The content is about 10% by weight of resin. In order to reduce the brittleness of the curing product, plasticizers can be added, such as phthalate esters and phosphate, etc.

2) The performance of furan resin

Furan resin belongs to thermosetting resin and can cross-link with each other and cure when heated without adding the curing agent. In the curing reaction, acid is used as the catalyst and can reduce the temperature required in thermal curing. According to the special needs of construction process, adding catalytic curing agent can make Furan resin quickly cured at room temperature. Because curing cross-link will release off low-molecule compound, the cured volume shrinkage is high. The elongation of furan resin is very low and the cured resin shows brittleness.

Because the molecular chain links of curing product are basically methylene (—CH_2—) and the saturated C—C bond, there are not active functional groups. Therefore, furan resin does not take part in chemical reactions of corrosion medium. The cured furan resin has outstanding alkali resistant, solvent resistant and acid-alkali alternate resistant properties, and good corrosion resistance to the inorganic acid. Furan resin also has good heat resistance. Generally it can be used under 120 °C to140 °C for a long time, and can be used under 180 °C to 190 °C in some cases. However, because furan rings contains double bonds, and heterocyclic, which have tendency to open under certain conditions, oxidation resistance of furan resin is poor and furan resin will be destroyed in the oxidative nitric acid and concentrated sulfuric acid.

Furan resin is well miscible with a number of plasticizers, thermosetting resins, thermoplastic resin, so a variety of products with different performance can be produced.

Exercises

1. Please describe briefly the roles of matrix in composites.
2. How do strength, modulus and shrinkage ratio of matrix affect the properties of composites?
3. How does curing degree affect the nature of matrix and composite material? Why?
4. Choosing resin matrix for composites, which aspects should be given main consideration to?
5. Please describe briefly the development of resin matrix used for composites.

6. When preparing corrosion-resistant composites, what should we pay attention to in choosing materials?

7. What are curing characteristics of epoxy, phenolic and unsaturated polyester resin respectively? How do they affect the preparation property?

8. What are characteristics of bisphenol A type epoxy resin? Try to write the structural formula.

9. Preparing composites with weather resistance, which of epoxy resin should be selected in terms of structure? Why?

10. For epoxy resin curing at room temperature, which kinds of curing agent can be applied? Write the structural formula.

11. Epoxy value of epoxy resin $618^{\#}$ is 0.51eq/100g and phthalic anhydride is used as curing agent. Please calculate the amount of anhydride required to cure100 grams of epoxy resin.

12. Try to write the molecular formula of 2 - methyl- 4 - ethyl-imidazo (2, 4-MI), please state curing mechanism of epoxy resin cured by 2,4-MI.

13. At present, how many ways are there to toughen epoxy resin? Make a brief description about the toughening mechanism.

14. Compared with epoxy resin, what are advantages of bismaleimide resin? How many modifying methods are there?

15. What are the main features of modified bismaleimide resin matrix at abroad?

16. Enumerate structure and performance characteristics of five high-performance thermoplastic resin.

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4

Interface of polymer matrix composites

4.1 The basic concept of interface

From the basic knowledge of physical chemistry, we know that the interface exists between two phases in coexistent system of different phases. Polymer composite is composed of fiber and matrix, which has the attributes that the original composition does not possess. Moreover, due to the existence of interface, the roles of matrix and fiber are independent and interdependent. Interface is an important part of composites, of whose structure, properties, adhesion strength and so on are directly related to the performance of composites. Therefore, thourough research on the interface of composites is very important.

As we all know, the properties of composites are affected by the following major factors: ① the performance of reinforcing materials; ② the performance of matrix; ③ the structure of composites and molding technologies; ④ the binding status of interfaces between fiber and matrix in composites, namely the performance of interface layer. Fibers used in composites can be regarded as fine dispersed materials. For example, glass block of 1cm^3 is drawn into fiber in diameter of 8μm, and the total area will increase from 6cm^2 to 5000cm^2, by approximately more than 800 times. As a result, if composites of 1cm^3 contain 50% fiber in diameter of 8μm, the area of interface can be thousands of square centimetres. The role of interface in composites thus can not be ignored. Therefore, the study on the rules of interface is one of the basic theories in composite materials.

Interface, which was mentioned above, is not an ideal geometrical surface without thickness. Experiments have proved that the region between two phases is an interfacial layer with certain considerable thickness, namely the middle-phase, and the contacting of the two phases can bring about many of interface effects, which results in different structure and properties of the interface layer from the two adjacent structures.

The fiber in many composites is poorly compatible with matrix. In order to improve compatibility of the fiber and the matrix, some modifiers are added to the interface between two phases, such as coupling agents, which will form a new interface on the interface between fiber and matrix. The structure and properties of the new interface are different from the original one (see Fig. 4.1).

In this way, the quality of composite interface that we mentioned will directly affect the overall properties of composites. A large number of facts have proved that the overall properties of composites, consisting of many components, are not simple addition of the properties of every single component, but a linear relationship. In composites, each component is independent but not isolated; and they are interdependent, which is carried out by the interface of composites. Interface effects of composites include: ① physical effect, which causes changes of infiltration, diffusion, miscibility of each component, and interpenetrating network of the interface free energy structure; ② chemical effect, which results in a chemical reaction on interface to form a new interfacial layer structure; ③ mechanical effect, which cause the stress distribution on the interface. Interface plays a decisive role on fracture toughness of composites and reaction of composites in humid and corrosive environment. Composites with weak interfaces have low strength and stiffness but a high fracture resistance; composites with strong interfaces have high strength and stiffness, but it is very brittle. Such properties are attributed to the difficulty of debonding and pulling out of fiber from the matrix, which occurs in the crack growth course.

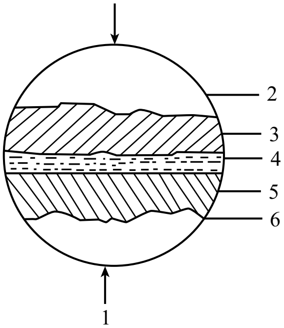


Fig. 4.1 Schematic diagram of interface region:
1-external force field; 2-bulk matrix; 3-matrix surface zone;
4-mutual infiltration region; 5-fiber surface zone; 6-bulk fiber.

A variety of effects on interface reflect comprehensive changes of properties and processing properties of composites, such as mechanical properties, corrosion resistance, energy absorption and rheological properties. Therefore, the studies on the interface of composites will play an important role in improving the performances of composites, designing materials, implementing process, pioneering applications of composites and developing new composites.

4.2 The formation and action mechanism of interface

4.2.1 Formation of interface

For polymer composites, there are two stages for the formation of their interface.

The first stage is the contacting and infiltrating process between reinforcing fiber and matrix. Since the reinforcing fiber has different adsorption capacity for each group of matrix molecules and each component of matrix, which only adsorb the materials that can reduce the surface energy preferably those that reduce more surface energy. Therefore, the structure of polymer layer on the interface is different from the polymer itself. The second stage is the curing stage of polymer. During this stage, polymer cured by physical or chemical changes to form a fixed interface layer. The curing stage is influenced by the first stage, and it directly determines the structure of the formed interfacial layer. Taking the curing process of thermosetting resin as an example, the curing reaction of resin is carried out by curing agent or reaction of its own functional groups. In the curing process by curing agent, the location of the curing agent is the center of the curing reaction: the curing reaction expand out from the reaction center radially, and finally form a non-uniform curing structure with high central density and low edge density. The part with high density is called micelles or glue particle, and the part with low density is called glue floc. Similar phenomenon also occurs in the curing process by the reaction of functional groups in resin.

There are some pre-requisites for preparation of fabricating composites that components can combine firmly, and have sufficient strength. It is generally agreed that, in order to achieve this goal, materials must form the combination of minimum energy on the interface, and there is usually a process for liquid infiltrating solid. The so-called infiltration is to drop different droplets on the surface of different solids. Sometimes droplets immediately spread out and cover the surface of solids, which is called infiltration; and sometimes droplets are still spherical, which is called “no wetting” or “poor infiltration”.

The wetting angle or contact angle θ can be used to express wettability of liquid on solid. If $\theta \leqslant 90^\circ$, it is called partial wetting; if $\theta \geqslant 90^\circ$, it is called not wetting; if $\theta = 0^\circ$ or $\theta = 180^\circ$, it is called complete wetting and totally not wetting respectively. See Fig. 4.2.

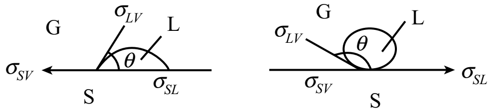


Fig. 4.2 Liquid wetting on the solid surface.

The wetting angle of liquid is related to the surface tension of solid σ_{SV}, surface tension of liquid σ_{LV} and interfacial tension of solid-liquid σ_{SL}. Relations among the above perameters and the wetting angle θ are expressed by equation (4.1)

$$\sigma_{SV} = \sigma_{SL} + \sigma_{LV} \cos\theta \tag{4.1}$$

Namely

$$\cos\theta = \frac{\sigma_{SV} - \sigma_{SL}}{\sigma_{LV}}$$

Where σ_{SV}, σ_{LV} can also be written as γ_{SV}, γ_{LV}, or simply γ_S, γ_L.

Following discussions are carried out according to equation (4.1): ① if $\sigma_{SV} < \sigma_{SL}$, then $\cos\theta < 0, \theta > 90°$, the solid can not be wetted by the liquid. If $\theta = 180°$, the surface cannot be wetted at all, and the liquid is spherical. ② If $\sigma_{LV} > \sigma_{SV} - \sigma_{SL} > 0$, then $1 > \cos\theta > 0, \theta < 90°$, the liquid can wet the solid. ③ If $\sigma_{LV} = \sigma_{SV} - \sigma_{SL}$, then $\cos\theta = 1, \theta = 0°$, the liquid completely wet the solid. ④ If $\sigma_{SV} - \sigma_{SL} > \sigma_{LV}$, when the liquid completely wets the surface of the solid ($\theta = 0°$), the liquid spreads before the equilibrium.

From equation (4.1), we know that if the surface tension σ of the research system changes, the contact angle θ can change, which means the change in wettability of the system. The wetting property of solid surface is related to its structure. Changing the surface state of solid, namely changing its surface tension, can change the wettability. For example, the surface treatment on the reinforcing fibers can change wettability between the fiber and the matrix materials.

The interface area of composites is constituted of the interface of fiber and matrix, together with the matrix and the surface thin layer of fiber. Matrix and surface layer of fiber mutually influence and restrict each other. They are also influenced by their structure and composition of the surface. The thickness of surface layer is not clear at present. It is estimated that the surface thickness of the matrix is about ten times of the surface thickness of fiber. Surface layer thickness of matrix is a variable, which not only affects the mechanical behavior of composites, but also affects its toughness parameters. For composites, the interface area also includes coupling compounds generated by treating agent, which combines with the surface layers of glass fiber and the matrix to form a whole.

From the micro perspective, the interface may be constituted of the surface atoms and sub-surface atoms, but it is still unclear that how many layers of sub-surface atoms there are that is affecting the interface area. The distance between matrix and surface atoms of fiber depends on the affinity between atoms, the size of atoms and groups, and the shrinkage on the interface after preparing composites. The interface layer thickness that Helfand calculated by the statistical theory is within the range of dozens of nanometers while S.Wu suggested that it is less than 0.1µm, but the value reported by Kwei and Troslyanshava is in a range of 200nm to 2µm, and Saglaz reported that the value of SiO_2/epoxy filler composite at 2.2µm. However, Songmujin and others reported that the value of system without adding silane coupling agent is less than 0.5µm, while the value of system added silane coupling agent KH-550 is larger than 0.5µm, but the thickness decreases while the amount of reinforcing materials increases. Sideridis and others also found that the same laws applied for the iron/epoxy filled composites. In addition, Wam Bach and others observed glass bead filled PPO composites by transmission electron microscopy, and found that the interface layer thickness is 7000nm.

The interface enables the fiber and matrix to form an integral, so that stress can be transferred through interface. If there is no stress on fiber surface and all surfaces have formed interface, stress transmission on the interface is uniform. It has been proved that stress is transferred through the adhesive bond between fiber and matrix. If the wettability between fiber and matrix is poor and bonding is not complete, the area of stress transmission is only a part of the total area of fibers. Therefore, to make the composites evenly transfer the stress and exhibit excellent performance, a complete interface zone is required to form in the preparation of composites.

4.2.2 The action mechanism of interface

In two phases of composites, in general, one phase in solution or melt flow status contacts with another phase in solid, and cures to make two phases combine. In this process, the mechanism and roles played by two phases are what people concern about, yet it is still not clear so far. The results from studies have been summarized in the following theory, including infiltration adsorption theory, chemical bond theory, diffusion theory, electron electrostatic theory, weak boundary layer theory and mechanical link theory, deformation layer theory and preferential absorption layer theory. Each theory has its own basis, but their existence can not explain all experimental facts. A problem perceived by two theories may contradict. Sometimes, it is necessary to combine several theories to summarize all the experimental facts.

1) Infiltration absorption theory

According to the infiltration absorption theory, there are two stages in the adhesive role of polymer. In the first stage, polymer molecules move from the solution or melt to the surface of adherent by means of macro-Brownian motion, and then the macromolecular chain gradually approaches the surface polar group of adherent by the micro-Brownian motion. When there is no solvent, the macromolecular chain can only partially approach the surface. However, reducing viscosity by pressure or heating can make macromolecular chain close to the surface. In the second stage, the adsorption happens. When intermolecular distance between adherent and adhesive is less than 0.5nm, the “van der Waals” forces take effect and form the dipole-dipole bond, dipole-induced dipole bond, hydrogen bond and so on. According to this theory, adhesive strength is determined by the second valence bond, which is based on: ① an adhesive material can stick a variety of materials; ② the general adhesive has a large inert with adherent, and it is difficult for chemical reactions to take place among them.

Bancroft noted that, the more intensively the adherent adsorbs adhesive, the higher is the adhesive strength. In the opinion of infiltration, matrix can spread on the fiber when the surface tension of the matrix is less than critical surface tension of reinforcing material or reinforcing material treated by coupling agent. It has been reported that the surface tension of the bisphenol A epoxy resin is 42.5×10^{-5}N/m, and the surface tension of polyester resin is 35×10^{-5}N/m. Therefore the critical surface tension of glass fiber with epoxy resin must be at least 42.5×10^{-5}N/m and above, and for the polyester it must be above 35×10^{-5}N/m, or otherwise the voids can be caused at the interface. It has proved that this theory is not like this in practice. When the basic demand for bonding are satisfied, further improvements should focus on improving the infiltration of the matrix and the filler. The limitations of the adsorption theory are: ① experiments showed that peeling the polymer film requires energy of as high as $10^4\sim10^8$erg/cm^2, (erg is an illegal unit, 1erg=10^{-7}J, similar in the follows), which greatly exceeds the required energy to overcome the intermolecular forces , indicating that there is more than the effect of intermolecular forces on the interface; ② experimental results show that the bonding power is determined by peeling speed of the adhesive layer, but the strength of intermolecular forces should not be determined by peeling speed of two bonding surfaces and as a result, bonding is not only determined by the intermolecular forces; ③ the theory is based on the interaction between polar groups of adhesive and adherent, so it can not explain why there is adhesive force between the non-polar polymers.

2) Chemical bond theory

Bjorksten and Lyaeger proposed chemical bond theory in 1949. The theory's main argument is that: molecule of coupling agent should contain at least two types of functional groups; the first functional group can react with reinforcing material theoretically, and the second functional group should be able to participate in the curing reaction of resin theoretically, and form chemical bonds linking with resin molecular chain. Therefore, the molecules of coupling agent act like "bridge" which firmly links the reinforcing material with matrix by the covalent bond. For example, methyl trichlorosilane, dimethyl dichlorosilane, ethyl trichlorosilane, vinyl alkoxy silane and diallyl alkoxy silane are used in unsaturated polyester/glass fiber system. The results show that the intensity of products containing unsaturated silane-based is almost three times of the saturated group, which remarkably improved the interface bonding between two phases in the resin/glass fiber system. The theory is powerless for complex systems without coupling agent or not being able to form chemical bond theoretically even with coupling agent.

3) Diffusion theory

Barodkuu proposed the diffusion theory of adhesive effect between two polymers. Its main argument is: the effect of bonding between polymers is the same as the self-adhesive effect (diffusion between the same molecules), and it is also caused by the diffusion (different molecules) between macromolecular chains or chain segaments, resulting in strong adhesive force. The theory is based on the macromolecular chain structure and flexibility that is the most fundamental characteristics of polymers.

Diffusion of two-phase polymer molecules is actually mutual dissolution that is determined by the solubility parameters, and the more similar the solubility parameters are, the more easily the two phases are miscible. The usage of coupling agents makes this theory apply in the field of fiber composites. The interpenetrating network theory proposed in recent year is actually a combination of the chemical bond theory and the diffusion theory to some extent.

4) Electron electrostatic theory

The electricity generates when two dielectrics are in contact. In addition, under certain conditions, the special sound and light-emitting phenomena arise because of the discharge and emitting electrons when adhesive film is peeled from the surface of the adherent. According to the phenomena, Dezayagin proposed a static theory: adhesives and adherent can be regarded as two plates of a capacitor; when adhesives and adherent contact each other, capacitor charges to form double electric layer. Thus, the bonding damage is equivalent to the separation of the capacitor, and adhesive power is equivalent to static gravity required to separate the capacitor. Double electric layer can be formed by directionally absorbing the polar group of a phase to another phase, which can be carried out by the electrons on the polymer functional groups going through the phase interface. In the case of dielectric-metal bonding, the double electric layer is a static electricity resulting from the changes of metal Fermi energy level and the electrons transferring to electronic media. Only under certain conditions, for example, if the sample is very dry and the peeling speed is more than 10cm/s, can such phenomenon occur. Therefore, the static theory agrees well with experiment results, but also has limitations. For example, it can not explain sufficiently that polymers with the similar property can be bonded solidly. According to the theory, non-polar polymers are not bonded, but in fact, they have a high adhesive strength.

5) Mechanical link theory

The theory indicates that the bonding between adherent and adhesive is purely based on mechanical action. The liquid binder infiltrated into the gaps of adherent, and then the adhesive solidifies or cures under certain conditions and is mechanically “embedded” in the pores, thus mechanical bondings like bolts, nails, hooks are formed. This shows that the mechanical bonding is mainly determined by the geometrical factor of the materials. In fact, mechanical bonding theory is the theory acting synergistically with other theories. There is no bonding system which is only formed by mechanical action.

6) Deformation layer theory

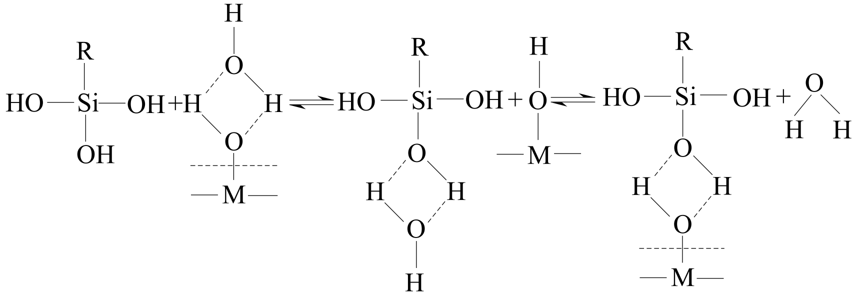
In the fatigue performance research of laminated composites, Hooper found that there is a coupling agent coating layer on the surface that makes the fatigue properties greatly improved. According to the theory, this is a flexible coating layer providing the chemical bond with “self-healing capabilities”, which is in the dynamic balance state of continuous formation and fracture under outer load. The stress-corrosion of low-molecular-weight compounds makes the chemical bonds broken. At the same time, the strength exists along the fiber and matrix under the stress. Stress relaxation arises in this change, which reduces stress concentration on the point. The dynamic balance not only prevents water and other low-molecular-weight compounds, but also relaxes partial stress of the interface because of the existence of these low-molecular-weight compounds.

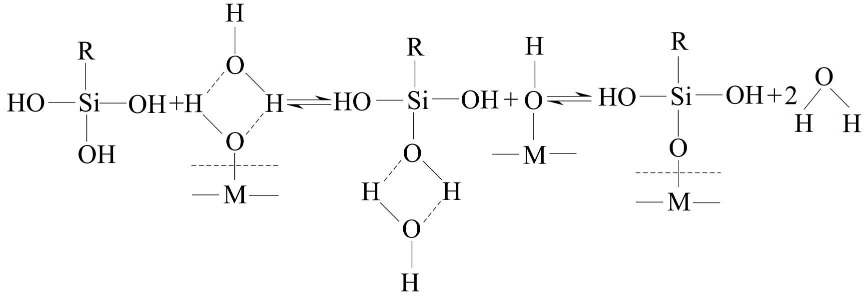
The polymer contracts in the curing process of polymer composites. Since the thermal expansion coefficient of matrix and fiber differs a lot, in the curing process, additional stress will be resulted on the interface of fiber and matrix. Additional stress could damage the interface and worsen the performance of the composites. In addition, the stress generated under static load is also unevenly distributed in composites. We found by observing the microstructure of composites that interface of fiber and resin is not smooth and some parts of the interface have concentrating stress higher than the average. This stress concentration will break the chemical bond between matrix and fiber, resulting in micro-cracks in the composite interior, and to decrease the performance of composites.

After treated by treatment agent, reinforcing materials can alleviate the effect of the stresses mentioned above. Therefore, some researchers proposed several theories about the formation and effect of the interface: one suggests that the treatment agent forms a plastic layer on the interface, which relaxes the stress of interface and reduces the effect of the interface stress; this theory is known as the “deformation layer theory”; another theory suggests that the treatment agent is part of the interface which is the modulus lying between the high modulus reinforcing material and low modulus matrix. It enables the stress to transfer uniformly and weakens the interface stress. This theory is called the “inhibition layer theory”. There is a relatively new theory known as “weakening interface local stress theory”, and we will introduce the theory in the following.

Weakening interface local stress theory suggests that the treatment agent in interface between the matrix and the reinforcement provides a chemical bond with “self-healing capabilities”. The chemical bond is in the dynamic balance state of continuous formation and fracture under static load. The stress-corrosion of low-molecular-weight compounds (one of them is water) breaks the chemical bonds. The treating agent can slide to a new location along the surface of reinforcing material under stress, and the broken bonds can reform new bonds, maintaining certain adhesive strength between matrix and reinforcing material. At the same time, stress is relaxed in the process, which weakens the stress concentration on certain points of interface. The dynamic balance not only prevents the destructing effect of water and other low-molecular-weight compounds, but also relaxes partial stress of the interface.

The basis of this theory is: when the post-hydrolysis treatment agent (silicon alcohol) approaches the surface of hydrophilic reinforced material covered with water film, because of its ability to generate strong hydrogen bonds, it can compete successfully with water to react with the surface of reinforced material, making it bonded with hydroxyl of reinforced materials surface. There are two reversible reactions in the process:





The R- group of silane treatment agent reacts with the matrix to form two stable membranes: rigid membrane and flexible membrane, they become a part of the matrix. The interface between the membrane generated by polymer and treatment agent and reinforced material represents the final interface between the matrix and reinforced material. The bonding between polymer rigid membrane and reinforced materials is shown in Fig. 4.3.

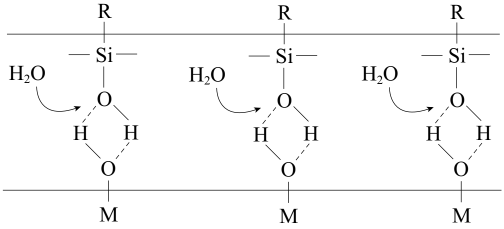


Fig. 4.3 Rigid membrane of polymer and adhesion with reinforcement.

As long as the interface is rigid or mobile, with the presence of water, the bond generated by treatment agent and the surface of reinforcing materials hydrolyzes to form free silicon alcohol that remains at the interface and finally restores the original bond. Or it will form a new bond with the group (active site) of the adjacent reinforced materials surface. So the formation and damage of chemical bond between treatment agents and reinforcing materials' surface is in a state of reversible dynamic equilibrium. As long as the rigid membrane generated between the treatment agent and the matrix maintains the integrity, then under the stress, after the chemical bond between the treatment agent and the reinforcing material damages, it will be re-formed in the adjacent position. The overall effect of the dynamic equilibrium makes the bonding between the matrix and the reinforcing material intact and can weaken stress, but this effect can be observed only in the large scale.

The above-mentioned theory is also confirmed useful by contrasting the performance of composites acting in acid, alkali and water. Acid or alkali is effective catalysts for hydrolysis of silicon oxygen bond (—Si—O—), if the bond (silicon oxygen bond —Si—O—) formed between the matrix and the reinforcing materials through treatment agent is covalent bond which is not durable and can reversibly change. Then the mechanical properties of composites at the role of acid or alkali will decrease, which should decline faster than in the water. But in the experiment the composites are formed by reinforcing materials treated with the silane, boiling test is in the acid or alkali solution for 24 hours, with the pH at 2,4,6,8 or 10 , respectively. The results show that bending strength of the material does not decrease normally comparing to the one treated by water. We see that bond formed between the surface of reinforced materials and the treatment agent is covalent bond that can change reversibly.

The above-mentioned theory is not feasible to explain the flexible membrane generated by polymer. That is because the bond formed between the flexible membrane and the reinforcing material can contract after the hydrolysis and no longer eligible of generating a new bond. Thus the water can spread on the surface of the reinforcing material, so that the bonding between the matrix and the reinforcing material damages completely. The bonding between flexible membrane and the surface of reinforcing materials is shown in Fig. 4.4.

7) Priority absorption theory

Different components of resin adhesive can have different ability in getting attached to glass fiber. The fiber surface first absorbs the auxiliary of matrix system. For example in the amine cure epoxy resin, the surface of fiber first absorbs amines. So the distribution of the interfacial layer in matrix is of gradient, and will finally affect the structure and properties of the interface layer also having a gradient change, which can eliminate stress and improve the mechanical properties of composites.

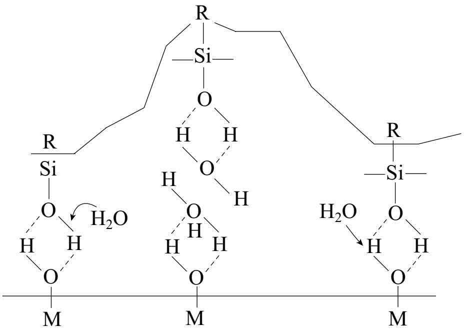


Fig. 4.4 The bonding between flexible membrane and surface of reinforcing materials.

In order to explain the process of interfacial adhesion, a variety of interface bonding theories were put forward. Every theory has the fact basis, but contradicts with other truths. Each theory can only explain a particular aspect of interfacial adhesion, but it can not explain the nature of phenomenon and all the process. Although there are many theories, the understanding of adhesion phenomena is still superficial and the essence has not been grasped. In order to deeply reveal the nature of bonding phenomena, there should be a comprehensive analysis of various theories, select the essence, summed up into a more complete theory that can well explain all the process and mechanism of interfacial adhesion.

4.3 Damage mechanism of interface

4.3.1 The factors that influence the bonding strength of interface

1) Size and specific surface area of fiber surface crystal

With the increasing surface crystal of carbon fiber, the graphitization degree of carbon fibers and modulus increase. This makes the surface smoother and more inert. Its adhesion with resin and reactivity become worse, so the bond strength of interface decreases. A large number of experiments have proved that interfacial adhesion strength of carbon fiber composites decreases with increasing the fiber surface crystal. This is consistent with the result that interlaminar shear strength of carbon fiber composites declines with increasing fiber modulus.

The specific surface area of fiber is big, the physical interface of bonding is big, and adhesive strength is high. However, fibers and surface treatment are different, its pore size distribution, surface reaction groups and the concentration are different. At the same time, molecular weight, viscosity, the ability to react with the surface reaction group of the different matrix system are not the same, therefore, specific issues should be in a concrete analysis.

2) Soakage

Bonding strength of interface increases with increasing the soakage, and decline with the increase in porosity, because reducing bonding interface area leads to the increase of stress concentration source. If infiltration is complete, the bonding strength generated by physical adsorption of resin on the interface is great, but in fact because fiber surface adsorbs gas and other pollutants, resin does not completely infiltrate, gas and pollutants can not be excluded, gap is formed on the interface, so that the porosity of materials rises and interlaminar shear strength declines.

3) Interfacial reaction

Interfacial adhesion strength increases with the increase of interfacial reaction that is closely related to interlaminar shear strength of composites. For example, using silane coupling agent to modify the surface of glass fiber can improve performance of composites. Using cold plasma to modify surface of fiber improves interfacial reaction and makes the interlaminar shear strength of composites greatly improved (Table 4.1).Thus, in the preparation of composites, it is necessary to introduce as many reactive groups as possible to interface and increase the proportion of interface chemical bonding, which can improve the properties of composites.

Table 4.1 Influence of carbon fiber and aramid fiber surface modification on properties of composites

Composites	Change of reactive groups on fiber surface		Interlaminar shear strength (MPa)		
	Increment of hydroxyl (%)	Increment of hydroxyl (%)	Composites without fiber surface treatment	Composites with fiber surface treatment	Increment rate (%)
Carbon fiber composites	2.34	3.49	60.4	104.7	72
Aramid fiber composites	Fiber surface grafted with allylamine		60.0	81.3	36

4) The influence of residual stress on bonding strength of interface

For polymer matrix composites, the interfacial residual stress is caused by heat contraction stress and chemical contraction stress produced by resin volume shrinkage in the curing process. As thermal expansion coefficient of fiber and resin are different, heat stress is major cause. The forming process of heat stress is indicated in Fig. 4.5, mainly because the thermal expansion coefficient of resin is high and thermal expansion coefficient of fiber is low. The resin is in the state of rubber at 150°C. When cooling to room temperature, the resin transits to glass state with volume greatly shrinking, but shrinkage of the fiber is less, bonding interfacial force attempts to prevent this shrinkage, the final result is that resin is subjected to tensile stress, fiber is subjected to compressive stress, the interface is subjected to shear stress. Heat stress can be obtained through the calculation.

$$\begin{aligned}&\sigma \text{ (heat stress) } = E \text{ (modulus) } \varepsilon \text{ (strain)}\\ &= E\Delta\alpha(\text{coefficient of thermal expansion difference})\Delta T \text{ (temperature difference)}\end{aligned} \tag{4.2}$$

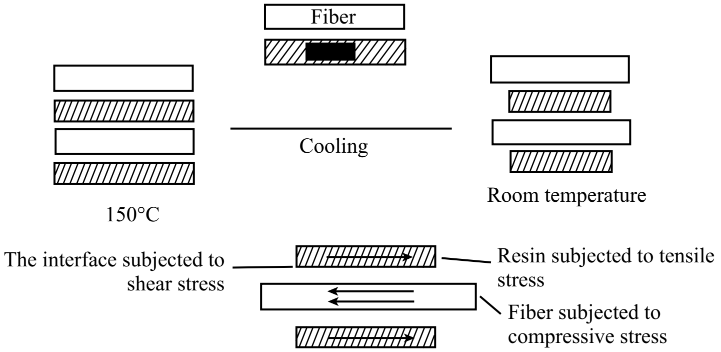


Fig. 4.5 Schematic diagram of the composite heat stress formation.

Because interface has internal stress, the external force needed to destroy the sample correspondingly declines, which is the reason that interface adhesion strength of composites is influenced by the residual stress. The extent of this influence depends on the fiber content, modulus ratio of fiber to matrix and the size of fiber. Generally, heat stress decreases with increasing fiber volume content, and it increases with the decrease of the modulus ratio of fiber to matrix.

4.3.2 Damage mechanism of interface

Damage mechanism of composites should be studied from the changes of fiber, matrix and interface under the load and medium, and understanding the damage mechanism of the interface is very important, because fiber and matrix forms a whole composite through the interface. In the study of interface damage mechanism, there are many theoretical reports about the energy change of interface crack propagating process and the interface damage arising from media. Now we introduce the two opinions: in the composites, micro-cracks exist in both fiber and matrix interface. Under external force and other factors, the micro-cracks will propagate in accordance with its own law, eventually resulting in the damage of composites. For example, the micro-cracks on the matrix (see Fig. 4.6), crack growth trend is that some are parallel to the fiber surface, and some are perpendicular to the fiber surface.

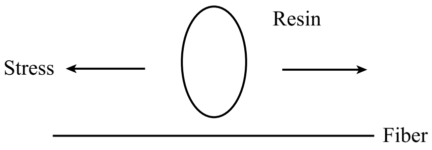


Fig. 4.6 Schematic of crack perpendicular to the fiber surface.

Micro-cracks gradually expand throughout the matrix under external factors and finally arrive at fiber surface. During this process, energy will be gradually consumed with the expansion of cracks. Because of energy consumption, the speed of expansion will slow down, and the crack vertical to surface will mitigate the impact to fibers because of energy consumption. Assuming that energy is not consumed, energy concentrates on the tip of cracks and the fiber is penetrated, which makes fiber and composites destroyed. This is characteristic of brittle damage. The brittle damage can be observed by increasing bond strength between the carbon fiber and epoxy resin. In addition, it can also be observed that damage of some polyester or epoxy resin composites is not brittle, but gradual damages which begin when load reaches in the range of 20% to 40% of the overall destructive load. The mechanism of this damage is that above mentioned energy dispersing (energy dissipation) in expanding process of crack slows the expanding speed of crack. Energy is consumed in the interface debonding (adhesion was damaged), which disperses the energy concentration on the tip of cracks, so fiber damage is not caused, making the whole damage process gradual. The crack energy dissipation at the interface is shown in Fig. 4.7.

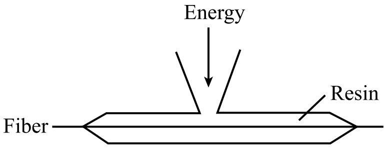


Fig. 4.7 Schematic of the crack energy dissipation at the interface.

When the cracks are prevented at the interface, energy is consumed because interface degums (bonding of interface is destroyed), which lead to debonding layer of a large area. It has been observed that the visual size of degumming layer is 0.5μm by high-resolution microscopy, which shows that the dissipation mechanism of energy is at work. At the interface, the bond formed between matrix and reinforcing material can be divided into two categories, one category is the physical bond, or van der Waals' force, the bond energy is about 6kcal/mol and the other is a chemical bond, the bond energy is about 30kcal/mole. We see that the energy consumed in damaging chemical bonds is greater when the energy disperses. The distribution of chemical bonds at the interface can be centralized, decentralized, and even disordered. See Fig. 4.8.

If the chemical bond on the interface is centralized, the dissipation energy is small when the crack expands. More energy is focused on the tips of cracks, which may cause the fiber's breaking down even before the focused bond has not been damaged. In this case, composites damage in brittle manner. See Fig. 4.9.

There are other cases in the chemical bonds focusing on the interface: in the expanding process of crack tip, fiber failed to be thrusted but the focused bonds are damaged, because the energy dispersion caused by damaging focus bonds only damage the interface bonding. See Fig. 4.10. If energy concentrated at the tip of crack is large enough, or continues to increase the energy, not only will the focus bonds be damaged, but also will fiber breakage be triggered. In addition, damages of physical bond also consume a certain amount of energy focusing at the tips of crack in the damage process of chemical bonds.

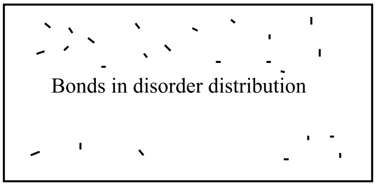


Fig. 4.8 Chemical bond distribution diagram on the interface of matrix and reinforced materials.

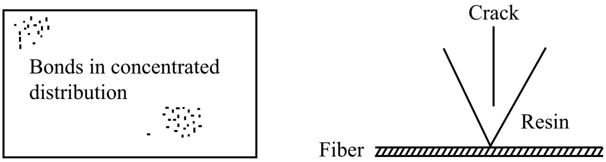


Fig. 4.9 Schematic of energy concentration of cracks causing fiber fracture.

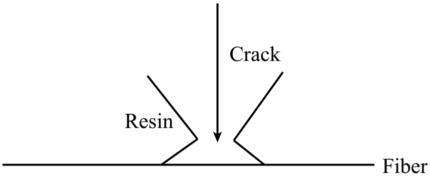


Fig. 4.10 Schematic of damage of focused bond caused by crack propagation.

If the chemical bonds on the interface are scattered, when the cracks expand, the chemical bonds will be gradually destroyed to make resin gradually detached from the interface and energy gradually dissipated, resulting in debonding damage (interface bonding damage). Schematic diagram of interface debonding damage is shown in Fig. 4.11.

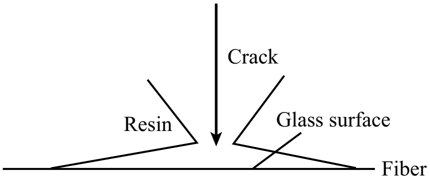


Fig. 4.11 Schematic of interface debonding damage.

4.3.3 Damage of water to composite materials and interface

When water adsorbed on the surface of glass fiber reinforced composites infiltrates into the interface, it causes damage of the interface bonding by triggering chemical reactions among water, glass fiber and resin, resulting in damage of composites. Data are listed in Table 4.2. The glass fiber reinforced composites has great sensitivity to water, its strength and modulus decrease with increasing of humidity.

Table 4.2 Changes in properties of glass fiber reinforced composites at different humidity air

Relative humidity (%)	Tensile strength (MPa)	Tensile elastic modulus (GPa)	Tensile proportional limit (MPa)
Dry	322	17.3	176
55	269	15.6	143
97	223	11.3	112

1) Water infiltration

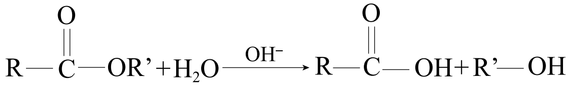
It is well known that water is in the form of water vapor in the atmosphere. Especially in humid and hot areas, there is very high vapor content is in the atmosphere. Water molecule is small in size, and polarity is large, so it is easy to enter the interface. Clean surface of the glass fiber has big ability of absorbing water, and because of the action force between water molecules, water on fiber surface can be transfered through the absorbed water film. Therefore, absorption of water by the surface of glass fiber is a multi-layer adsorption, forming a thick water membrane (the thickness is about 100 times of the diameter of water molecule). Glass fiber surface on the adsorption process of water is very rapid. It only needs 2 or 3 seconds to complete adsorption at relative humidity of 60% to 70%. The finer the fiber is, the greater the specific surface area is, the more adsorption of water. The water is firmly adsorbed on the surface of glass fiber, if heating up between 110°C and 150°C, only the half water can be excluded, if heating up between 150°C and 350°C, only three-fourths of the water can be excluded. In addition, it is proved in many experiments that there are three ways for water get into interface through diffusion process. The first way is by the cracks of resin, which is generated by chemical stress and thermal stress in resin curing process. The second entering way is by micro-cracks which are produced in high-pressure zone. Because of the existence of impurities in resin, particularly water-soluble inorganic impurities, high-pressure zone will be formed resulting from osmotic pressure when they contact with water. The third one is by inner bubbles that remain in composite materials processing. They are to be broken by stress and form the perforative channel along which water can easily reach to the deep place of composites.

2) Chemical corrosion of water on the surface of glass fiber

When the water enter into the glass fiber composite materials to reach the surface, alkali metal of the surface of glass fibers will dissolve in it. Alkaline aqueous solution accelerated the corrosion of the surface. Finally, the silicon oxide skeleton of glass fiber will be disintegrated, which decreases the strength of fiber and thus performance of composite materials. Such corrosion, especially in structural defects of the glass fiber surface is more serious.

3) The degradation of water on resin

There are usually two effects about the role of water on the resin: one is physical effects, that water molecules can damage the internal polymer hydrogen bonds, and other non-chemical bonds, so that the role of plasticization occurred, which lead to the decrease of thermo-mechanical performance. This effect, however, is reversible. Once the water dries off, performance can recover. The other is chemical effects, that is, water molecules can react with the polymer bond (such as ester, ether, etc.) by chemical reactions to make it fracture, leading to polymer degradation and strength of bonded joints lost. This degradation reaction is irreversible, but there are different degradation abilities of water for different resins. For polyester resins, the hydrolysis of its activation energy is in the range of 11kcal/mole to 12kcal/mole. Polyester glass fiber composite materials under the effect of the water produced hydroxide ion, so that the water shown alkaline. Alkaline water accelerated the role of hydrolysis of polyester resin, the reaction is given by.



$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR'+H_2O\xrightarrow{OH^-}R-\overset{\overset{\displaystyle O}{\|}}{C}-OH+R'-OH$$

As macromolecular chain degrades by hydrolysis, it will result in the destruction of resin layer, and thereby it causes damage of the interface bonding. Damage caused by hydrolysis is a non-uniform damage from a small piece to another. As different opportunities for resin to contact water, hydrolysis of resin is more damaged near the site of the surface layer in the composite material, and it is less damaged in the center of composite materials.

4) Water swelling in resin to interface debonding damage

After water enters the interface, resin swelling occurs. The swelled resin causes a shear stress on the bonding interface, and once it is greater than the bonded interface strength, the interface debonding damage will occur.

5) Interfacial debonding destruction by osmotic pressure from water into the pore

In the bonding process, the binder is not always ideal to the exclusion of surface adsorption of all gases and spread, so it is hard to avoid the formation of some micro-gaps. When the water entered into bonded joints through the diffusion, it can be gathered in the micro-gap to form the micro bag of water. The water of micro bag contacts with resin and some of impurities dissolves in water. In this case, the concentration difference is formed inside and outside the bag, resulting in osmotic pressure in micro-water bag, which has the following relationship with the concentration of solution:

$$\pi = cRT \tag{4.3}$$

Where c is the concentration of the solution in the bag; R is the mole gas constant; T is thermodynamic temperature.

Under certain temperature, with the time delaying, the concentration of aqueous solution in bag is increasing. When osmotic pressure is greater than the interface bond strength, bonding interface will debond, leading to the breach.

6) The expansion of crack by water

The water immersed in the interface of glass fiber composite materials, first damages the interface bonding, and then decreases the strength of glass fiber and makes resin to degradate.

Water absorption of composite materials, the initial is sharp, and then gradually slows down. Water absorption with time is generally according to the following relationship.

$$R_{pc} = R_\infty(1 - \mathrm{e}^{-\alpha t}) \tag{4.4}$$

Where R_{pc} is the water absorption, %; R_∞ is the saturation absorption rate, %; α is a constant; t is time.

Water in composite materials not only renders destruction of interface, but also accelerates the expansion of crack. When composite material is stressed, if the energy δ_E that stress caused by the consumption of elastic strain is more than the total of energy δ_σ that required for the formation of new surface and the energy δ_W that caused by plastic deformation, the damage of crack will be the rapid expansion, the relationship is given by

$$\delta_E \geqslant \delta_\sigma + \delta_W \tag{4.5}$$

The above relationship does not adapt to the slow development of cracks, but we can apply to the discussion of the relationship between water and crack propagation. Water reduces the cohesive energy of the fiber, which reduces the δ_σ. When the water is inside the tips in the crack, it embrittles the glass fiber, which reduces the δ_W. Therefore, under relatively small stress, the crack of the glass fiber surface will extend to the internal as a result of water. Besides the reduced δ_σ and δ_W, there are two other reasons why water contributed to the expansion of cracks: first, the new surface flaws generated by the corrosive effect of water on fiber surface; another is the agglutination of the water in the tip of the crack that generates a lot of capillary pressure, which boosts the original micro-crack to propagate in the fiber. This encourages the crack expansion.

The above failure mechanism of the interface is not perfect. The topic is still under intense exploration by the current domestic and foreign researchers. From the available information, there are generally the three theories: theory of micro-cracks damage, theory of interface damage and theory of destruction of the chemical structure.

4.4 Surface treatment of fiber

Inorganic reinforced materials and organic polymer matrix is in essence two types of non-miscible materials, so direct combining of the two will not attain the ideal interface bonding. For glass fiber, in order to facilitate the textile processes, to reduce the mechanical wear and prevent water erosion, it is often coated with textile-based sizing on the surface in the preparation of fibers. The applied coating is a paraffin emulsion agent. If it is not removed, the bonding of interface between fiber and resin will be hampered. In addition, for glass fiber not coated by sizing agent or had it removed, its surface tension is large, and it can easily absorb a layer of water film from the air. The existence of water not only damages fiber itself, but also resisted the interface bonding of fiber and resin. For high modulus carbon fiber, its surface is chemically inert, and the infiltration of resin matrix is poor, which results in the low interlaminar shear strength (ILSS) of carbon fiber composite material.

The formation of an ideal interfacial adhesion between treated fibers and matrix, will act asnumerous micro-bridges between the two planes, bridging communication between materials with starkly different performance, joining them together in synergy. Therefore, surface treatment of inorganic materials is particularly important.

4.4.1 Surface properties of reinforced materials

The surface properties of reinforced material generally refer to the physical properties of the surface (including surface micro-structure, surface area and morphological structure), chemical properties of the surface (including surface chemical composition, surface functional groups and surface reactivity) and the surface Gibbs free energy.

1) The surface physical properties of reinforced materials

Micro-structure and morphological structure of the surface of reinforced materials belong to surface morphology. Ideal smooth surface does not exist. Every solid surface is covered with micro-cracks, voids, empties and so on. Through optical and electron microscopy it is shown that glass fiber surface is smooth, its roughness is relatively little, and its cross-section is symmetric circular. PAN-based carbon fiber surface is lightly grooved, smooth and regular, and its cross-section is round and has shape of kidney. Rayon -based carbon fiber has very smooth surface with irregular bands and trenches in the longitudinal direction and round cross-section. This is not conducive to bonding. Boron fiber surface structure is similar to cob, but it is still smooth. The specific surface area is small, and cross-section is circular, with tungsten boride (WB_5 and WB_4) in the inner core, and pure boron (B) on the outer layer. Silicon carbide fiber surface is in a shape of concave valley groove, but it is still smooth. It has small surface area, larger diameter, a circular cross-section. The core is a tungsten wire, and the outer edge is the composite structure of silicon carbide.

Some physical properties and the surface size of fibers are listed in Table 4.3. Table 4.3 shows surface area of carbon fiber is the largest, and of boron fibers, silicon carbide fiber is small, of glass fiber is intermediate. Surface area includes the inside and the outside surface area. There are holes and empties in carbon fiber, thus it has a high surface area. However, they are usually inner holes with their orientation along the fiber axis. Such holes generally do not extend to the fiber surface, so the inner surface does not adsorb gas, and has nothing to do with resin adhesive. Therefore, the surface of carbon fiber utilization rate is low. According to the bonding mechanism, the greater surface area, the better bonding situation between fiber and resin, but in reality this is not the case. Practice has proved that by surface treatment, the changes of fiber surface area are little, but composite interlaminar shear strength has greatly improved. While some fiber only pointed out the surface state, the adhesive interface of composite materials is mainly decided by the surface chemical properties.

Table 4.3 Physical properties of some reinforcing fibers and their surface size

Fiber types	Density (g/cm^3)	Diameter (μm)	Specific area (m^2/g)		The total surface area of composites in100cm^3 (m^2)
			Calculated value	Actual value	
S-glass fiber	2.50	10.0	0.160	0.13	19.5
Boron fiber	2.70	101.6	0.015	0.01	3.1
Silicon carbide fiber	3.50	101.6	0.012	0.01	1.8
Silicon carbide fiber coated with boron	2.80	105.4	0.014	0.01	2.16
Thorne 150	1.63	6.6	0.370	0.55	54.0
Hitco HMG-50	1.71	6.8	0.340	0.83	89.0
Magnamite I	1.99	7.5	0.260	0.11	31.0
Courtaulds B	1.93	7.5	0.270	0.31	34.8

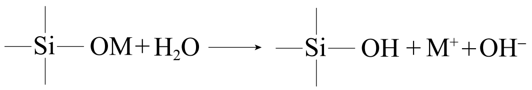
2) The surface chemical properties of reinforced materials

The surface chemical properties of reinforced materials are mainly referred to the chemical surface composition and surface reactivity.

Surface chemical composition and functional group structure determines the size of fiber surface free energy and surface reactivity, which determines whether the fiber used should carry through surface treatment or not, whether fiber and resin can form a chemical combination, whether the surface is easy to react with the environment and other issues.

(1) Surface chemical properties of glass fiber.

Studying chemical composition on surface of glass fiber, we found that the chemical composition of their body is not exactly the same as surface chemical composition. Such as E-glass fiber, the bulk chemical composition are Si, O, Al, Mg, B, F, Na, etc., and the surface only contains Si, O, Al. On the glass fiber's surface, cation and anion are imbalance in the force, and the cation can't obtain oxygen ions in necessary number, resulting in surface free energy. This causes the glass fiber's tendency of adsorbing materials from the outside. In glass fiber's structure, alkali metal oxides with size of 1.5nm to 20nm scatter in SiO_2network and these oxides has great hygroscopicity. In addition, there are a large number of polar groups —Si—OH on the surface of SiO_2 network, resulting in strong hydrophilicity. Therefore, the pure glass fiber in the atmosphere can absorb a layer of water molecules very quickly. Surface physical adsorption ability can transmit across continuous water layer; thus water molecule layer on fiber's surface is not a single molecular layer, but a water film with approximately 100 molecules' thickness. Adsorbed water on glass fiber surface reacts with alkali metal or alkaline earth metals of glass composition and forms hydroxyl, which is shown below.



$$-\overset{|}{\underset{|}{Si}}-OM+H_2O \longrightarrow -\overset{|}{\underset{|}{Si}}-OH+M^{+}+OH^{-}$$

Hydroxyl turns the adsorbed water on glass fiber surface alkaline and OH^- further reacts with the network, reducing the fiber strength.

In addition, partial adsorbed water and —Si—OH on glass fiber's surface, as well as among adjacent —Si—OH, can combine to form hydrogen bonds.

Therefore, there are a large number of —Si—OH groups on clean glass fiber's surface, which have the reactability of general substance with active hydrogen group. This is good for surface modification and chemical bonding.

(2) Surface chemical properties of carbon fiber.

The chemical composition of graphite fiber body is C, O, N, H and trace metal impurities, while its surface chemical composition is C, H, O. Experiments show that PAN-based high modulus type I and high-strength type II carbon fiber contain at least two different kinds of oxygen atoms in combining on surface at depth in a range of 100∼150nm. The existence of these components is caused by the nature of precursor fiber and the reaction activity of carbon fiber surface.

There are polar high reaction groups on fiber's surface such as ketone, carboxyl and hydroxyl, which cause combination of resin by secondary bonds force and chemical bonds. It can greatly increase shear strength of carbon fiber composite materials.

(3) Surface chemical properties of other fibers.

There is boron oxide on boron fiber surface, silicon oxide on silicon carbide surface, so the existence of these oxygen groups greatly improves the wettability and reactivity of fibers.

3) Surface Gibbs free energy of reinforced materials

An important condition for bonding between reinforced material and the matrix is the close contact with each other and the completely wetted surfaces. This is depended on their surface free energy, that is, the surface tension. When the solid surface tension is greater than the liquid, the liquid will wet the solid. The surface tension of the commonly used matrix material is between 3.5×10^{-4}N/cm and 4.5×10^{-4}N/cm. If these matrix materials are required to wet reinforced material, the surface tension of the reinforced material should be larger than 4.5×10^{-4}N/cm. Carbon fiber, boron fiber, silicon carbide fiber have evident oxidation surface, it is conducive to the formation of high surface free energy. If the surface is contaminated, the surface energy will be reduced, and have the impact of wettings of polar matrix on their surface. Such as surface monolayer adsorption of water of glass fiber will affect wettability of the polar matrix on their surface.

For carbon fiber, its untreated surface is inertial. After it was treated in air at 500°C for 15 minutes, the wettability between the carbon fiber and epoxy resin will be greatly changed.

The size of the contact angle θ can also be used to express surface tension between solid and liquid. For example, untreated surface of E-glass fiber, the contact angle is $45^\circ \sim 60^\circ$ with water, by heat treatment and cooling to room temperature, the contact angle becomes 160°; the contact angle is $0^\circ \sim 8^\circ$ by acid treatment, and 12 hours' placement after washing with acid, the contact angle becomes 160°; 15 minutes drying at room temperature after E-glass fiber was treated by γ-aminopropyl triethoxysilane, the contact angle with water is 20° and the contact angle with epoxy resin is 25°.

4.4.2 Surface treatment of glass fiber

The bonding between glass fibers and the matrix depends on the surface composition, structure and property of the reinforced materials, and nature of bonding will have an important impact on composite materials. In order to improve the bonding between the matrix and the glass fiber, we can use surface treating agent for chemical treatment to the surface of the fiber. The so-called surface treating agent is the substance, that it has at least two types of reactive functional groups in the chemical structure: a class of functional group reaction with —Si—OH on the surface of glass fiber, other functional groups can participate in resin curing. In this way, treatment agents behave like the "bridge", linking the glass fiber and resin together so as to obtain good adhesion, therefore, it is also called coupling agent.

1) Dewaxing treatment

During fiber spinning process in order to achieve cluster, soakage and removal of electrostatic adsorption, glass fiber is coated by in a single layer of textile-based sizing. Such sizing is a paraffin emulsion, which will prevent the bonding between the fibers and the matrix, thus reducing the performance of composite materials. So these sizing agents must be removed before compounding with the matrix.

The extent of such sizing's remaining is showed by residue, which is the residual wax content (in percentage) in the surface of glass fiber fabric material.There are two methods to remove sizing, washing and heat treatment. See Table 4.4.

Table 4.4 Methods of removing sizing agent

Processing method		Treatment conditions	Appearance after treatment	Strength retention (%)	Residue (%)
Washing method		Sizing agents are dissolved and cleaned by hot water, acid, alkali, detergents, organic solvents, etc.	White	60∼80	Less than 0.3
Heat treatment	Discontinuous process	Place a large number of glass cloth in heating furnace to heat up gradually, so that the sizing agent evaporate slowly.	Dark brown	80∼120	Less than 0.5
	Batched method	For 65 or 75 hours, the maximum temperature at 300°C. Glass cloth is placed in hot stove discontinuously to treat. The first stage: at 230°C for 10 to 20 hours; the second stage: at 350°C for 60 hours or more.	White	40∼60	Less than 0.1
	Continuous process	Glass cloth is put in hot stove continuously for heat treatment between 550°C and 650°C, at a rate of 3∼8m/min.	White	30∼50	Less than 0.1

Washing method is to get rid of the sizing agent by using lye, soapsuds and organic solvent according to the composition of sizing agent. After treatment, the wax remainder of the glass cloth is between 0.3% and 0.5%.

Heat treatment method is using heat to get rid of the sizing agent on the surface of glass fiber and textile through evaporation, carbonization or burning. According to the level of heating temperature, heat treatment method includes low-temperature (250∼300°C), medium temperature (300∼450°C) and high temperature (>450°C) heat treatment. The higher the temperature, the longer the time, the smaller the sizing residues, but also the greater decline in fiber strength. At 500°C the treatment of within a minute will decrease strength by 40%∼50%.

According to whether the process is continuous or not, there are intermittent method, batch method and continuous method.

Intermittent method is by adding a large number of glass fabrics rolls to furnace and warming up gradually, so that the volatile sizing on the glass cloth goes out slowly. The furnace heats with the circulated hot air and the maximum temperature is at 300°C. The processing time is for 65~75 hours. Generally we use low and middle temperature, this method is more convenient, but each volume of cloth is non-uniform processing from the inside to the outside, the processing time is long and residue is large.

Batch method is by putting the glass cloth in hot stove in batches, and treats in different stages. At the first stage, at 230°C for 10h to 20h; at the second stage, at 350°C for more than 60h. It is the best when the treated matter is still white.

Continuous method is that on the joint handling units the glass cloth goes through a gas or electric heating furnace to a certain temperature, for baking, and then is automatically rolled up. Processing temperature between 550~650°C, the glass fabric in the heater is stayed only in a few dozen seconds. As soon as the fabric entered into a heat treatment furnace, it is heated rapidly. So in place not far from the entrance, partial sizing starts to decompose, volatilize and go into spontaneous combustion. The heat treatment degree is usually controlled by location and color of the flame in practical production.

The effect of heat treatment can be quantitatively determined by the residual sizing and the strength loss of glass fibers. After heat treatment, the color of glass cloth can qualitatively reflect the content of residues, i.e brown>golden yellow>white. General requirement for the treated fabrics both retain a high strength and a low residue. Under the circumstance to ensure the fabric strength, it is better with lower content of residues.

After heat treatment of glass fiber, it is easy to adsorb moisture in the air; therefore we should coat it with coupling agent as quickly as possible.

2) Chemical treatment

The so-called chemical treatment, that is, to treat glass fiber using coupling agent, so as to form chemical bonds between matrix and fiber to obtain good adhesion, and effectively reduce the water erosion.

(1) The structure and mechanism of siloxane coupling agent.

At present, the general structure of the siloxane coupling agent used in industry is:

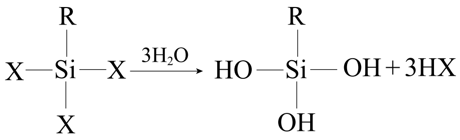
$$\mathrm{R(CH_2)}_n\mathrm{SiX_3} \quad (n = 0 \sim 3)$$

Where X is the hydrolysis groups, which can react with the surface of inorganic materials; R is the organic functional groups, which can react with matrix resin.

The mechanism of coupling agent is shown in follows.

① Organic silane hydrolyzes to generate silicon alcohol.

This is the most commonly used coupling agent.



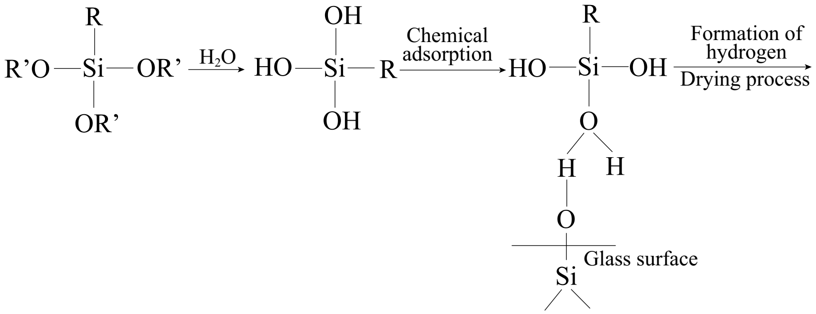
$$\mathrm{X{-}\overset{\displaystyle R}{\underset{\displaystyle X}{Si}}{-}X} \xrightarrow{3H_2O} \mathrm{HO{-}\overset{\displaystyle R}{\underset{\displaystyle OH}{Si}}{-}OH} + 3HX$$

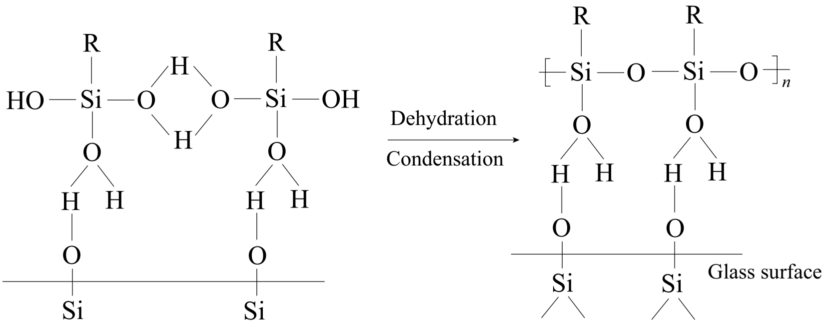
② React with glass fiber surface.

We can get trisilanol by the hydrolysis of silane, and its structure is the same as that of glass fiber surface, and thus it is very accessible for adsorption. The trisilanol adsorbed on the surface of glass fiber has only one —OH group to combine with silicon alcohol, and the other —OH groups dehydrate with neighboring molecules to form Si—O—Si bond.

③ Action with resin matrix.

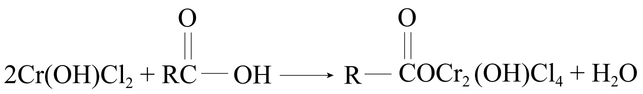
The R group of silane coupling agent is the active group which has an effect to couple with the resin. For different resins, it has different effect. In the thermosetting resin, R group is generally to participate in the curing reaction and become the part of the structure. In the thermoplastic resin system, based on the principle of miscibility of the same or similar structures, there happens dissolution, diffusion and entanglement between the thermoplastic resin molecules and coupling agent. Or we may achieve crosslinking by adding crosslinking agent. For different resin matrix, it is necessary to choose different R groups of the silane coupling agent. If R is —CH═CH$_2$, it entangles and is firmly bonded.





(2) Structure and mechanism of organic chromium complex coupling agent.

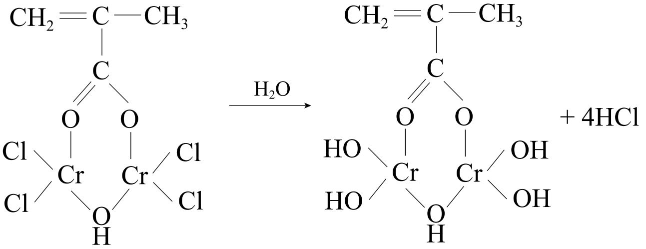
Organic chromium complex is fabricated with chromium chloride and organic acid, equations are given by



$$2Cr(OH)Cl_2 + R\overset{\overset{O}{\|}}{C}—OH \longrightarrow R—\overset{\overset{O}{\|}}{C}OCr_2(OH)Cl_4 + H_2O$$

If R is $—CH_2{=}\overset{|}{C}—CH_3$, it is the common "Volan" (chromium complex of methyl acrylic and chromium chloride), the mechanism is shown in the following.

① Hydrolysis of volan.

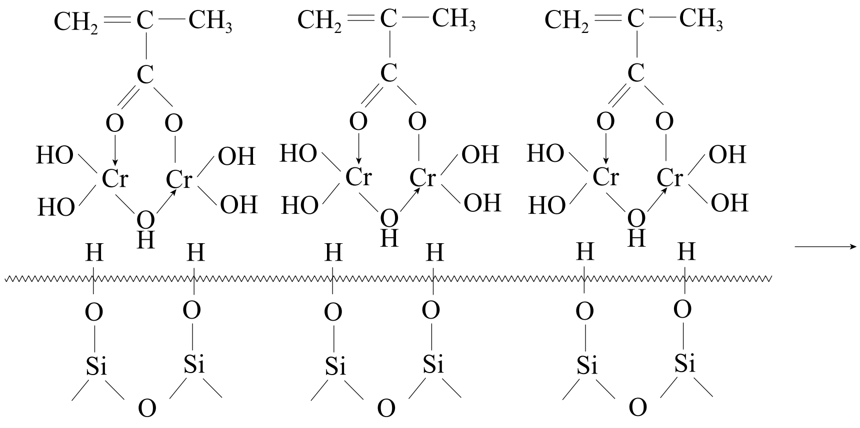


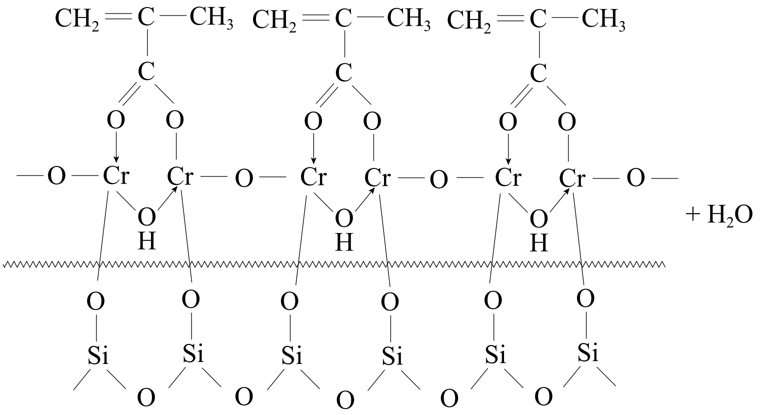
HCl is generated after hydrolysis, so Volan solution shows acidic.

② Action with glass fiber surface.

Volan is adsorbed on the surface of glass fiber, and dehydration condensation of it with —Si—OH occurs on the glass fiber surface, forming anti-water —Si—O—Cr bond. Meanwhile, Volan molecules dehydrate and condensed to form Cr—O—Cr bond, the process is shown in follows:

Equations are given by





The above-mentioned physical and chemical actions make Volan molecular aggregation to gather on glass surface. The surface of glass has the role of removing adsorbed water, so that the glass surface is hydrophobic. Combination with the chemical bonds accounts for 35% and plays a major role.

③ Action with resin.

In Volan, $CH_2{=}\overset{|}{C}{-}CH_3$ may copolymerize with the polyester participating in the curing reaction, and Cr—Cl, Cr—OH may participate in the curing epoxy and phenol-formaldehyde condensation reaction. Therefore, Volan can be applied to unsaturated polyester, epoxy and phenolic resin.

For thermoplastic resin, PP, PE, PMMA, etc., with the similar structure of $CH_2{=}\overset{|}{C}{-}CH_3$ can be applied.

(3) Preparation of coupling agent.

A majority of coupling agent in aqueous solution can be used. In order to achieve the purpose of treatment, the coupling agent must be stable in aqueous solution.

For the silane coupling agent, the coupling agent molecules gradually generate from monomer to the low polycondensation prepolymer and then get into a high polycondensate. Among them, the polycondensation of monomer and low prepolymer can be dissolved in water and react with glass-fiber surface —Si—OH. High polycondensate, however, is not soluble in water and will precipitate from the solution. The longer the time is, the more precipitation there will be, worsening the treating effect. Therefore, silane coupling agent should use as soon as it is mixed in water to prevent invalidation. The properties of the R group and pH value of solution of silane coupling agent determine its stability. When the R group is the methyl acrylate, epoxy, vinyl and other neutral groups, it is best to be prepared in dilute acetic acid of pH = 4. When the X group, i.e. the hydrolysis group is —Cl or —O—CO—CH_3, the generation of HCl or CH_3—CO—OH after hydrolysis will make silane self-polymerize to form high polymer. Therefore, such agents should be prepared in organic solvents. When the hydrolysis group is alkoxy such as —OCH_3,—OC_2H_5, hydrolysis reaction is very slow and the resulting substance has low solubility.That makes the hydrolyzate solution neutral and stable. For example, fresh vinyl trimethoxysilane aqueous solution is 82% of monomer, 15% of dimer and 3% of trimer, and after placement precipitation comes forth, it becomes 34% of monomer, 23% of dimer, 30% trimer and 13% tetramer. Once silane in the system completely condensates to siloxane polymer, it will lose the effect of surface treatment.

HCl is generated after hydrolysis of Volan, producing acidic aqueous solution. Besides, HCl can be catalytic to polycondensation, which ultimately makes hydrolyzate dehydration polycondensation and forming insoluble polymer film. In practice, we should strictly control the pH value of aqueous solution of Volan. Experiments show that solution is stable if pH = 4∼6.

Coupling agent in glass fiber surface orientation is not simple single-molecule layer coverage, but multi-layer non-uniform sediment. Schrader, who uses radioactive tracer atomic technology for study, thinks that the adsorption layer can be divided into three parts: the first part can be washed away by cold water, known as physical adsorption layer, accounting for 98% of the total, thickness is about 270 single-molecule layers; second part cannot be washed away in cold water, but boiling in hot water for 2 hours can remove this layer; this layer is called the chemical adsorption layer with about 10 single-molecule layers thickness; the third part, cannot be removed anyhow; it is chemical adsorption of the single-molecule level. The latter two parts contribute to interface bonding, while the physical adsorption layer is not only ineffective, but also leads to the weak interface layer to reduce the interfacial adhesion strength of composite materials. Therefore, for the coupling agent preparation solution, it is meaningless to make the concentration too high. Generally the concentration is 0.1%∼1.5%.

(4) Surface treatment technology of glass fiber.

When using coupling agent to treat the surface of glass fiber, there are three main process methods: pre-treatment method, post-processing method and the migration method.

Pre-treatment method: in the glass fiber spinning process, we use enhanced glass fiber sizing method. As the sizing agent contains coupling agent, it not only meets the requirements of the textile process, but also will not prevent the infiltration and bonding between fiber and resin. At the same time, coupling agent is coated to the glass fiber surface in the spinning process. Glass fabric treated by this approach is called the pre-treatment fabric. If using this fabric to process glass fiber reinforced plastics, we do not need any treatment. This approach is simpler than post-processing method, and it avoids the loss of fiber strength caused by the heat treatment.

Post-processing method: it is also called the general approach. This method has two steps, the first is to remove the textile-type sizing on glass surface coated in drawing process, and then impregnate coupling agents, wash and dry, so that layer of coupling agent is coated on glass surface. All glass fibers that use the textile-type of sizing adopt post-processing method.

Migration method: it is also called potential treatment. Coupling agent is directly added to liquid resin. While the glass fiber is in the dipping, the coupling agent is coated. Coupling agent in the adhesive resin glue will migrate to the glass surface, and then react with glass fiber surface, resulting in coupling effect.

Treatment effect of migration in general is worse than that of the other two methods. But its biggest advantage is that the technology is simple, and does not require complicated processing equipment.

4.4.3 Surface treatment of carbon fiber

Carbon fiber, especially high modulus graphite fiber has an inert surface. It has poor infiltration, poor adhesion with resin, so the prepared composite materials have low interlaminar shear strength and interface adhesion strength. It has been a long time since people start to research on the surface treatment of carbon fiber in order to improve the carbon fiber and matrix adhesion, or to protect carbon fibers in the composite process from the damage. In the more than ten years from the 1960s to the 1970s, people used a variety of carbon fiber surface treatment methods to improve the interface bonding strength and interlaminar shear strength, and achieved different degrees of effectiveness. In recent years, a study of surface modification of carbon fiber has been launched. Composite materials by these methods not only have a good interface bonding strength, interlaminar shear strength but also obtain a marked improvement of water resistance of the interface, fracture toughness and dimensional stability. Carbon fiber surface treatment methods are mainly gas oxidation, liquid phase oxidation, anodic oxidation, plasma oxidation, surface coating modification, surface electro-polymerizaton and surface plasma polymerization grafting modification.

1) Gas oxidation

This method is the surface oxidation treatment of carbon fiber in the oxidant gases (such as air, O_2, O_3). In normal conditions, its surface will be oxidized by general oxidant gas, but in order to achieve oxidation of the surface modification of carbon fiber to generate a number of active groups (such as —OH, —COOH, etc.), we must create some external conditions, such as heating, adding a catalyst to promote the gas oxidant oxidizing carbon fiber surface, to form oxygen-containing active functional group.

(1) Air oxidation.

In the presence of salt catalyst of Cu and Pb, at 400°C or 500°C, we use O_2 or air oxidation treatment of carbon fiber surface where a number of active groups can be formed on oxidized carbon fiber surface. This treatment increases composite interlaminar shear strength to twice.

(2) Ozone oxidation.

Using strong oxidation of O_3 in gas, oxidation treatment is directly on the CF surface. This activates the formation of oxygen functional groups (such as —COOH,—OH, etc.). However, the oxidation conditions (such as O_3 concentration, environmental temperature, oxidation time) have great influence on the effects of oxidation. Among all conditions, the processing time has the greatest impact and the concentration of O_3 is secondary. The tensile strength of CF itself is improved by 11%~13% by O_3 oxidation treatment reaching 3.36GPa. The surface concentration of oxygen functional groups increases by 16%~45%. Interlaminar shear strength of CFRP increases by 36%~56% reaching 106MPa.

2) Liquid-phase oxidation

There are many types of liquid-phase oxidation, such as concentrated HNO_3 method, sodium hypochlorite oxidation and strong oxidizer solution oxidation.

(1) Concentrated HNO_3 method.

In accordance with strong oxidation of HNO_3, at a certain temperature, oxygen functional groups (such as—COOH,—COH, etc.) are formed by oxidation on the inert surface of CF. If use 65% concentrated HNO_3 to reflux for oxidation treatment on CF, it will lead to the following results in Fig. 4.12. The loss of strength is great after the fiber is treated with HNO_3.

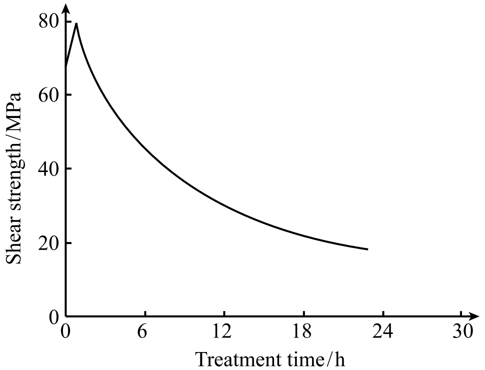


Fig. 4.12 Relationship between the treatment time with HNO_3 and interlaminar shear strength.

(2) Sodium hypochlorite oxidation.

Add sodium hypochlorite aqueous solution with a concentration of 10% to 20% and pH = 5.5 into acetic acid to generate hypochlorous acid. Then control the solution temperature at 45°C. Immerse CF in the solution for 16 hours and then wash the dipped fiber to remove the acid remained on its surface. CF gone through this treatment will have its interlaminar shear strength of composites increase from 21MPa to 70MPa. Also, its bending strength and modulus are increased.

3) Anodic oxidation

Take CF as the anode and graphite as the cathode of electrolytic cell. By electrolyzing water, generate oxygen in the anode which oxidizes carbon fiber surface. A small amount of electrolyte is added into general pure water in order to enhance conductivity and reduce energy consumption. Electrolytes are usually NaOH, H_2SO_4, $(NH_4)_2CO_3$, and Na_3PO_4. Take carbon fiber as the anode and stainless steel as the cathode, CF in NaOH aqueous solution of 5% undergoes continuous anodizing treatment; the results are shown in Table 4.5.

Table 4.5 Impact on ILSS and physic-chemical properties of carbon fiber surface by anodizing

Treatment time (min)	Current density (mA/cm^2)	Surface area (m^2/g)	Total amount of oxygen-containing groups (%)	ILSS (MPa)	Failure mode
0	0	1.8	42.11	56.5	Multiple shear
2	1.5	1.6	44.29	90.5	Simple shear

4) Plasma oxidation

Plasma is another aggregative state different from solid, liquid and gas, which is called the fourth state of material. The aggregative state of matter with sufficient approximation and equal number of charge of positive and negative charged particles is called the plasma. Plasma surface treatment refers to the physical and chemical action processes of a non-polymeric gas on the surface of materials. Non-polymeric gas is divided into reactive and non-reactive. Plasma belongs to reactive, it has high-energy and high-oxidability, and when it hits the surface of carbon fiber, it will oxidize crystal angle, the defects such as grain edges, or parts of the double bond structure to form active groups such as —COOH, —C═O, C—OH and so on.

The effect of this treatment is good. There is almost no loss of fiber strength; the surface energy increases by 22.25%, surface-active functional group increase by 11.33%, therefore by enhancing infiltration and reactivity to the matrix, interlaminar shear strength of composites has improved significantly.

5) Modification of surface coating

By coating a polymer on carbon fiber surface which changes structure and properties of the interface layer of composite material, the interface polarity is adapted to improve the interface bond strength, and to provide a plastic layer interface which can eliminate internal stress. If using thermoplastic polyquinoxaline (PPQ) as a coating agent of CF to enhance epoxy resin, the interlaminar shear strength of CFRP is increased from 64.4MPa to 78.9MPa.

6) Modification of surface electro-polymerization

Electro-polymerization is monomer polymerization or copolymerization on electrode where free radicals are generated from electrochemical processes of electrode. The mechanism of polymerization depends on the location of polymerization, i.e. CF being the anode or cathode electrode; different polymerization mechanisms can result from different electrodes.

(1) The mechanism of anode-initiated polymerization.

Monomer (M) polymerization is triggered by Kaeble reaction in potassium acetate solution.

$$\mathrm{CH_2COO^{\cdot}} = \mathrm{CH_3COO} \xrightarrow{-\mathrm{e}} \mathrm{CH_3COO^{\cdot}} \xrightarrow{-\mathrm{CO_2}} \mathrm{CH_3^{\cdot}} \xrightarrow{\mathrm{M}} \mathrm{CH_3M^{\cdot}} \xrightarrow{n\mathrm{M}} \text{Polymer}$$

(2) Cathode-initiated polymerization mechanism.

When monomer is in sulfuric acid aqueous solution, polymerization on the cathode surface is shown in follow.

$$\mathrm{H^+} + \mathrm{e} \longrightarrow \mathrm{H\cdot} + \mathrm{M} \longrightarrow \mathrm{HM\cdot} \xrightarrow{n\mathrm{M}} \text{Polymer}$$

The monomer for polymerization is a variety of containing alkene compounds such as acrylic, acrylate, maleic anhydride, acrylonitrile, vinyl ester, styrene, vinyl pyrrolidone, as well as cyclic compounds. The monomer can be homopolymerized or copolymerized to form a polymer with CF carboxyl, hydroxyl groups to generate graft polymer by chemical bonding, which has a strong interface bonding. In addition, we can choose the flexible chain monomer copolymerization to improve the brittleness of CFRP. Electro-polymerization time should be appropriately controlled, if the time is too short, thin polymer coating of CF surface should not serve any role in the reinforcement; interlaminar shear strength will decreased if the time is too long and the coating is too thick. Because long time produces a multi-layer polymer, the inner surface with the CF is combined very firmly, but bonding between the second layer and the first layer is not strong by polymer's own cohesion combining, which is a weak interface layer and led to interlaminar shear strength decreasing.

United States Patent uses methacrylic ester, sulfuric acid and hydrogen peroxide system, takes CF as the anode, electro-polymerization for 30 seconds, and the ILSS of CFRP reaches 71.16MPa.

7) Surface plasma polymerization grafting modification method

Under the glow discharge plasma, the surface generates a large number of active free radicals and monomer molecules will be triggered in contact with them, grafting polymerization occurs on the surface. The grafting polymerization method does not need any of initiator and solvent, and has less pollution, short time-consuming, simple equipment, high efficiency, and good safety, so it is better than the chemical methods of surface grafting.

4.4.4 Surface treatment of aramid

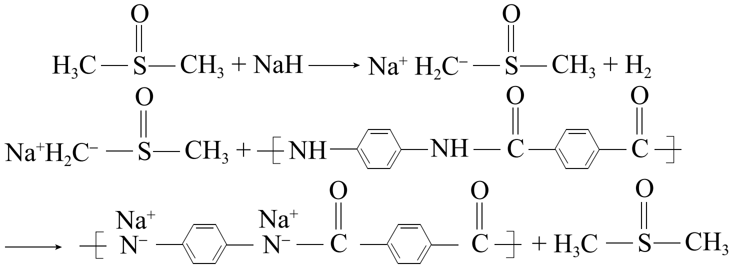
Compared with other fibers, aramid fiber has high strength, high modulus and high heat resistance; low creep rate, small contraction rate and expansion rate, thus very good dimensional stability. Fiber surface is inertial and smooth, low surface energy, and when compounding with the resin matrix, composite materials has low interfacial bond strength. ILSS (interlaminar shear strength) of the aramid composite material is thus low, limiting the superiority. PPTA surface treatment methods include oxidation-reduction treatment, the surface chemical grafting treatment, and cold plasma surface treatment.

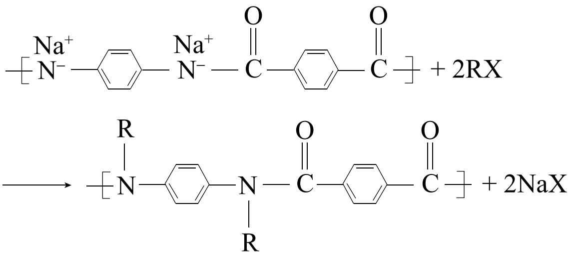
1) Oxidation-reduction treatment

Chemical active groups may be introduced on Kevlar surface by oxidation-reduction reaction, but using HNO_3 or H_2SO_4 for oxidation will result in a sharp drop in tensile strength of fiber, and hence a serious impact on composite materials ILSS. Pem etc studied a new method of the oxidation-reduction, and increased the interface bond strength by introducing amino reaction with the epoxy resin. This oxidation-reduction method, the amino is introduced by deoxidizing nitryl after nitrification in the first step. Under the premise that number of amino on the fiber surface is no more than $0.6 / 100\text{Å}^2$, the tensile strength of fiber does not essentially reduce. However, after treatment of this method, Kevlar and epoxy resin matrix interface bond strength almost double. By this oxidation-reduction method, although the interface bond strength has been greatly improved, the operation is complex, the best conditions are not easy to master, and at the same time it is still difficult to avoid damaging the fiber.

2) Surface chemical grafting treatment

We use crown ethers to dissolve NaH homogeneously in dimethyl sulphoxide (DMSO), and then it reacts with Kevlar, making metallization on fiber surface, and then reacts with halohydrocarbon, polymerizing monomer or multi-functional epoxy compound for grafting.





Here R is the alkyl or aryl alkyl containing functional group, which increases chemical bonding between fiber and matrix interface.The result showed that the grafted epoxy group improved interlaminar shear strength of composites for about 3 times. However, this method is complicated and difficult to industrialize.

3) Cold plasma surface treatment

Cold plasma surface treatment is a better method, because the modified process is without adding initiator, solvent, less pollution, less time-consuming, simple equipment, easy operation, high efficiency, and very safe. The tensile strength of fibers is increased by plasma treatment for two reasons: firstly, the role of plasma treatment on the surface only occurs in shallow surface, leaving the body strength untouched. Not only that, plasma's slow etching will completely eliminate the surface crack, which reduces the stress concentration source, hence increases the tensile strength fibers indirectly. Secondly, the fiber is repeatedly impact of plasma at high-frequency, which relaxes the internal stress accumulated during the production process and indirectly increases the tensile strength of fibers. Aramid-1414 surface was modified by plasma treatment and graft polymerization, and it has been found that the tensile strength of aramid-1414 increases by treating in different time. Fig. 4.13 shows the results. We can see from it, no matter which type of plasma treatment on aramid-1414, its tensile strength is improved, and increases with the increase of processing time. The upward trend is different resulting from the different activity and quality of plasma. After aramid-1414 is treated by air plasma treatment and grafting, Table 4.6 shows the surface energy and interlaminar shear strength.

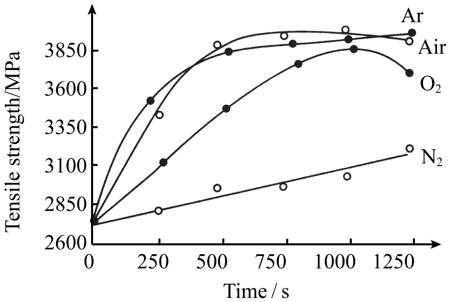


Fig. 4.13 The relationship between processing time and tensile strength.

Table 4.6 Surface energy of aramid-1414 fiber surface by air plasma treatment and grafting of allylamine and its impact on ILSS

Treatment conditions	Surface energy (mN/m)	ILSS (MPa)
Untreated	34.05	46.0
Plasma: air Pressure: 0.15 torr1); Power: 200W; Time: 120s	41.65	60.5
Plasma: air + allylamine Pressure: 0.15 torr; Power: 200W; Time: 600s	42.48	81.2

Note: 1) 1 torr $=1.33322\times10^2$Pa, the same in follow.

4.5 Study on composite interface

4.5.1 Determination of surface wettability

The properties of composite materials are greatly determined by the soakage property between reinforced material and matrix. In general, good wettability can lead to high interface bond strength. If it is full infiltration, the bond strength only produced by physical adsorption can be even greater than the cohesion of adhesive resin itself. A good bonding interface can well transfer stress, so materials have better mechanical properties. If soakage is not good, it will leave gaps in the interface, which is not a good bonding interface to transfer stress and also a source of stress concentration, hence deteriorate the material properties. Therefore, in order to produce high performance composite materials, it is very necessary to determine the infiltration properties of reinforced materials. The relevant methods are introduced in follows.

1) Determination of contact angle

(1) Sokage method of monofilament.

The monofilament sample is affixed to the grip head by using adhesive tape, and then hanged on the sample rack. There is a heavy hammer pulling on the bottom of fiber and the vertical fiber contacts with resin surface. As a result of surface tension, there presents a meniscus at the contact part. Then image it. Under a magnifying glass we may read fiber diameter and maximum height of the resin climbing along the fiber surface near meniscus. With these data, contact angle can be obtained according to (4.6).

$$\frac{Z_{\max}}{a} = \frac{R}{a}\cos\theta\left[0.809 + \ln\frac{a}{R(1+\sin\theta)}\right] \tag{4.6}$$

Where

$$a = \sqrt{\gamma/\rho g}$$

$$R = \frac{b}{\cos\theta}$$

Where $Z_{\max}$ is the maximum height of liquid rising along the fiber wall; γ is the liquid surface tension; ρ is the liquid's density; g is the gravity acceleration; b is the radius of fiber.

Transform (4.6), we get:

$$\frac{\cos\theta}{1+\sin\theta} = \frac{b}{a}\exp\left(\frac{Z_{\max}}{b} - 0.809\right) \tag{4.7}$$

If $\gamma, \rho, Z_{\max}, b$ are known, then a constant on the right of equation (4.7), i.e.

$$\frac{b}{a}\exp\left(\frac{Z_{\max}}{b} - 0.809\right) = k$$

$$\frac{\cos\theta}{1+\sin\theta} = k \tag{4.8}$$

Let $t = \sin\theta, \cos\theta = \sqrt{1-t^2}$, transform equation (4.8), then we get:

$$\sqrt{1-t^2} = k(1+t) \tag{4.9}$$

Measure k through experiment, and put it in (4.9) to get t, and get contact angle $\theta = \sin^{-1} t$.

(2) Monofilament contact angle test method.

We can use the detector to measure monofilament contact angle directly. The processes are: making one end of fiber go through the receptacle, using adhesive tape to fix both ends of the fibers on the filament position of sample seat, rotating the tension adjustment nut, exerting tension on the fibers until tight, forming the film on the receptacle with a small amount of droplet. And then install fiber detector flatwise on the microscope platform, calibrate focal length. Slowly rotate angle adjustment knob to make the liquid receptacle turn, until the contact circular arc between the liquid surface film and the fibers suddenly disappeared and liquid surface is just in the horizontal. At this time the angle between surface and fiber is the contact angle we measure.

(3) Tilt method.

Tilt method is to tense the measuring fiber on sample bow, and then insert it the test solution. Start contact angle meter rotation motor, so that the contact point between fibers and liquid aligning in the optical axis is slowly rotating, and take pictures each 2°. On the basis of photographs of the rise of liquid along the fibers and the prescript of tilt method, the contact angle is measured.

(4) Test method of monofilament wetting force.

Measure the wetting force of pulling out monofilament from liquid by microbalance, and then get θ according to (4.10):

$$\cos\theta = \frac{F}{P\gamma_1} \tag{4.10}$$

Where θ is the contact angle (°); F is the measured wetting force of fiber pull-out from liquid, dyn (1dyn=10^{-5}N); P is the fiber girth, cm; γ_1 is the surface tension of the tested liquid, mN/cm.

(5) Dynamic capillary absorption method.

This method is by measuring the change value of surface free energy in the capillary absorption process, and then finds the wetting contact angle. That is, the change of surface Gibbs free energy is exactly the work consumed in overcoming the viscousness, gravity and inertia for moving in soakage liquid plane. Through some mathematical treatment we can get the relationship between infiltration mass and the change of the surface free energy $\Delta\gamma$.

$$\Delta\gamma = \frac{64(1-\varepsilon)^2 H^2 \rho_f \eta}{k^2 \varepsilon^3 w_f d_f \rho_1^2}\left(\frac{m^2}{t}\right) \tag{4.11}$$

$$\varepsilon = \frac{V_1}{V_T}$$

Where V_1 is the total volume of liquid absorbed in the fiber bundle; V_T is the total volume of the system; ρ_f is the fiber's density; η is the viscosity of infiltration solution; H is the length of the fiber bundle; k is a hydraulic constant (4.4); w_f is the weight of the fiber bundle; d_f is the fiber's diameter; ρ is the density of infiltration solution; m is the capillary infiltration weight of fiber bundle; t is the capillary time.

The infiltration curve is measured by infiltration detector, and we can get m and t value at soakage equilibrium by the curve and put them in the (4.11) to get $\Delta\gamma$, and then by the Young's equation $\cos\theta = \dfrac{\Delta\gamma}{\gamma_l}$ (γ_l is the surface tension of infiltration liquid) we may calculate the infiltration contact angle. It should be noted that the method of critical surface infiltration tension value obtained by Zisman is related to the polarity of the solution used, as well as the presence or absence of the hydrogen bonds. In addition, the geometric mean equation pointed out by Fowkes can also be used.

$$\gamma_l(1+\cos\theta) = 2(\gamma_s^d \gamma_l^d) + 2(\gamma_s^\gamma \gamma_l^\gamma)^{\frac{1}{2}} \tag{4.12}$$

Also assume that the solid surface tension is made up of polar and dispersion, we may measure the surface tension of fiber.

$$\gamma_s = \gamma_s^d + \gamma_s^p \tag{4.13}$$

2) Determination of the dynamic infiltration rate

Infiltration rate is the contact angle of liquid on the surface varying with time, by formula (4.14):

$$\ln\left(1 - \frac{\cos\theta_t}{\cos\theta_\infty}\right) = -Kt \tag{4.14}$$

Where θ_t is the contact angle at time t; θ_∞ is the contact angle at equilibrium; K is the rate constant of soakage.

Draw $\ln\left(1-\dfrac{\cos\theta_t}{\cos\theta_\infty}\right)$ to t, the infiltration rate constant K is obtained by the slope of a straight line.

3) Determination of the critical surface tension of resin curing system

In the study of effect of soakage on strength of interfacial adhesion of composite material, it is incorrect to regard the surface tension of the resin as the surface tension of the cured resin system. For this reason, Dearlore invents the concept of dynamic surface tension in recent years, and uses dynamic surface tension at equilibrium of resin curing process to stand for the value of the surface tension of cured resin system.

It is more difficult to determine dynamic surface tension, and we can use Zisman contact angle method to determine the critical surface tension γ_c of the cured resin system, and use the same value to express the surface tension of cured resin system.

Zisman thought that relationship between critical surface tension of solid γ_c and liquid surface tension γ_l is given by:

$$\cos\theta = 1 + b(\gamma_c - \gamma_l) \tag{4.15}$$

Where θ is the contact angle of the liquid on the solid; γ_c is the critical surface tension of solid; γ_l is the surface tension of liquid; b is the characteristic constant of the matter.

If $\theta = 0°$, that is when liquid is completely wetting on the solid surface, in accordance with equation (4.15), we get $\gamma_c = \gamma_l$, i.e. , the surface tension of liquid is equivalent to the measured critical solid surface tension.

The specific method using Zisman contact angle to measure critical surface tension of cured resin system is shown: determine the contact angle θ of a series of liquids with the known surface tension in the surface of resin curing system (that is, resin compositions with curing agent, plasticizer), and θ at the very moment when the resin system reaches the critical cured state (that is, the viscous fluid into a solid state). Assuming that it is a linear relationship between liquid surface tension and $\cos\theta$, use $\cos\theta$ and γ_l value to plot a graph, and extrapolated to $\cos\theta = 1$ (that is $\theta = 0°$), the corresponding liquid surface tension γ_l, i.e., is the critical surface tension γ_c of the cured resin system. We use this data to express the surface tension of the cured resin system.

4.5.2 Microscope observation

This method is the most straightforward way of studying the surface and interface of composite materials. It is mainly used in observing the surface morphology of the fiber, and the structure and state of composite materials fracture surface.

According to the instruments, it can be further divided into scanning electron microscopy and optical microscopy observation.

Scanning electron microscope has much better resolution than the optical microscope. It can observe the details about the structure with large depth of field, large field of view, rich stereoscopic images, easy to adjust magnification and simple requirements of the sample. Scanning electron microscopy can observe the damage state of the composites fracture section. When there is a good adhesion between the fiber and matrix, we can see the matrix adhesion on fiber at the fracture section; when the adhesion is not good, we then see the fibers pulling out from the matrix, leaving holes in the cross section of matrix. For example, using treated glass fibers to compound with the PP, on the cross-section we can see polypropylene fiber adhesion and better cross-section without holes. When the untreated glass fibers are compounded with polypropylene, due to poor adhesion between them, we see that fiber pull-out in the section and the existence of holes.

4.5.3 FT-IR and Raman spectroscopy

Infrared spectroscopy method is a tool for us to study surface and interface in depth. By infrared spectroscopy data, we may know whether matrix attaches on the reinforcement surface by the physical adsorption or chemical reaction. For example, through infrared spectroscopy, the chlorine silane under room temperature attaches on the glass fiber surface by physical adsorption. But under 300°C, or placed in CCl_4 solution after drying between 120°C and 150°C, there happens irreversible chemical reaction between chlorine silane and the glass fiber surface.

Raman spectroscopy is the usage of argon laser excitation to study surface and interface. It can be used to study the bonding between treatment agent and glass fiber. For example, glass fiber is immersed in the concentration of $2\%\sim3\%$ vinyl triethoxysilane (VTES) aqueous solution, and then dried. Using Raman spectroscopy we find that chemical bondings are established between silane treatment agent and glass fiber surface. Then we compound the treated fiber with methyl methacrylate (MMA), at the same time MMA was initiated and polymerized. Through Raman spectroscopy, we found that about 5% of VTES copolymerized with MMA, thus confirming the role of the treatment agent coupling between reinforcement and matrix.

4.5.4 Determination of interface force (strength)

The materials with poor interfacial properties are mostly shear failure, and in the material section we can see debonding, fiber pull-out, fiber stress relaxation, and so on. Strong interface bonding material behaved on the unexpected brittle fracture. Generally, it is recognized that the best state of the interface bonding force is, when the cracks occur, this crack can transfer to regionalization instead of a further interfacial debonding, and at this case the composite material has the largest fracture energy and a certain degree of toughness. There are many methods of measuring interfacial forces, but there is not a convenient and high credibility method. In addition to the existence of different results through different ways, the most vexing problem is that the material failure is not a result of the separation of interface, but is due to the damage of the matrix or enhanced material near the interface. The common method of testing interface bond strength is monofilament pull-out test.

Monofilament pull-out test is to bury the reinforcing material monofilament or rod vertically in resin matrix cast wafer, and then pull out the monofilament or thin rod from the matrix to determine the interface shear strength between them. There is the following relation between interface shear strength and the maximum pull load of the monofilament or thin rod:

$$\tau = \frac{P_{\max}}{2\pi r l} = \frac{\sigma_{\max} r}{2l} \tag{4.16}$$

Where τ is the average interface shear strength; $P_{\max}$ is the maximum load imposed on the monofilament or fine rod; r is the radius of a single wire or a small rod; l is the length of monofilament or thin rod buried in the matrix; $\sigma_{\max}$ is the maximum tensile stress of monofilament or thin rod.

Transform the equation (4.16) to get the calculation of length of monofilament or thin rods embedded in the matrix.

$$l = \frac{\sigma_{\max} r}{2\tau} \tag{4.17}$$

When the length of monofilament or thin rod buried in the actual matrix is larger than the calculated value in equation (4.17), the monofilament or thin rod will fracture before pulling out, on the contrary, when the experimental length in the matrix is less than the calculated value, the monofilament or thin rod will be pulled out from the matrix. If the tensile strength of monofilament or thin rod is known, based on the critical length of monofilament or thin rod pulled out from the matrix, we may compute the average interface shear strength with (4.16). For example boron fiber in a diameter of 100μm, its tensile strength at 2100MPa, critical length buried in matrix is 760μm, the equation of calculating the average interface shear strength between boron fibers and matrix is given by:

$$\tau = \frac{\sigma_{\max} r}{2l} = \frac{2100 \times \dfrac{100}{2}}{2 \times 760} = 69.1(\mathrm{MPa})$$

We used the above-mentioned method to determine interfacial shear strength of glass fiber polyester resin buried in the cast wafer. The results are: if glass fiber is only washed by using acetone, the average interface shear strength of polyester composite is 42.4MPa; if the glass fiber is treated by the vinyl-silane, its the average interface shear strength is 47.7MPa.

There are also radioactive tracer method, stress corrosion method, etc., for studying interface.

Exercises

1. What is the interface effect of composites? How to affect the performance of composite materials?
2. How many stages are there in the formation of interface?
3. What are the factors that affect the interface bonding strength?
4. What is the effect of interface bonding strength on mechanical properties of composite materials?
5. What are the ways to improve interface bonding strength?
6. Describe the damage mechanism of water on composite materials.
7. What are the surface characteristics of glass fiber and carbon fiber?
8. What is coupling agent? Make a brief description on coupling agent types and mechanism for glass fiber.
9. Which three types do the commonly used coupling agents have? What is the mechanism?
10. How many ways of surface treatment do carbon fiber and aramid fiber have? List separately.
11. How to study composite interface by microscope?
12. What is the range of temperature in dewaxing processing? How to affect properties of composite materials, if the temperature is too high or too low and the time is long or short?
13. Make an analysis of the reason why use different treatment methods for carbon fiber and glass fiber according to physical and chemical properties of fiber surface.
14. Using silane coupling agent can improve the wet strength of composite materials, why?

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5

Fabrication of the half-finished products for polymer composites

As we learned previously, a composite material is a new kind of material which is made from at least two elements (named component materials) working together in suitable methods to produce material properties that are superior to the properties of these elements on their own. Composites processing is a proper method which makes component materials work together. There are usually two methods in the preparation technology of polymer composites, one-step method and two-step method. One-step method is to mix and soak fiber and resin directly and at the same time cure and mold to get the composites. Two-step method, however, is to first mix and wet fiber and resin to form a middle product and then make the composite product from it. Fig. 5.1 shows the flow chart of typical production technology of thermosetting resin composites. As we may see, there is a sophisticated process in preparing semi-product in working procedure. Specialized companies usually handle the process and supply the semi-product as a special type of raw material to the manufacturer of composites. The process of preparing dry state or semi-dry state semi-product with proper processing is called semi-product preparation technology, which is a subtopic of composites processing just like composites forming (see Chapter 6).

In early stages of composite material development, one-step method (also called wet method) is usually adopted. For example, compression molding product is fabricated by first laying the fiber or textile in the mold, then pouring the confected resin glue and forming under pressure. Advantage of the one step method is simplicity in both technology and equipment. Nonetheless, it has some fatal disadvantages. Firstly, the volatiles such as water and solvent are difficult to remove, which can easily get into the product and form void holes. Also, the resin will not distribute uniformly in products, resulting in poor glue regions and rich glue regions. In serious cases, it even shows the “white thread” phenomenon due to incomplete impregnation of the fibers. Moreover, the production efficiency is usually low and the working environment is poor. In order to avoid these disadvantages, two-step method is invented. By dipping the fiber in resin or mixing the fiber and the resin together completely first with proper treatment, a dry state or a slightly tacky material is produced i.e., the semi-finished material. Naturally, the

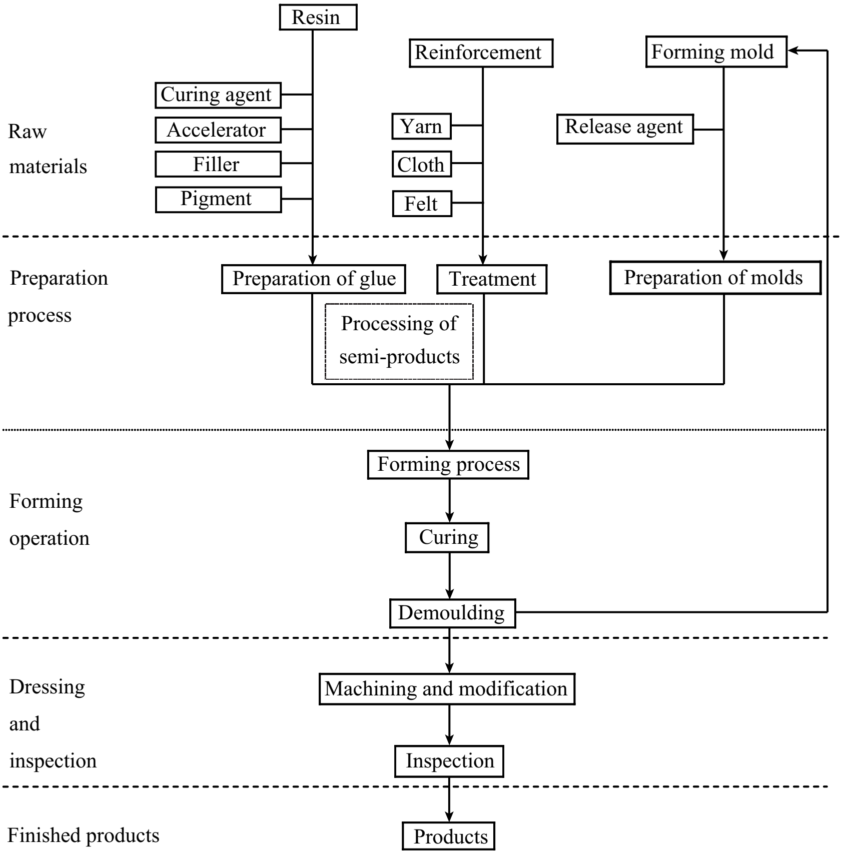


Fig. 5.1 Flow chart of the typical production technology of thermosetting resin composites.

second step is to use the semi-finished material for forming composite materials. The two-step method is also called dry process. Since two-step method advances the dipping process, it enables controlling over the percentage of resin content and the problem of resin distribution is henceforth solved. Additionally, in the process of making semi-product, solvent, water and other low molecular components are eliminated, which reduces the void. The working environment is improved too. The quality of the composite materials can be ensured by controlling the quality of semi-finished materials.

Polymers are scarcely used alone. To improve properties of composites, they are usually combined with additives such as fiber and particle to form multi-phase composites. Instead of being added in the molding process, these additives are usually mixed with other fillers such as fiber and resin during the production of semi-products, which are later made into composite products by compression molding or injection. The semi-products are customarily called granules or pellets in thermoplastics, molding plastics or compounds in thermosetting plastics and prepreg in continuous fiber reinforced plastics (composites). They are the important middle phase in manufacturing plastics or composites. Their quality affects molding technics conditions and product performance. The quality not only depends on the types and ratio of resin and fiber, but also relates to the manufacturing method.

The commonly used manufacturing methods of particle and fiber reinforced semi-product are briefly introduced in this chapter.

5.1 The manufacturing method of thermoplastic granules

5.1.1 The manufacturing method of particle-filled thermoplastic granules

The particle fillers and resin can be well distributed by using emulsion or suspension liquid, but because of the characteristics of continuous production in thermoplastics, usually mixing or milling (powder granulation method) is used in industrial production. It develops to be airtight, continuous and more efficient. Fig. 5.2 shows the technique flow chart.

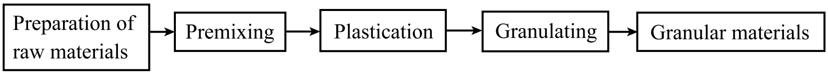


Fig. 5.2 Technique flow chart of particle-filled thermoplastic granular materials.

1) Preparation of raw materials

The preparation of raw materials includes these contents:

(1) Filtration. Remove granular impurities and large particles, make particles be well distributed, which protect the machining equipment.

(2) Magnet absorption. Remove metal impurities.

(3) Drying. Remove the water absorbed in resin and additives, to ensure the quality of product.

(4) Grinding. Ensure properties such as stability, reliability and homogeneity of granule, as well as the smoothness and consistency of color. We can use three-roll mill, ball mill and so on.

(5) Preheating. Decrease the viscosity in mixing and speed up mutual diffusion rate. Meanwhile strengthen heat transfer process and improve mixing efficiency.

(6) Weighting. Weigh the amount of each component according to formula strictly.

2) Premixing

Premixing is a process of initial mixing which is carried out below the melting point of polymer and under low shear stress. This process only improves the spacial disorder of all kinds of little particles. Depending on the difficulty of mixing, proper devices are to be selected such as kneader and high-speed blender. Kneader is mainly made up of a mix chamber with saddle shape bottom and a pair of Z-shape agitators. When mixing, two Z-shape agitators circumgyrate in opposite directions and at different speeds and agitate up and down to get a well distribution of materials. An additional sheath can be used for heating and cooling, so as to achieve uniform temperature and qualities. On the other hand, high-speed blender is made up of a circular mix room and a high speed impeller which is in the bottom of the mix room, and with a heating and cooling equipment. Large clustered particles will be broken up and well distributed when mixing because of high speed (80∼860r/min) of the impeller. Moreover, the mixture can be wetted in a short time through internal friction and outer heating.

The feeding order is important in mixing. Raw materials are usually fed in following sequence: resin; partial plasticizer; the mixture composed of stabilizer, lubricant, coloring agent with the other partial plasticizer; and some solid materials (fillers). The end of mixing is usually judged by experience, and can also be controlled by mixing time. By the time mixing is considered complete, a well distribution must be obtained and plasticizer must have fully permeated into the macromolecular chain. This is crucial because effective kneading improves the processability of plastics.

3) Plastication

Plastication is a very important process. In the process, materials are thermally melted and mixed by shear to achieve appropriate softness and plasticity on the dedicated equipment at a temperature higher than the melting point of resin and under a large shear stress. In this way, each component is dispersed evenly. Meanwhile, inner volatiles are eliminated, which facilitates transmission and molding and consequently contributes to the quality of products.

The conditions of plastication are very stringent. Each type of plastics has its own affordable plastication condition, which is determined by experiments. The main manipulative conditions of the process are plastication temperature, time and shear stress. Shear stress is adjusted through the speed ratio of rollers. The time condition of plastication is sensitive. If the time is too short, the plastication will not be uniform. It would lead to instability and sometimes excessive fluctuation in targeted properties, which undermines the quality of products, resulting in all sorts of deficiencies such as surface roughness, nep, lack of brightness, knob-and-tubed model, uncontrolled external diameter, eccentricity, and the decline of mechanical properties. Inversely, if it takes too long a time for plastication, it will not only reduce efficiency, but also cause polymer degradation, and thus lower quality. The proper end of plastication can be determined by uniformity and dispersivity of the sample, but the best practice is to measure the tear strength of sample.

Plastication equipments include twin cylinder mixer (exoteric mixer), internal mixer (obturated mixer), and single screw extruder and etc.

4) Granulation

The uniform plastics sheet plasticated from plastication mixer is transported to granulator and cut in longitudinal and cross-sectional direction successively to obtain granule. If extruder is used during plastication, a rotary blade can be installed on its head for cutting. Alternatively, we may first extrude the material in bar shape, and then granulate it by granulator.

5.1.2 Manufacturing methods of fiber reinforced thermoplastics pellets

There are many methods for manufacturing fiber reinforced thermoplastics pellets. Choices are determined by the morphology and properties of resin, glass fiber and other raw materials, as well as the equipment availability in workshop. No matter which method is adopted, however, the ultimate goal is always to add glass fibers with huge size and loose structure into the resin to form granular semi-product in uniform dispersion for injection molding. There are some requirements for fabricating the reinforced pellet. They are: ① glass fiber can be dispersed in the resin uniformly; ② glass fiber and resin should be wrapped or bonded firmly to avoid the dust of the glass fiber flying in packaging, transportation, feeding and molding process, which will affect environment and operating conditions; ③ mechanical damage of the glass fiber and degradation of the resin molecules during manufacturing process should be minimized as much as possible.

It is well-recognized that the reinforced thermoplastics pellets are classified into two categories: long fiber and short fiber. The manufacture of the long fiber reinforced pellet usually use classical cable embedded method, it is suitable for screw type injection molding. The so-called short fiber reinforced pellet (or called dispersion reinforced pellet) is made of glass fiber and polymer by mixing. During this process, the glass fibers are cut into short fibers with the length of 0.25~0.5mm and are dispersed in the resin uniformly. It is suitable for plunger-type injection molding (of cause also be used in screw type injection molding).

Ever since the day fiber reinforced thermoplastic pellet is invented, with the expansion of its application and the market demand, the manufacture methods also emerged endlessly. Table 5.1 summarizes the manufacture methods.

Table 5.1 Manufacture methods of fiber reinforced thermoplastics pellets

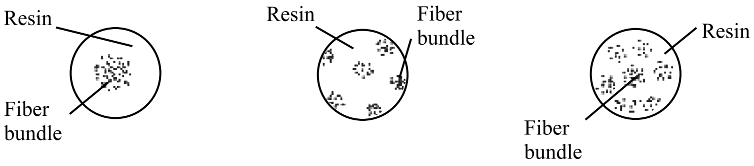
Method	Name	Technique course	Advantages	Disadvantages	Remark
Manufacture methods of short fiber reinforced pellets	Single screw extrusion method of chopped strand	Mix the resin and short fiber in extruder in proportion, repeated for 2 or 3 times. Granulation for powder resin can be finished in one time.	The glass fiber and resin can be mixed uniformly, for plunger-type injection molding.	① Serious damage of fiber. ② Serious abrasion of screw and barrel. ③ Slow production speed. ④ Bad working environment.	At present, protection is better than before.

(Continued)

Method	Name	Technique course	Advantages	Disadvantages	Remark
Manufacture methods of short fiber reinforced pellets	Re-extrusion granulation method with vented single screw extruder	Feed the long fiber reinforced pellet in vented single screw extruder, re-extrude for 1 time for granulation. Use ordinary extruder if material has a little low molecular volatile.	① Continuous production. ② Good appearance, tight texture. ③ Good protection of labor.	The resin aging with heat. Its appearance is not as good as the one made by vented twin-screw extruder.	It has been widely used in domestic because of low requirement of equipment.
	Method of vented twin-screw extruder	Feed the resin through the resin orifice and add the continuous or chopped fibers automatically into extruder in proportion by the fiber mouth separately, then be extruded for granulation.	① Continuous production. ② Good appearance, tight texture. ③ Good protection of labor.	① Not high requirement for the equipment and materials. ② Noisy.	It is a developing trend.
Manufacture methods of long fiber reinforced pellets	Electric cable enwrapping method	To enwrap the glass roving with melted resin when the rovings go through the cross extrusion head. Then cooling, traction and granulation.	① Continuous production. ② Pellet with high quality. ③ Good protection of labor.	The pellet is not fit for plunger-type injection molding.	The method is used commonly at home and abroad.
	Channel reaction method	Feed monomer and glass fiber in pipeline through the inlet simultaneously. By the pipeline polymerization, the reinforced bar (such as nylon MC) went out from the outlet.	① Simple technique. ② Continuous production.	① Polymer with bad quality. ② The strength is lower than that by electric cable enwrapping method.	
	Enwrapping method of polymer at discharge mouth	Set an enwrapping head at the discharge mouth of polymerizer, and it will wrap the fiber when polymer comes out.	① Reducing the times of resin heat aging. ② Simple technique.	Deceleration in discharge of materials. Reduction in yield.	Try this way when produce PA6 by VK method.

1) Manufacture methods of long fiber reinforced thermoplastic pellet

The production experience demonstrated that it is better to use the electric cable enwrapping method for long fiber reinforced plastic pellet. Its equipment is simple, the operation is continuous, and the quality is outstanding. This method is widely used at home and abroad. At present, there are three structures of long fiber reinforced plastic pellet on sale in the market (Fig. 5.3).



(a) (b) (c)

Fig. 5.3 Structure types of cross section of long fiber pellets.

In the particle structure of Fig. 5.3(a), the glass fiber forms a big bunch of package in the particles. Usually they are untightly wrapped, easy to fluff when pelletizing, and the glass fiber can fly easily. Besides, it is not conducive for the glass fiber to disperse in the resin during injection molding. In the particle structure of Fig. 5.3(b), the glass fiber forms several small bundles and scatter in the surrounding of particles. Although scattered, fibers are too close on the edge and resin wrapping force is not enough, so this is also easy to fluff when pelletizing and glass fibers fly. The ideal form is the particle structure of Fig. 5.3(c), in which glass fiber is well dispersed. It has thick external resin and wrapping force is firm. So in this form, the surface is smooth, glass fibers are not easy to fluff and fly.

Fig. 5.4 shows technique flow chart of manufacturing enwrapped long fiber reinforced plastics. Glass fiber roving is enwrapped by melted resin when the rovings go through the cross extrusion head (or set a wrapping head at the discharge mouth of polymerizer). Then it goes through cooling, traction and granulation to final product. As resin is poor at wrapping long fibers, which leads to uneven distribution of fibers and hence low hardness in pellets, only screw type injection molding can be used. Screw injection disperses fibers well in resin by mixing them with the screw during the molding.

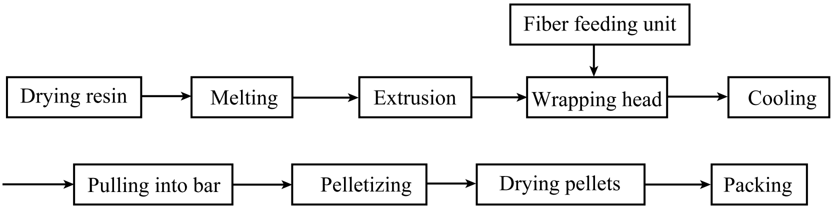


Fig. 5.4 Technique flow chart of wrapping long fiber pellet.

Here, we should know clearly: the long fiber reinforced pellet does not really show the properties of fiber reinforced plastics, it has a low hardness. In injection molding machine, glass fiber disperses evenly in the resin with the help of screw mix effect, and under the coupling effect of surface treatment agent, the two phases can yield a comprehensive effect, such that the injection products can really reflect properties of the reinforced plastics. For short fiber reinforced pellet, as glass fibers are mixed evenly with resin, surface treating agent has already exerted its full effect, so the pellet has embodied the performance of the reinforced plastics. Their hardness is large, and easy to burst when feed. Moreover, they accelerate the abrasion of screw and barrel, and are capable of damaging the machine. Therefore, it is appropriate to make the short fiber reinforced pellet as small as possible in forms of small pellet or small tablet.

2) Manufacturing methods of short fiber reinforced thermoplastic pellet

Short fiber reinforced plastic pellets are produced to solve the problem of poor dispersion of the long fiber in high melt viscosity resin, which will lead the poor performance and appearance, so it is also called distributed reinforced pellet. It is firstly to mix chopped fibers and resin, and then extrude the mixture by the screw extruder, in which the fiber is broken into short fiber about 0.25~0.5mm and uniformly dispersed in resin. Fig. 5.5 shows the technique flow chart.

Short fiber reinforced plastic pellet has good molding processabilty and smooth surface character, which is molded by plunger-type or screw-type injection machine. However, because of the serious wear and tear of fibers during the granulation and the shortness of the fiber, and the products have low strength. Because of good processing fluidity, short fiber reinforced plastic pellet is suitable for manufacturing thin-walled and complex shaped products.

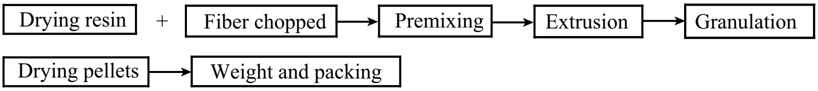


Fig. 5.5 Technique flow chart of short fiber plastic pellets.

For resins with high melt viscosity such as polyolefin, polystyrene, chlorinated polyether and so on, since long-fiber reinforced plastics products have poor performance and appearance for poor dispersion of glass fiber in the resin, it is required to use the distributed reinforced pellet to mold the products. Consequently, the production process of short fiber reinforced plastic pellet is developed. In addition, some plastics processing unit does not have the screw-type injection machine (essential for manufacturing long-fiber reinforced plastic pellets), and thus it has to make some resin with good fluidity performance to short fiber reinforced resin pellet. As is suggested in Table 5.1, the ideal manufacturing method is vented twin-screw extruder for mixing (Fig. 5.6).

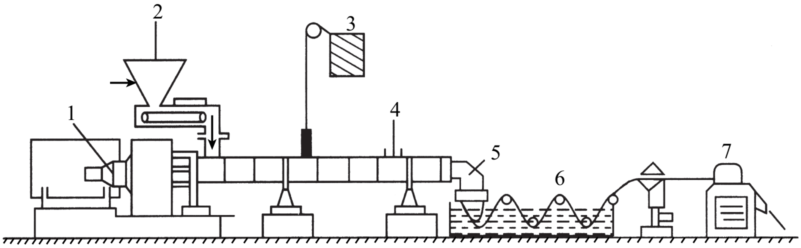


Fig. 5.6 Technical flow chart of thermoplastics reinforced by glass fiber rovings: 1-measurement feeder ZSK/V; 2-thermoplastics; 3-glass fiber rovings; 4-vent port; 5-strip die; 6-water bath; 7-strip cutter.

Fig. 5.6 shows the technique flow chart of fiber reinforced thermoplastics, which use the deformable twin-screw compounding extruder ZSK/V made by the Federal German Werner and Pfleider Machinery Factory. The dosed polymer is fed into the feed opening of ZSK/V extruder and then begins to melt. The glass fiber rovings are fed into the second mouth at downstream and mixed with the melted polymer. As the resin is completely plasticized, it provides lubricating protection to the glass fiber, which will reduce abrasion of the machine. In the beginning, the glass fiber roving are introduced to the second mouth by hand, and then they are pulled into machine continuously by using the force of screw rotation.

The content of glass fiber is controlled by the number of feed-in rovings and speed of the screw. The rovings are broken and mixed evenly by levo screw and kneading devices, and then after removing the volatiles the mixture was extruded through die, cooled, dried and pelletized. The barrel and screw of the extruder adopt building-block structure, the average length of the glass fiber can be changed in a certain range by changing the compages of different screws and the length of screw segment after the glass fiber is fed in. For some sections of the barrels and the screws which are easy to be abrasion, we can replace them and need not discard the whole barrel and the whole screw. The different screw can be used for processing different types of polymer. The design of the screw makes the stuff in the screw thread root be cleaned out by the top of the adjacent screw thread, which is called self-cleansing. And this process avoids the dead-point inside the extruder, which ensures simultaneity of all the materials staying in the extruder. Along the screw, the thread can be discontinuous, and can add some kneading components with special structure in these discontinuous regions. And this adapts the complex technological requirements. There are one or more vents along the barrel, so that the water, decomposition product of polymer and lubricant can be excluded, and it is favorable to wetting of resin to glass fiber. This twin-screw extruder brings some characteristics to compound processing which are: ① the twin-screw plays the role of booster pumps, which transfer the pressure to the materials, the stay length of the materials in the extrusion machine can be adjusted; ② in specific load, we can control the pressure along the length of the barrel by the reverse thread or the throttle; ③ by changing the configuration of the kneading segment, adjusting the throttle valve and controlling the temperature, we can adjust the shear rate of each cross-section along the barrel; ④ there is a nice heat exchange system in the extruder, which can freely control the temperature; ⑤ because of effect of the double-screw, the material in the barrel can be formed as thin layer, so the surface of the material is in constant updating, and it has a very large function in mixing and quick formation of homogeneous melts.

For reinforced thermoplastics, it is more effective to extrude the loosened composite material by using the double-screw extruders than using the single-screw extruder. The single-screw extruder can make the homogeneous melt, which relies on the nose pressure in a large degree, while the double-screw extruder almost relies on the screw effect which makes the resin plasticize fully and mix with fiber evenly.

Now, in domestic industry, we still widely use the Φ45-type vented single-screw extruder. We use the technique of re-extrusion of long fiber reinforced pellet.

Fig. 5.7 shows the structure of double-vented single-screw extruder. Fig. 5.8 shows the geometric parameters of the vented screw.

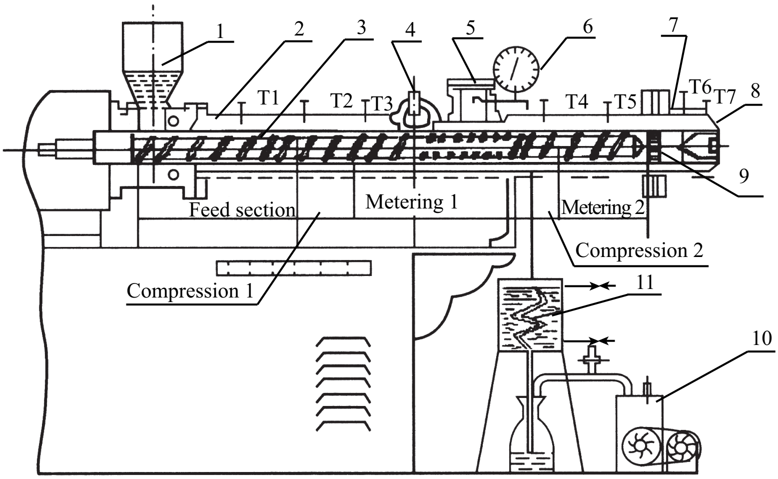


Fig. 5.7 Structure of double stages vented extruder for vented re-extrusion granulation method:
1-feed hopper; 2-barrel; 3-screw; 4-throttle valve; 5-vent port; 6-vacuum; 7-head; 8-die; 9-grid plate; 10-vacuum pump; 11-condenser.

We can regard the vented screw that is made coaxially in series by two single-screws with different length. When the long-fiber reinforced pellet become molten fluid after heating from the hopper, the pressure gradually increased from zero. When it continues to advance to the second conveying segment (exhaust section),

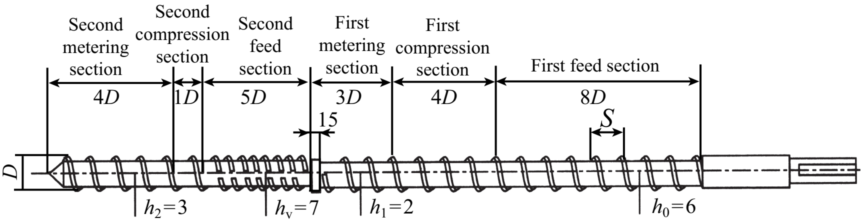


Fig. 5.8 Geometric parameters of vented screw:
diameter of screw $D = 45$; aspect ratio $L : D = 25 : 1$; screw pitch $S = D$;
compression ratio is 3 : 1 in the first section, and 2.3 : 1 in the second section.

as a result of a suddenly deep of spiral groove, the melt pressure suddenly steps down. The material expands and meanwhile the water and other low molecular weight volatiles within materials escape. This screw thread is double-headed design and milled two axial troughs along the axes. It enhances the agitation and facilitates the gas escape from the melt. There are exhaust vents in the exhaust section of the screw, which are connected to the vacuum pumps and hence the low molecular weight volatile compounds can escape from the melting materials extremely fast. The material free of the low molecular weight volatile materials continue to be forwarded by the screw, through the second compression section and the second metering section to the nose, then they are extruded into a dense strip and cut into pellet by granulator after cooling.

Usually we add a throttle value between the first metering section and the second transport section in order to regulate the extruder's workload, to balance the input and output of materials, and to prevent the material overflow from the vent.

As the time for the molten materials in the vented section is very short, some vacuum is needed to suck out the low molecular weight volatiles to the greatest extent within the limited time. A rule of thumb adopted by engineers in the industry suggested that when the vacuum is higher than 600mmHg ($1\text{mmHg} = 1.33322\times10^2\text{Pa}$), the glabrous and dense short fiber reinforced pellet can be obtained.

One step granulation with chopped fiber and resin powder by the single screw extruder method is common domestically, for example, in reinforced plastics such as PP, PC and POM.

5.2 The manufacturing of thermosetting molding compound

5.2.1 Manufacturing methods of molding powder

Molding powder is powdered thermosetting plastics which is made from particle additives and synthetic resin (either containing curing agent or not). There are two types of molding power: compression molding powder and injection molding powder, which aims for compression molding and injection molding respectively. Typical resins used in practice are phenolic resin, urea-formaldehyde resin, melamine resin, epoxy resin and so forth. At present, linear phenolic resin molding powder called bakelite is in the largest production, and has been the most widely used.

The manufacturing methods of molding powder mainly take technologic measures to mix each components evenly, so that every component can be impregnated fully in resin and the materials have an appropriate liquidity and volatiles content, which meet the requirements of molding and performance. The commonly used two types of manufacturing methods are dry process and wet process.

1) Dry process

When we use solid resin for fabricating the molding powder, dry process is usually adopted. There are two methods: roll mixing method and squeeze mixing method. In China, roll mixing method is usually used. This method will bring a lot of dusts, but has low energy consumption, and is less costly. Fig. 5.9 shows the production technique flow chart of the rolling method.

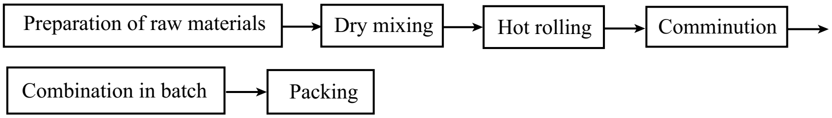


Fig. 5.9 The production technique flow chart of the rolling method.

(1) Preparation of raw materials.

Preparation of raw materials includes crushing and sifting of resin. If the resin is grinded into too thin powders, not only will the energy efficiency and productivity be undermined, but will the rolling operation become much difficult. Conversely, if the resin is too thick, the molding powder's quality is uneven, which will affect the compression technique and quality of the product. The criterion is usually more than 30% of resin passing through 60 eyes of mesh. Other components which are vulnerable to moist, such as wood powder, lime, and hexamethylenetetramine, should be dried before use to achieve the water content requirements. Too dry or too wet materials will bring difficulties to the rolling process and affect the quality of the product. All the components should be ground, sieve, and meet the required degree of fineness. Finally, we must strictly weigh all the components according to the formulations.

(2) Dry mixing.

In dry mixing, we can use a variety of equipments to mix each component evenly such as ball mill, Z-type kneading machine, columniform turn canister, and so on. The order of component feeding greatly affects the degree of uniformity. Usually we first put all the components except the fillers in the equipment and mix evenly, and then add the fillers and mix. This is because the amount of molding powder's fillers is large, especially the wood powder, its volume is very large.

If all the components are fed at the same time, the efficiency of mixture and the degree of uniformity will be affected. When mixing with ball mill, there are further grinding effects on the materials. The material after mixing has a certain degree of uniformity. However, since the density of each component is different, the uniformity will be destroyed when vibrating. The resin in the compound is not able to impregnate filler and other additives fully and retains good fluidity. If the compound is used to mold the products directly, the quality of appearance, mechanical properties, water resistance and heat resistance will be all low, making the product unusable. Therefore, another step, hot rolling, must be conducted before molding.

(3) Hot roll mixing.

Hot-roll is the key step in the process of molding powder. Under the premise of the established formulation, the quality of molding powder depends on the temperature and time of hot roll mixing.

Roll mixing is carried out in the roll mill. Roll mill is made up of two hollow steel rollers, which can be heated or cooled by steam or water, and also can use electric heating. Roller's diameter is generally from 400mm to 600mm, and length from 1000mm to 1200mm. When working, the two rollers rotate with different rolling speeds (for example, at 18r/min and 13∼24r/min), the relative roll speed ratio at about 1.3. The temperature of the two rollers is also different. The temperature of the low temperature roller is slightly higher than the dropping point of resin. The high temperature roller is 30∼50°C higher than the low temperature roller. In the linear phenolic molding powder production, the temperature is 70∼110°C and 90∼130°C respectively. The roll gap between the two cylinders can be adjusted, and the size determines the thickness of the material, it usually between 3mm and 7mm.

The material on the heat roller is melted when rolling. After the effect of squeezing, shearing, kneading between the gaps of the two rollers, each components are well mixed and impregnated. Viscous material formed from melting resin evenly attached to the surface of one roller (low temperature and high speed roller).This roller is called the working roller, and the other one is called idling roller. This method we described above is known as reverse-roll type. If temperature of the rapid roller is high, and temperature of the slow roller is low, the method is called as positive-roll type. When using positive-roll type, the material doesn't enwrap the roller. Instead, the materials drop down from the roller instantaneously and need to be continuously re-fed on the roller. This method is labor-intensive, but the degree of rolling materials can be controlled, so as to avoid excessive rolling. The material always enwraps the roller when using the method of reverse-roll type. Less heat emits from the roller when a "coat" is on and thus the utilization of the roller is higher compared to positive-roller type. In practice, the linear phenolic molding powder is usually used the reverse-roller type, while a first-stage phenolic molding powder used the positive-roll type.

The purpose of hot rolling is to impregnate the additives with the resin well, so that each component will mix evenly. Hot rolling also incorporates a certain degree of polycondensation, which increases the degree of crosslinking to the second stage and shortens the molding cycle, and increase the productivity. Moreover, hot rolling removes some volatile compounds (including by-product of low molecular weight in the polycondensation), and improve the compression technics and product's quality. Besides, it makes the molding powder more close-grained. Reducing the volume can facilitate the molding operation. Table 5.2 shows the rolling effect. The main indicators of rolling quality are the fluidity, the content of the volatile and the quality of the appearance.

Table 5.2 Rolling effect of molding powder

Indicators	Mixture in ball mill	Roll mixed molding power
Fluidity (mm)	186	140
The content of volatile (%)	2.78	1.98
Specific volume (cm^3/g)	3.21	1.90
Impact strength (kJ/m^2)	2.68	4.42
Flexural strength (MPa)	33.7	62.0
Heat resistance (°C)	90	138
Water absorption (%)	9.247	0.170

(4) Grinding, combination in bath and packaging.

The flake after rolling is removed from the roll and should be rapidly cooled, so that the polycondensation can be terminated. Then the material proceeds to grinding and sieving. The particle size of molding powder must not be too large or too small either of which will be negative to compression molding either. In order to regulate the quality of the molding powder, the molding powders of different batches should be fed in a same mixer and mixed at the same time.

There is also a screw squeeze method abroad in the dry methods. It enables continuous production and the degree of mechanization and automation is high, so the quality of the products is good. This method is suitable for mass production of the molding powder with the same brand and the same color.

2) Wet process

When we use liquid resin, resin solution and resin emulsion to produce the molding powder, the wet method, also called the latex method, is used. This method is clean with less dust, but it consumes large quantities of energy and solvent. We take the urea-formaldehyde molding powder as an example. The urea-formaldehyde molding powder can be made of products with light colors and many other colors. The main filler is α-cellulose and the most commonly used material is the sulfite paper pulp. The manufacturing method of this molding powder is: first, feed the solution of urea-formaldehyde condensation with the low-molecular-weight, curing catalyst (usually oxalic acid), lubricants (usually zinc stearate), brightener and colorant into the kneader which has the Z-shape double blades and mix evenly. Then we add the α-cellulose in several groups, and the kneading temperature is controlled between 55°C and 60°C. After mixing evenly, the mixture is sent for drying. The drying is at the temperature of about 85~90°C until the content of moisture is between 2% and 3% and the fluidity is good. Drying of the mixture is critical for the wet type method. In drying process, the moisture and part volatiles will be removed. The resin also takes further polycondensation, until it is close to the B stage. The mixture then proceeds to grinding, sieving, and combination in batch, yielding the molding powder.

The latex method requires resin to be low in viscosity and easy to impregnate the fillers. Mixed with other components, the relatively loose fillers can ensure drying uniformly. The drying equipment is the atmospheric pressure or vacuum dryer, which is inefficient and difficult to uniformly control the temperature. It is difficult to prepare a molding powder with good fluidity and low volatile percentage, so the method of latex rolling was developed. The production process is shown in follows: latex resin mixed with other components→rolling→cooling→drying→batch combination→the products. The rolling is a key process. It replaces the drying process of the latex method. The viscosity of the resin used this method is high, and it is easy to form dough after mixing with other components. The role of rolling is similar to the drying in the latex method. Both of them are capable of further mixing, dipping and removing volatiles, so that the resin can be further polycondensed. The material after rolling can be crushed, but the percentage of volatile is still large, further drying is often carried out to reduce it. The weaknesses of latex rolling method are: low efficiency, high labor intensity, and volatile pollution.

5.2.2 Manufacturing methods of short fiber reinforced thermosetting molding plastics

The short fiber molding material, i.e., short fiber prepreg, is a kind of fiber reinforced thermosetting molding compound made and composed of the short fiber, other additives and synthetic resins (with or without curing agent). Since it is usually used in the compression molding, we call it compression molding compound. Common resins in practice are phenolic resin and amino resins, unsaturated polyester resins, silicone resins, epoxy resins and so on. The fibers used are usually glass fiber, cotton fibers, asbestos, organic fiber, carbon fiber and so on. Depending on the different fibers and resins, there are a wide variety of manufacturing methods. The most important manufacturing methods contain three categories, premixing, pre-impregnating and extrusion method.

1) Manufacturing the short fiber molding compound by premixing method

The method of premixing is to mix short fibers (such as cotton fibers, asbestos fibers, etc.) or long fibers (such as glass fibers, synthetic fibers, etc.) that have been cut into 15∼50mm with a certain amount of resin glue evenly and then tear loose and dry the mixture, which yields the molding compound. It is usually a discontinuous operation of batch mixing. The yield of this method is large, so it is suitable for mass production. This molding compound has the following characteristics: fibers are loose and without orientation; the fluidity is good; it is suitable for molding the product with a small size and a complex shape. Drawbacks are that the strength loss of the fiber is great during the manufacturing, so it is not suitable for the product that requires high strength. Also, the quality uniformity of molding compound is poor. The large specific volume requires large loading room which makes it difficult to fill the compound into mould. The working condition of this method is poor too. Fig. 5.10 shows the production technique flow chart of premixing method.

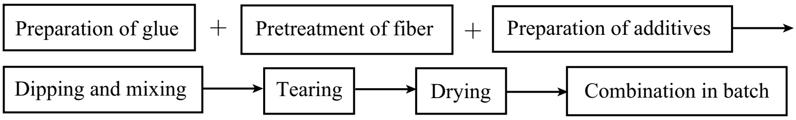


Fig. 5.10 The production technique flow chart of premixing method.

Each process described below can be either handled manually or mechanically in batches or continuously.

(1) Preparation of glue.

Make the resin glue according to the formulation, and then dilute to the required viscosity.

(2) Pretreatment of fiber.

The fiber should be cut and torn to be loosened. The fiber with paraffin sizing should be heated to remove the paraffin first. The pretreatment of asbestos fibers should include the removal of impurities and then drying.

(3) Preparation of additives.

The additives should be fined, screened, dried and so on.

(4) Dipping and mixing.

The purpose of this process is to allow the resin to fully impregnate the fiber and other additives, and to mix all the components uniformly. Small bulk can be repeatedly kneaded by hand, while large bulk should be processed by Z-kneader. The cotton fiber is usually processed by the disk-type mixer, which is also called round grinding machine. For asbestos fibers, we needs to compress the kneaded material in the press and then roll mix the material. The aim is to split the large bundle of asbestos fibers into smaller bundles, so that the resin can infiltrate the fibers fully.

(5) Tearing.

The major role of tearing is to make the kneaded material into fluffy ones. Small amount of molding plastic can be torn by handwork. Large amount can be processed by the tearing machine. The tearing machine consists of the feed roller and a pair of tearing rollers, the material can be torn loosely through the effect of reverse movement of the tearing rollers.

(6) Drying.

Put the premix after tearing on the clean metal net uniformly, and spreading is not too thick. Air it at the room temperature first until most of the solvent evaporated and then dry it. During the drying process, the volatile evaporated more thoroughly, and the resin can be prepolymerized to a certain degree.

(7) Combination in batch.

Cool the dried material rapidly, and mix the different batches of molding plastics thoroughly in order to ensure the uniform quality. At last, the material is ready for packing.

Premixing manually is mostly used in small-scale preparation. Since damage of the fiber is small when using this operation, it is also adopted in the production of special materials, for example, high silica fiber reinforced. That is because of the significant mechanical loss of silica fiber when it is mixed mechanically.

2) Manufacturing short fiber molding compound by pre-impregnation method

Pre-impregnation method is the process in which continuous bundle of fiber passed through the resin trough, dipped and then scraped by roller, and after drying in the oven, it was cut into unidirectional molding compounds with the required length. This method supports continuous production. The molding compound produced by this method is in bunches and relatively compact. During the production process, fiber is less damaged. Its quality is uniform, and the specific volume is small. The mold doesn't require large loading room and the filling process is simple. It is easy to lay the materials in the filling process according to the different stress status that the product bears. Therefore, using this method we can manufacture the product with complex shape and high-strength. The output of pre-impregnation method is generally lower than the premixing method, and the liquidity of molding material and the miscibility among bundles are not good.

Pre-impregnation method can be further divided into manual type and mechanical type. Usually mechanical pre-impregnation method is used in industrial production.

The pre-impregnation method generally uses the continuous untwisting rovings except the hand-impregnating method. In the preparation process, the fibers are not kneaded, teared and agitated as in the premixing method, so the original strength of the fiber will have no heavy loss. In addition, the molding compound made by this method is of small size, easy to handle, and has good fiber orientation, which fits the directed laying of compression molding. The degree of mechanization is high and the operation is easy; labor intensity is small and equipment is simple.

It also supports continuous production. Nonetheless, the output is smaller than the premixing method, so it is only applied for continuous fiber products (such as untwisted rovings). In order to facilitate the rapid infiltration to fiber bundles and the miscible among the fibers, there are some special requirements for the rovings and little ribbon-bonding is needed.

Fig. 5.11 shows the summarized flow chart of pre-impregnation process.

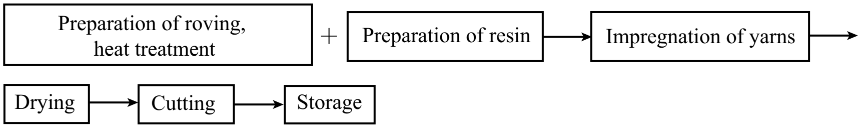


Fig. 5.11 The flow chart of pre-impregnation process.

The adopted equipments are fiber dipping machine and prepreg cutting machine in the mechanical impregnating method for molding compound.

The process flow chart of the glass fiber prepregs is: ① the fiber is derived from the yarns creel, colligating and passing through the concentrated ring into the resin bath for impregnating; ② after the fiber is impregnated by the resin, it goes through the scraping roller and is then sent into oven I and II for drying; ③ after drying, the prepregs are towed from the traction roller; ④ then the prepregs are immediately led to the cutting machine, then be cut into the required length or cut directly or sometimes after a few days of airing. We can also use punch type cutter to cut prepregs.

In the mechanical impregnation method, the main controlled parameters are density of resin solution, temperature of drying oven in all stages and traction speed.

The process of felt dipping is mainly similar to the rovings impregnation method. The structure principle of the machine used for the felt dipping is basically the same as the pre-impregnation machine. The only difference is that first spread the chopped glass fiber evenly on the bottom glass cloth and then be covered by a glass cloth on the surface. After that, we send the sandwiched felt to dip, dry and then become the product. Fig. 5.12 shows the technique flow chart of felt dipping method.

3) Quality control of molding compound by premixing and pre-impregnation methods

The quality of molding compound has a great impact on the properties of the molding process and molding products. The raw materials and every process during the production should be strictly controlled in order to get the molding compound with good quality. Moreover, the three quality aspects of contents of resin, volatile and non-soluble resin should accord with the specifications of the technics. Table 5.3 lists the quality indicators of some typical molding compounds.

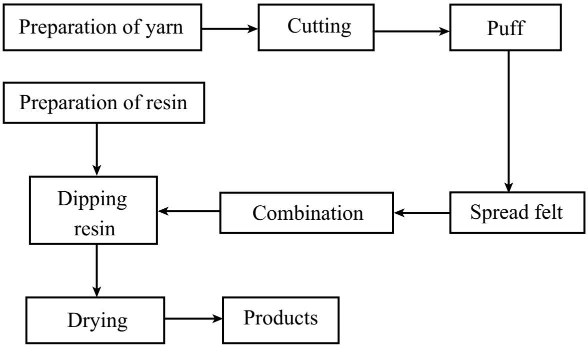


Fig. 5.12 The technique flow chart of felt dipping method.

Table 5.3 Quality indicators of some typical types of molding compounds

Types of the molding compound			Indicators		
			Content of resin (%)	Content of volatile (%)	Content of insoluble resin (%)
Prepregs	Mechanical method	Mg phenolic/Glass	40±5	<3	<8
		Epoxy phenolic/Glass	40±3	<1.5	<4
	Manual method	Epoxy phenolic/Glass	42±4	<2	<5
Premix	Continuous mechanical method	Mg phenolic/Glass	40∼50	5∼9	<5
	Mechanical method in batches	Mg phenolic/Glass	40∼50	2∼3.5	5∼10
		Ammonia phenolic/Glass	40±4	2∼4	<15
	Manual method	Ammonia phenolic/Glass	35±5 (Glass) 40 ± 4 (High silica)	<4	3∼20
Molding felt materials	Mechanical method	Epoxy phenolic/Glass	35∼40	2.5∼3.0	Weight is 1.7kg/m^2. Thickness is 3∼4mm.

(1) The main factors that should be controlled in preparing the molding compound.

① Viscosity of the resin solution.

In preparation of the resin glue, in order to make the resin dip and adhere into the fibers evenly and fast, besides correctly calculating and weighing all the ingredients, we also need adding an appropriate amount of solvent (i.e., dilutent) into the resin to regulate the resin's viscosity. Reducing the viscosity of liquid resin is conducive for the resin to impregnate the fibers and reduce the strength loss of the fiber. But if the viscosity is too low, the fibers may be led to segregation in the process of premixing, it also impact the quality of resin adhesion to the fibers, and will affect the quality of molding compound. Since there are the relation between viscosity and density, and testing the density is simpler than testing the viscosity, people usually use the density as the control indicator of viscosity in industry production, e.g., the density of phenolic resin premix solution is controlled in the range from 1.00 to 1.025.

② Length of the chopped fiber.

The length of fiber should not be too long in preparation of the molding by premixing, otherwise it is easy to cause entanglement between fibers, and get agglomerate materials. In premixing machine, the length of fiber generally should not exceed the range of 20∼40mm. While in the manual premixing method, length of the fiber does not exceed the range of 30∼50mm.

③ Dipping time.

The soaking time should be as short as possible in case that the fiber can be dipped uniformly. Particularly in the premix preparation process, the long kneading time can lose the original strength of the fiber. Excessive solvent evaporation will make the process of tearing more difficult.

④ Drying conditions of the molding compound.

The drying condition is an important factor to control the percentages of volatiles and insoluble resin. Drying conditions include drying temperature and drying time.

⑤ Other factors.

In the preparation process of prepregs, the density of resin solution, the location of scraping roller, oven temperature, traction speed, fiber tension and other factors should be coordinated in order to ensure the effective control of quality indicators.

In addition, equipment design, such as the type of kneader blade, the space between kneading blades and the wall of kneader, the structure and speed of tearing-loose machine, are the important factors for controlling the quality of molding compound and the performance of plastic products.

(2) Storage of the molding compound.

① Storage conditions.

Under normal circumstances, molding compound is packed with plastic bags. It should avoid light, heat, moisture and also contamination of external impurities.

② Operation time of the molding compound.

Molding compound cannot immediately be used after preparation. It takes 3 to 7 days before it begin to behave well in its designed properties. During the period, the volatile content of molding plastics reduced, and the quality of uniformity and stability were improved. A longer period of storage for certain molding plastics also has some effects on ripening, and thus improved the quality of molding compounds and products in some extent.

③ Storage life of the molding compound.

The molding compound is not permanent. It has a limited period of time in storage (storage life or shelf life). Climatic condition and storage condition will affect the storage life of the molding compound.

4) Manufacturing of short fiber molding compound by extrusion method

Both the premixing method and the pre-impregnation method introduced above are using the way of impregnating of resin glue to fabricate the fiber molding compound. They are the traditional production methods. The extrusion method is a relatively new approach. The screw extruder is used for manufacturing the glass fiber molding compound by extrusion method. It overcomes the issue of large use of organic solvent in dipping process, improves the sanitary conditions of labor and at the same time reduces the costs. The quality of product is uniform and steady, and the production can be continuous and automated. The disadvantage is that the glass fibers in the screw extruder should be seriously worn and torn even cut, which will reduce the strength of plastics.

The extrusion method is only applicable to the glass fiber molding compound which has no the low molecule by-product release. For example, it is very suitable for glass fiber reinforced DAP (diallyl phthalate) molding compound. The production method is: the pre-crushed DAP prepolymer and other components are premixed according to preliminary formulations, and then mixed with glass fiber. The initial mixture is continuously added into a single screw extruder. With the effect of heating and shearing, the resin is melted. The rotating screw makes all the components impregnate fully and be mixed evenly, and extrudes the melted compound into a bar. After cooling and cutting, we get the glass fiber reinforced DAP molding compound.

5.2.3 Manufacturing methods of sheet molding compound SMC

Sheet molding compound (SMC) was developed in the 1960s. It is a new type of molding compound for a dry method to manufacture glass fiber reinforced polyester. Its physical form is a sandwich material which is similar to “rubber”. It uses multi-component of unsaturated polyester resin paste to impregnate the chopped glass fiber (or felt) and covers with polyethylene film to get the molding compound with sandwiched sheet. Resin paste contains unsaturated polyester resin, initiator, chemical thickeners, low-shrinkage additives, powder fillers, pigments, release agents and so on. Reinforcing material generally is untwisted glass rovings, which are chopped into the length of 20$\sim$50mm. The covered polyethylene film is to prevent air, dust, water vapor and impurities from polluting the material and to avoid the polyester resin’s cross-linking agent (styrene) to evaporate. When use the SMC, we simply tear up the covered polyethylene film, then cut to the corresponding size and lay-up. Lastly, we put them into the mould and cure to get the required product.

Because the composition of sheet molding compound is complex, and the types, qualities, properties and ratio of each component have a significant impact on the production process, the properties of product and the cost.

In the sheet molding compound, resin system (including polyester resin, initiator, thickener, low-shrink additive, release agent, inhibitor, etc.) accounts for about 30%; filler accounts for about 40%; glass fiber is 30%. Filler $CaCO_3$ is the most commonly used incremental filler (extender) in SMC. It is white and has a low oil absorption value. The usage of $CaCO_3$ has greatly reduced the cost and the shrinkage of the material, and also improved the surface quality of products. Hydrated alumina is the flame retardant, and it can improve the electrical insulation and water resistance of the products. MgO and $Ca(OH)_2$ are the thickeners of the resin, they increase the molecular weight of resin as ligand complex, but do not promote the gel of SMC. Low-shrinkage additives are generally thermal plastic resins such as polyethylene, polystyrene, copolymer of vinyl chloride and vinyl acetate.

Fig. 5.13 shows the production process of sheet molding compound. Firstly, resin and filler components are fully pre-mixed into resin paste. There are two methods for preparing the resin paste which are the batch mixing and the continuous mixing metric method. The batch mixing method is to mix resin and all the fillers except thickener uniformly by stirring, and to add the thickener at the end of the process. After a measurement, we deliver the mixture by pump to a conveyor belt or carrier film. The resin paste for batch mixing method has a restriction of 30min work life. If the work life is too short, the resin will rapidly thicken, which has an impact on the impregnation of glass fiber, only suitable for experiment or small batch production. In the continuous mixing measurement method, the thickener and resin can be prepared separately, and then through a static mixer with a metering device, directly mix the two parts as the proportion and feed them continuously to the paste area. Continuous mixing measurement method can guarantee the same approximate viscosity at the settlement point of roving cutting unit.

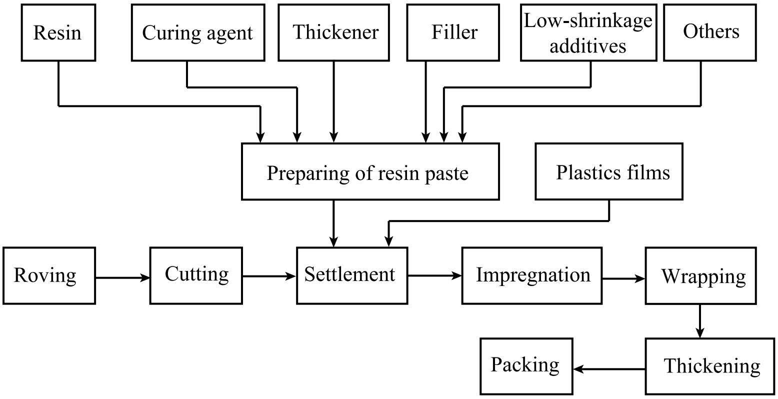


Fig. 5.13 The production process of sheet molding compound.

The resin paste is transported to the upper layer and lower layer of polyethylene film, and we use the scraper to make a certain thickness. Then the continuous glass fiber rovings go through a short-cut cutter. They uniformly deposit on the resin paste of the lower film. At the same time, we cover it with the upper film which also has resin paste. Now a resin paste-chopped glass fiber-resin paste sandwiched material has formed. Through a series of kneading roll, the resins will impregnate the fiber and dispel the bubbles in the sandwich, and the sandwiched material will be pressed into a sheet with uniform thickness, which will finally be made into roll. The sheet material after a period of time of ripening under certain condition becomes thick, and the viscosity achieves stable and is suitable for compression molding.

The production process of sheet molding compound can achieve a high degree of mechanization, automation and continuous production, whose extent depends on the characteristics of each component and the formulations. More importantly, it depends on the type and structure of production equipment (sheet production unit) of sheet molding compound.

At present, there are many different types of the production equipments at home and abroad. But from their structure and function, the main difference lies only in the pull-in system of reinforcing material and impregnating and defoaming unit. For the pull-in system of reinforcing material, the use of glass fiber rovings and glass fiber felt has a great difference. When using the felt, just a few of the rolls can realize combination of felt layers; when using fiber rovings, we need a set of roving chopper, subsidence and anti-electrostatic system.

From the impregnation and defoaming units, there are mainly two types of equipments, the roll type and the belt type, and the former evolutes to the drum wheel type. The roll type relies on the pressure from winding tension on the roll's surface to achieve impregnation and defoaming; the belt type relies on the grooved roll on the conveyor belt to achieve impregnation and defoaming.

The roll type can save space and reduce staff because of its compact structure. Both sides of sheet molding compound can be impregnated and defoamed at the same time. Also, the quality surveillance is convenient. Furthermore, it is easy to implement the change of the unit weight of sheet molding compound and high speed production.

Figs 5.14, 5.15, 5.16 and 5.17 show schematic diagrams of SMC production unit of the glass fiber felt, the belt type, the roll type and the drum wheel type, respectively.

In SMC production unit, the main role of impregnation, defoaming and compaction is to impregnate fibers, eliminate bubbles and press the sheet molding compound tightly into uniform thickness. These happen under the effect of kneading from the rolling and the extension of the SMC itself. In order to achieve this goal,

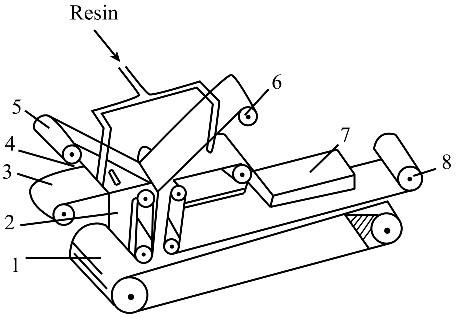


Fig. 5.14 Schematic of the SMC production unit by glass fiber felt:
1-conveyer belt; 2-glue tape; 3-bottom PE film; 4-scraper; 5-glass fiber felt; 6-glass fiber felt; 7-heater; 8-product of SMC.

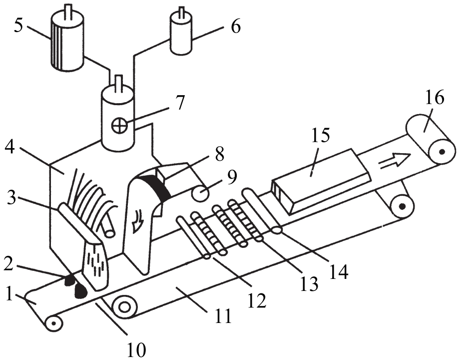


Fig. 5.15 Schematic of the belt type SMC production unit:
1-bottom PE film; 2-scraper; 3-roving cutter; 4-rovings; 5-resin mixture; 6-thickener; 7-mixer; 8-doctor blade; 9-platform; 10-platform; 11-conveyer belt; 12-disk tpye roll; 13-thrust roll; 14-extrusion roll; 15-heater; 16-rolling-up.

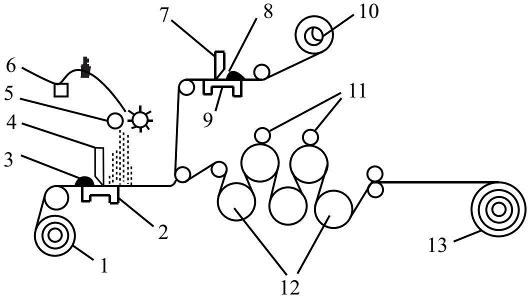


Fig. 5.16 Schematic of the roll type SMC production unit:
1-bottom PE film; 2,9-platform; 3,8-resin paste; 4,7-scraper; 5-roving cutter; 6-rovings; 10-top PE film; 11-press roll; 12-hollow roll; 13-product of SMC.

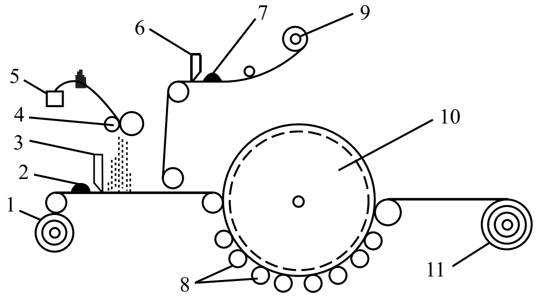


Fig. 5.17 Schematic of the drum wheel type SMC production unit:
1-bottom PE film; 2,7-resin paste; 3,6-scraper; 4-roving cutter; 5-rovings; 8-compaction roll; 9-top PE film; 10-hollow steel drum; 11-product of SMC.

there are various types of rolls (such as flat roll, slot roll, thrust roll and screw roll, etc.) in the device, which can be designed to different sizes, so the sheet molding compound can get through from the upper, the lower of roll, and around the roll. When it goes through the curving course, the sheet material is impregnated by the effect of bending and extending. Sheet material can also be impregnated directly along the direction of machine movement by the compression and kneading.

The quality of impregnation relies on the volume of the cut roving. The greater the volume suggests the worse the initial impregnation. The large hardness of roving, the small diameter of monofilament, the large cut length, and the strong electrostatic effect are all factors that may cause the too large volume of the cut roving.

During the impregnation, when the resin paste's viscosity is too small and fiber content is too low, the resin paste is prone to the phenomenon of outflow, resulting in the uneven quality of sheet molding compound.

In addition, in operation, we should prevent air to be wrapped as much as possible and control an appropriate viscosity of the resin.

The most important issue in wrap-up is to ensure constant winding tension which will facilitate to the automatic replace of coil.

Sheet molding compound generally must go through a maturation period when unloaded from the production unit. When the viscosity reaches the viscosity range of molding and remains steady, it can be used for molding. If the molding compound is stored at room temperature, it can be used after about 1∼2 weeks. In order to achieve the best molding viscosity as soon as possible, we often use the method of accelerating thickening. Condition of thickening is 40°C for about 24∼36 hours or 72 hours in the thickening room. At present, a more advanced approach is to set up an additional thickening area in the SMC production line or using new high-efficient thickening agent, so that the molding process can proceed immediately as soon as the sheet molding compound is made.

The storage life of sheet molding compound is related to their status and conditions of storage. In order to prevent the evaporation of styrene, sheet molding compound should be stored sealed with non-permeable film packaging. Ambient temperature has a great impact on the storage life of sheet molding compound. Taking the Scott Bard in the United Kingdom as an example, the sheet molding compound can be stored for three months below 15°C. If preserved in the cold rooms or in the temperature about 2∼3°C, its storage life can extend to six months. Conversely, if the storage temperature is more than 20°C, the storage life will shorten significantly.

The storage life is also related to the formulations of sheet molding compound. If we add the inhibitor in the formulations, the storage life will be longer. When we use the benzoyl peroxide as an initiator for instance, the life is less than using the tertiarybutyl benzate peroxide, and it is more instable during storage.

SMC has various advantages. The operation of SMC is easy, molding time is short, the production efficiency is high, and it improves the processing environment and working conditions; the fluidity of forming is good, so that it can form the complex structure parts and large parts while keeping the good surface quality of the products; the types of component and the ratio can be redeployed, and we can reduce the costs and make the products lighter; glass fibers are not damaged during the process of forming and production, the length is uniform and the strength of products is high. Therefore, from the 1960s, the production has maintained an annual growth rate about 20%.

5.3 Manufacturing method of continuous fiber prepregs for molding composites

Fiber prepreg is a kind of semi-product stored for using, which is made by coating resin system on the continuous fiber or fabric and through a certain treatment process. It is an important intermediate product for manufacturing continuous fiber reinforced composite materials.

5.3.1 Types of prepregs and the basic requirements for prepregs

There are different varieties and specifications of prepregs. According to different forms of fiber arrangement, there are fabric prepreg (impregnated cloth, impregnated belt), unidirectional fiber prepreg (unidirectional tape, non-weft prepreg) and impregnated yarns, and they are widely used in lamination, rolling, winding, hand lay-up, vacuum bag, autoclave, compression molding and pultrusion process. They are divided by two types of thermosetting prepreg and thermoplastic prepreg in accordance with resin types. According to curing temperature grade of thermosetting resin, there are prepreg cured at 120°C, prepreg cured at 177°C and prepreg cured at even higher temperature. According to the different types of fibers, there are carbon fiber prepreg, aramid prepreg, glass fiber prepreg and cotton fabric prepreg.

Prepreg is an intermediate product of composite material, and is also the basis of the composite materials' performance, since it is directly related to the quality of composite materials. Prepregs for advanced composite materials should satisfy these strict requirements: ① the state and chemical nature of the resin in the prepregs should be in accordance with the specific requirements of the target products (including the degree of prepolymer, molecular weight and distribution, gel time and curing conditions, etc.); ② the outflow volume of resin, tack and drape, should meet the requirements of use; ③ in prepregs, the degree of fiber alignment is that in the length of 1m the deviation shall be no more than 0.25cm, and the deviation of straightness of the edge is no more than 0.1cm in the length of 1m; ④ the deviation of resin content should not be more than ± 2%, and the volatile content is less than 2%.

5.3.2 Preparation method of fiber prepregs

There are three methods for preparing fiber prepregs according to the manner of resin impregnation in fiber which are: ① solution impregnation method; ② hot-melt impregnation and resin film rolling method; ③ powder technology method.

1) Solution impregnation method

It is the same with preparing short fiber molding material, in which each components of the resin are dissolved in the solvent according to the scheduled solid content. Then the fiber (yarn or fabric) goes through the resin solution where it is adhered with a certain amount of resin. After removing the solvent by drying, we get the prepreg. Here, the fiber is impregnated by the resin solution, so this method belongs to the wet process (solution method).

The fabric prepregs that are used for laminating, rolling, and winding of cloth tape are usually prepared using solution impregnation method, and its preparation is processed continuously in the horizontal or vertical dipping machine. Fiber (fabric) moves at a constant speed. Firstly it passes through the heat treatment furnace to remove the moisture and paraffin sizing agent. Then it goes into the resin bath so as to impregnate resin solution to a certain amount, after which most of solvents and volatiles are to be removed in drying oven and the resin is led to a certain curing degree. Finally we coil the end product for storage. Narrow tape which is cut from fabric prepreg can be used for the filament winding. Unidirectional fiber prepreg, according to the different preparation of equipment, there are roller winding type and continuous row array type. Roller winding method is often used in wet process, while continuous row array has gradually become the dry process from the wet process. Fig. 5.18 shows chart of fabricating non-weft unidirectional

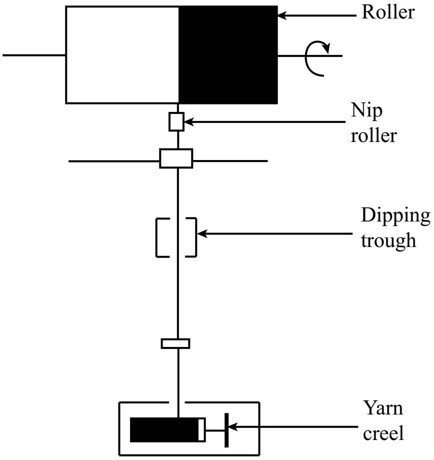


Fig. 5.18 The chart of manufacturing unidirectional tape by roller winding method.

tape by roller winding method. The continuous fiber coming from the yarn creel enters the dipping trough for impregnating by the resin, and after squeezing excess resin by nip roller, fiber is neatly hoop winded on the roller which is wrapped with release paper by the yarn-feeding equipment. Finally, we cut through generatrix of the roller and spread it to get the unidirectional fiber prepreg. Because there is no fiber in the direction of latitude and the longitudinal fibers are only adhered using the resin, the product is often called non-weft fabric. Only simple equipments are needed in this method, and they are easy to operate, but the length of the prepreg is restricted by the roller's diameter, and the production rate is low, so it generally applies for laboratory or small-scale production.

The basic process of row array type is shown: a lot of parallel fibers (or fabrics) are continuously dipped by the resin at the same time. After the processes such as drying and rolling, the continuous prepreg is made. The production is of high efficiency and suitable for mass production. Fig. 5.19 shows the chart of fabricating

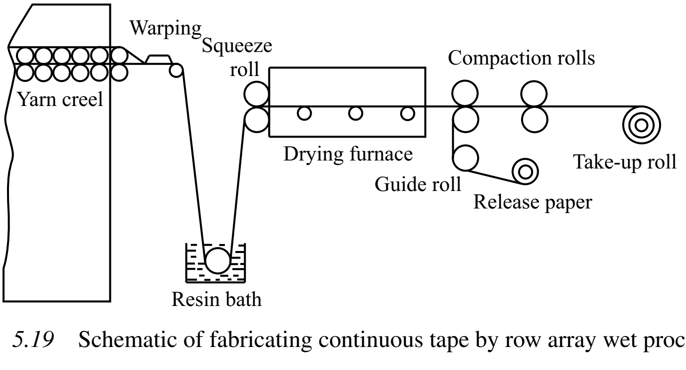


Fig. 5.19 Schematic of fabricating continuous tape by row array wet process.

continuous tape by wet process. A certain number bundles of yarns are led from yarn creel. After warp coordination, they neatly enter the resin solution in parallel position. By squeezing the resin, drying, laying the release paper and compaction, we get the continuous prepregs in rolls. In order to obtain the prepreg with good quality, the environmental temperature, resin solution density, roll gap and moving speed of fiber must be strictly controlled.

2) Hot-melting impregnation method and film rolling method

There are two dry methods to manufacture prepregs, which are hot-melting method and film rolling method. Since we do not use solvent, the environment will not be polluted and fire hazard is improbable. It saves solvent too. Furthermore, the prepregs will contain less volatiles and hence fewer voids in fabricating composites. The process of hot-melting is shown in Fig. 5.20. The molten-resin leaked out from the resin funnel by heating is scraped on the release paper, and is then transferred to the fiber yarns in parallel which are warped and arranged trimly. At the same time, a layer of release paper is labeled on the other side of the fiber. A sandwich structure is formed. By rolling thermally the structure, fiber is impregnated by the resin. Ultimately, the product is pressed compact and it is ready for rolling-up. The process of resin film rolling method is shown in Fig. 5.21. Similar to the hot-melting impregnation method, a certain number of yarn bundles are arranged trimly among glue films to form sandwich structures, which are squeezed by heat-roll to make the fiber embed in resin membrane. After adding release paper and being pressed compact, it could be cut and rolled. By hot-melt film method, we can obtain the prepregs with very low content of resin and uniform resin distribution in product. The content and the quality of resin are affected by thickness of the film, roll clearance and temperature. The film rolling method has a high requirement for processabilty of the resin system, which should have a good film-forming property, and the film should have appropriate flexibility,

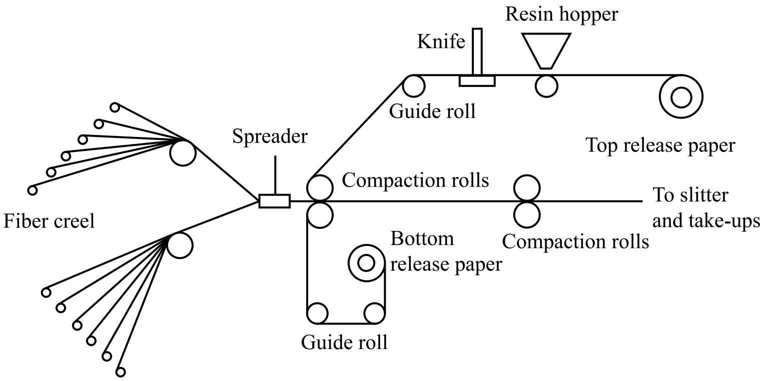


Fig. 5.20 Schematic of the hot melt resin impregnation process.

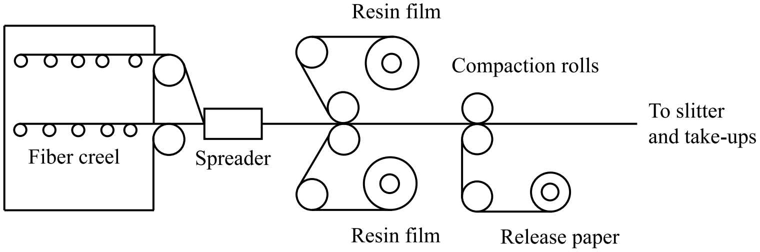


Fig. 5.21 Schematic of the hot melt prepreg from resin film.

tacky property and a long storage life. The manufacture problem that the resin can't dissolve in common solvent with low boiling point can be resolved by dry method. Film forming and flexibility properties can be obtained by adding certain amount of thermoplastic resin or linear thermosetting resin with high molecular weight and at the same time toughness of the cured resin is improved.

When using fiber fabric as raw material for manufacturing prepregs, the process is simple and there is no need of warping arrangement of yarns.

3) Preparing prepregs by powder method

Powder method includes powder electrostatic method and powder suspension method, which is mainly used to prepare prepregs of thermoplastic resin or insoluble resin with high melting point. Powder electrostatic method is by depositing electrified resin powder on the surface of continuous fibers, and adhering polymer powder permanently on the fiber surface by radiation heating method. This method does not cause stress on the interface between fiber and resin, and also does not lead to the deterioration of properties owing to the polymer overtime at high temperature. This method needs to mill the polymer into extreme fine particles, with typical size of 240μm, 110μm and 80μm. Soft prepregs can be prepared by using ultra-fine grain. Powder suspension includes water suspension and gas suspension. The former is by adhering suspended resin grain in water on the fibers which are moving instantly. The later is that polymer grains with fineness about 10∼20μm being suspended in fluidized bed adhere on continuous fibers, which afterwards are encased in a polymer sheath to prevent the powder from breaking away from the fiber surface. Fig. 5.22 shows the process of preparing prepregs by powder bed method.

5.3.3 Quality control of prepregs

The quality of prepregs decides the quality of composites in a great extent. So we must strictly control the quality of prepregs in the process.

Controlling quality includes three steps. They are, check and acceptance of raw materials, process control and batch inspection.

First of all, according to norms, we check various raw materials such as fiber,

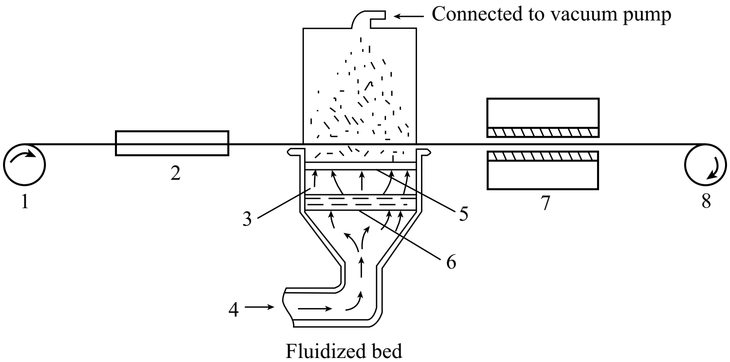


Fig. 5.22 Powder coating process for thermoplastic tow:
1-fiber spool; 2-tow spreader; 3-ionized air; 4-dry air input; 5-porous plate;
6-charging media; 7-oven; 8-take-up.

resin, curing agent, solvent, strippable paper and other accessorial materials. The resin system is the key to control quality, such as water content in resin and curing agent, film-forming properties of resin, binding state between fibers and resins etc. Since resin is a material that is sensitive to temperature, humidity, time and medium, the physical and chemical changes of the resin must be monitored throughout the process. The mixing of resin components must be quite precise and be controlled strictly, and after mixing, the resin system is needed to check by FTIR, DSC, LC, and HPLC according to norms.

Checking of the process of preparing prepreg is mainly to check whether the ratio of fiber and resin is suitable or not. We usually use a fluorescent light to irradiate the prepreg upward and check the clearance among fibers, or use penetrating radiation instrument to repeatedly scan the prepreg horizontally to show the relative change in thickness in the screen thus to give the suitable continuous curve of the ratio of fiber and resin. If the clearance emerges or the thickness is out of the range set beforehand, warning is issued and the signal will be fed back to resin impregnation equipment controlled by computer so as to adjust parameters in real time.

The properties of strippable paper or release paper exert a significant effect on qualities of prepreg. This is because glue film is coated on the strippable paper and it is the carrier of glue film. When strippable paper suffers a tensile force, non-uniform strain might appear in width. This will cause an inflex or excessive extension and lead to fibers non-conforming. When strippable paper encounters solvent, it will swell and its thickness will increase. The weight per unit area and thickness uniformity of strippable paper will affect prepreg and its quality control.

For engineering controlling, routine checking items include: gelation time, fluidity of resin, content of volatile, content of resin and change of viscosity with temperature, etc.

The life of prepregs must be noted here. Since the resin in prepreg could have chemical reaction during the process of storage, and cause the deterioration of the performance of prepreg, the storage and rechecking of prepregs must be carried out carefully. For example, T300/913 prepreg must be stored in fridge at $-18°\mathrm{C}$, with a valid period of half a year. Expired prepregs must be re-inspected. During storage life, every time when the prepregs are taken out from the fridge, they must be kept at room temperature for 24h to make sure that the rolled prepregs recover to room temperature. Otherwise, the differential temperature of hot and cold parts will cause adsorption of moisture and lead to deterioration.

5.3.4 Properties of prepreg and test

Structure parts of advanced composites are usually produced by vacuum bag-autoclave method which has a strict requirement about the quality of prepregs. The technology indices of prepreg include: volatile content in prepreg, fiber mass per unit area, resin content in prepreg, gelation time of prepreg resin system, resin outflows of prepreg, tacky adhesion of prepreg, drapability of prepreg and storage life of prepreg etc. The meaning and test method of each technology index will be introduced in the following.

1) Volatile content in prepreg

Volatile content refers to volatile mass percentage in prepreg. It usually has some volatiles in prepreg and it is good for prepreg to contain an appreciate amount of volatile components. For example, in processing, it provides the resin certain fluidity and improves the tack and drape of prepreg, but if the volatile content is too high to be removed completely in processing, it will lead to the formation of void and the increase of the void content.

Volatile content is tested by weighing method: cut three 100mm$\times$100mm quadrate prepregs randomly and test the weight loss after roasting in oven at a constant temperature ($125°\mathrm{C}$ of oven for epoxy prepreg) for 30min.

$$\text{Volatile content } = \frac{w_1 - w_2}{w_1} \times 100\% \tag{5.1}$$

Here w_1 and w_2 are the mass of prepreg samples before and after roasting, respectively.

2) Resin content of prepregs

Resin content of prepregs refers to the mass percentage of resin, curing agent, plasticizer and other additives all together. It is also called glue content, recorded as w_m. Fibers, other reinforcing materials or fillers are not counted in the calculation (since they are no "glue"). The methods used for testing resin content of prepreg include: air burning method, acid decomposition method, solvent method, and calculation method etc. Among these, solvent method is commonly used, as it is simple, convenient, accurate and suitable for quality control of prepregs.

In fact, the method simply extracts the resin from an 80mm×80mm quadrate prepreg sample by placing it in solvent. Choice of solvent is paramount here. The chosen solvent must be able to dissolve the resin well. The solvents used for ASTM 3529-76 prescriptively include: acetone, butanone, dimethylformamide etc, which are suitable for most resin system existed.

$$\text{Content of resin with volatile } = \frac{w_1 - w_2}{w_1} \times 100\% \tag{5.2}$$

Here w_1 and w_2 are the mass of prepregs before and after extraction, respectively.

$$\text{Resin content = Content of resin with volatile – Volatile content} \tag{5.3}$$

Another method we should pay attention to is the calculation method. In the method, before preparing prepregs, we test the mass of carbon fiber in per unit length. According to the parameters of prepregs and the size and mass of samples, we may calculate the resin content by equation (5.4).

$$w_m = \left(1 - \frac{S \times G_f}{G_b}\right) \times 100\% \tag{5.4}$$

Where w_m is the resin content of prepregs; S is the area of prepreg samples, cm^2; G_b is the mass of prepreg samples, g; G_f is the fiber mass per unit area of prepregs, g/cm^2;

$$G_f = \frac{G_s \times n}{100 \times h} \tag{5.5}$$

Where G_s is the mass of fiber bundles per meter, g; h is the winding clearance of prepregs, mm; n is the bundle number of winding yarn.

3) Fiber content in prepreg per unit area

Fiber content of prepreg per unit area is also called fiber areal density, recorded as G_f. Its value reflects the amount of fiber in single layer of prepreg, i.e. fiber thickness in single layer; with a known resin content, it also reflects the thickness of single lamina of composites. For carbon fiber unidirectional prepreg used in preparing aeronautical structure composites, thickness of the single layer is 0.125mm, i.e. the required G_f is (135±10)g/m^2.

The volume percentage of composites V_f is related to fiber areal density G_f (g/m^2), layer number n, thickness t (mm), fiber density ρ_f (g/cm^3). The relationship is shown in equation (5.6).

$$V_f = \frac{G_f \times n}{1000 \times \rho_f \times t} \times 100\% \tag{5.6}$$

4) Gelation time of prepreg resin system

The technology parameters of composites must be adjusted according to the length of gelation time. Otherwise, the prepreg's quality will be affected. The basic principle used in testing is to put prepreg between two cover glasses on the electric heating plate under a given temperature; when resin begins to flow out, it will be poked by a probe until it can't be spun the thread because of gelation. The time interval starting from putting on the plate to achieve the specified temperature and ending at the point not spinning is called gelation time of this temperature.

5) Resin outflow volume of prepregs

During the curing molding of composites, the resin will flow in mold and some resin will flow into absorbent materials. The resin outflow volume from composites is usually used to characterize fluidity of resin in processing. During the molding process of composites, excessive fluidity will bring inconvenience of processing and cause serious loss of resin in the early stage of curing and lead to lacking of glue and it also could cause irregular fiber arrangement. On the other hand, insufficient fluidity will cause bad contact between layers and uneven resin distribution. So suitable fluidity of resins can reduce void content and make the fibers to distribute uniformly and to improve some performances of composites.

ASTM 3531-76 and overseas corporation of prepreg prescribed the testing method of fluidity of resin. The standard is to cut sample from prepreg and cross lay-up; put it for a certain time under the prescribed temperature and pressure to squeeze some resin. Resin outflow volume is found to be the mass percentage of resin extruded in the process above. The equation for computing is shown in (5.7).

$$\text{Resin outflow volume with volatile} = \frac{w_1 - w_2}{w_1} \times 100\% \tag{5.7}$$

Here w_1 and w_2 are the mass of prepreg samples before and after extrusion.

$$\text{Resin outflow volume = Resin outflow volume with volatile – Volatile content} \tag{5.8}$$

6) Tack of prepregs

The property of prepreg slowly deteriorates during storage. Tack usually bears the brunt of such deterioration. The decrease of tack affects the lay-up of prepregs, and thus influences the molding processability and properties of composites. Among all situations where the tack fails to comply with requirement, the expiration of prepreg almost always bears the blame. The tack test must be carried out to check whether the prepreg is fine. Consequently, the storage life of prepreg is almost synonymic to storage life of its tack.

In the tack test, we lay-up two prepreg slices with prescribed size such as 150mm×25mm (0° direction) onto the test board in a stack; put the testing board vertically for 30 minutes, and watch the adhesion state of the slices under a specified environmental temperature and moisture. If there is no separation between the slice and the board or between two slices, its tack is to be qualified.

Tack of prepreg refers to the viscosity property among itself at certain temperature, which depends on the value of softening point of resin and test temperature.

7) Draping property of prepreg

The draping property of prepreg refers that in lay-up complex parts, prepregs are easily laminated and there is no back jump in bending part of the products. If fabric is fluffy and softening point of resin is low, prepregs will have good performance of deformation, i.e. good draping property.

5.4 Manufacturing of reinforced thermoplastic sheet

5.4.1 Summarize

Compared with thermosetting composite, thermoplastic composites have the advantages of good toughness, rapid forming and being recyclable and they are drawing people's attention more and more. A new processing method has been developed in recent years, in which we first make the reinforcing materials and thermoplastic resin into semi-finished board and then cut the semi-finished board into flan which will be used to form products by compression molding or stamping. This semi-finished product is called reinforced thermoplastics sheet, abbr. RTPS, of which 90% is glass fiber mat reinforced polypropylene or other thermoplastics, abbr. GMT.

1) Classification of reinforced thermoplastics sheet

Reinforced thermoplastics sheet can be classified according to the form of matrix materials and reinforcing materials. Any thermoplastic resin can be used as matrix for reinforced thermoplastic sheet, but the most widely used thermoplastic is PP, and HDPE, PBT, PET, PC, and nylon, etc. There are many forms of reinforcing materials in sheet, such as continuous fiber mats, stitched felts, chopped strand mats, unidirectional fibers, and so on.

(1) Continuous fibers reinforced thermoplastic sheet.

① Continuous fibers reinforced thermoplastic sheet. Continuous fiber mat is a kind of non-woven reinforcing materials, with continuous fibers taken on non-directional ring-shaped distribution, in which carpets are formed by mutual entanglement among fibers or fibers sticked by binders. The typical example of RTPS reinforced by continuous fibers for melting molding is PP reinforced by continuous fiber felts produced by PPG Corporation, for short, AZDEL sheet.

② Unidirectional fibers reinforced thermoplastic sheet. For this kind of reinforced composites, the fiber orientation is the same, and the performance is anisotropic. The manufacturing methods of this sheet include: electrostatic powder method, gas fluidized bed method, liquid fluidized bed method and melt extrusion method, etc.

(2) Moderate-long fibers reinforced thermoplastic sheet.

Moderate-long fibers refer to the fibers with length between 5mm and 50mm.

80% of RTPS are made by moderate-long fibers. According to different structure forms in sheet processing, there are two different categories:

① Chopped fiber stitched mats reinforced thermoplastic sheet, such as "ISO—GMT". They are manufactured by melting method which is also called dry method.

② Chopped strand mats reinforced thermoplastic sheet, such as "STC" and "TAFEN". The main manufacturing methods include: suspended deposition method (also called wet method or papermaking method), fluidized bed method and electrostatic adsorption method etc.

2) Characteristics of reinforced thermoplastics sheet

(1) Unidirectional fibers reinforced thermoplastic sheet.

This kind of sheet often adopts high-performance engineering plastics and is suitable for preparing of high-performance composites. They have high tensile strength and impact toughness and good resistance towards chemical corrosion. However, they are difficult to process and costly.

(2) Glass fiber mats reinforced thermoplastic sheet.

The reinforcing materials used here include stitched glass fibers mats and strand mats, usually with 1∼4mm in thickness and they can be transported, stored and processed like lamella. The characters are as followed.

① Compared with metal board, GMT has many advantages, such as its light weight (density of GMT is about 1/6∼1/7 of the density of metal), anti-corrosion, rustless, heat insulation, sound insulation and good electrical insulation property. Moreover, GMT can be formed into complex products in one process.

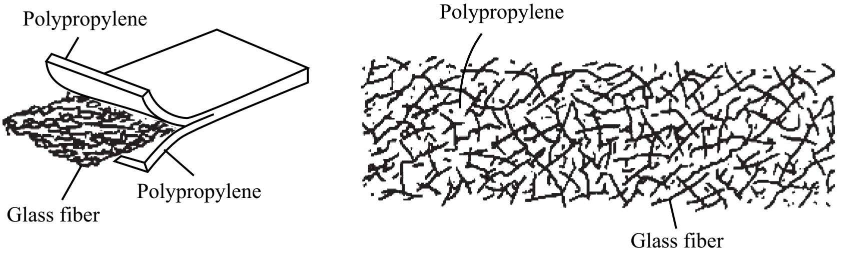
② Compared with sheet molding compounds (SMC), the storage life of GMT is extremely long; molding cycle is short, which is about 1/3 to 1/4 of SMC. GMT is recyclable, pollution-free and has good toughness.

③ Compared with short fibers reinforced thermoplastics, GMT has the advantages of high-strength, good stiffness, long service life and good dimensional stability of product.

Because of the above advantages, the field of application of GMT has becomes wider and wider, it will gradually take the place of metal and reinforced thermosets.

5.4.2 Manufacturing method of reinforced thermoplastic sheet

Different forms of reinforced materials will lead to different manufacturing technologies of RTPS. Here we only discuss the manufacturing methods of GMT. There are two kinds of GMT: one is formed by lamination between continuous glass fibers mats or stitched mats and thermoplastic [Fig. 5.23(a)]; the other is a sheet made of randomly distributed staple fibers and thermoplastic resin powder [Fig. 5.23(b)]. The former is usually formed by stamping and flow compression molding, and shape of the product is simple, and can be made into various structure parts. The latter has good fluidity and is suitable for molding parts with complex shape. The different sheet structures have different manufacturing technologies. The adopted technologies mainly include melting impregnation method, suspension deposition method, and electrostatic absorption and hot compression method, etc.



(a) Laminated sheet structure (b) Sheet structure of random distribution fibers

Fig. 5.23 Sheet structures of GMT.

1) Hot-melt impregnation method

Hot-melt impregnation technology is also called dry technology (Fig. 5.24), it is the earliest industrialization method used for processing sheet. Firstly, we make the continuous fibers or chopped fibers into felt or stitched felt, which after preheating, was laminated with resin film from extruder, then hot pressed and dipped, thermal consolidated by double belt press and cooled, and finally cut into sheets with required specification as semi-finished products for molding. When thermoplastics were extruded from an extruder, the preheated reinforcing materials will touch both sides of the resin film, then with hot-pressing, impregnation and thermal consolidation in double-belt press. The reinforcing materials in sheets could

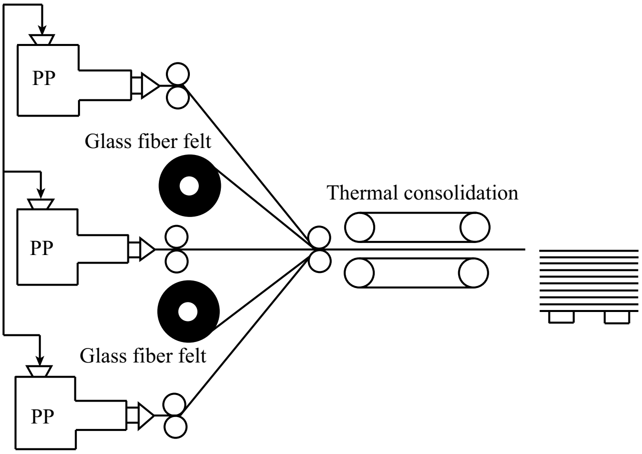


Fig. 5.24 The schematic of the hot-melt impregnation method.

be one or more layers (less than 6 layers). The length of glass fiber in felt is to be chosen arbitrarily based on needs, and so is the thickness of felt. The void ratio of glass fiber felt ranges 0.40 to 0.90. The major technical problem of hot-melt impregnation is the permeating rate of thermoplastics resin into glass fiber felts.

2) Suspension deposition process

Suspension deposition process is also called wet method or papermaking method. In this method, chopped glass fibers with staple length (5∼50mm) are adopted. The length of the fibers must be moderate; fibers with too short length will lead to low mechanical property; fibers with too long length are difficult to be distributed uniformly in resin system. Matrix resin used here are thermoplastic powder with particle diameter of 100∼400μm and sometimes at 800μm. Suspension medium adopted is water or foam. The content of glass fibers is generally at 25%∼40% (weight percentage). If it is less than 20%, it will be difficult for fibers to distribute uniformly; if it is more than 40%, it will contribute to obvious anisotropy and hard technology.

The schematic for suspension deposition method is shown in Fig. 5. 25. Firstly, we add GF, thermoplastic powder and suspension agent into water. Then we stir them. With the help of the suspension agent, glass fibers and resin micro-particles, which are of large difference in their density, will be distributed uniformly in water to the extent that the glass fibers are distributed in single fibers and resin in single particle. Secondly, we make the uniform suspension to pass through slurry-flow box and forming net. The water will be filtered from the suspension to form a wet sheet which will become reinforced thermoplastic sheet by drying, adhere and rolling in turn. This sheet includes two forms which are carpet-like sheet and rigid

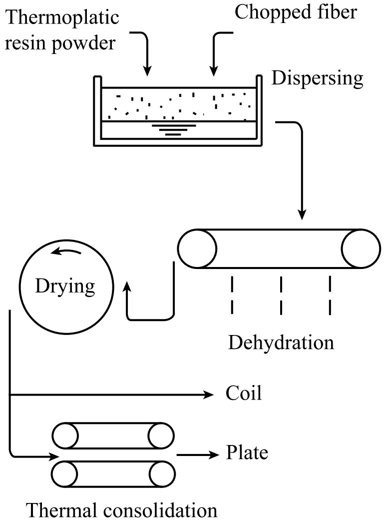


Fig. 5.25 Schematic of the suspension deposition process.

sheet. The latter is produced by hot consolidation with the former.

3) Fluidized bed method

Firstly, we put thermoplastic powder with a certain granularity on porous bed in vessel. It is then fluidized by pumping the air. Secondly, the distributed fibers pass through the vessel, which will be coated with resin powders around. Finally, the fibers with resin coating will be cut into a certain length by a cutter and dropped on conveying net belt. After passing through the hot-rolling area (be heated and rolled) and cooling, reinforced thermoplastic sheet is manufactured (Fig. 5.26). Electric heating or far-infrared heating is adopted in heating area; wind cooling is adopted in cooling area.

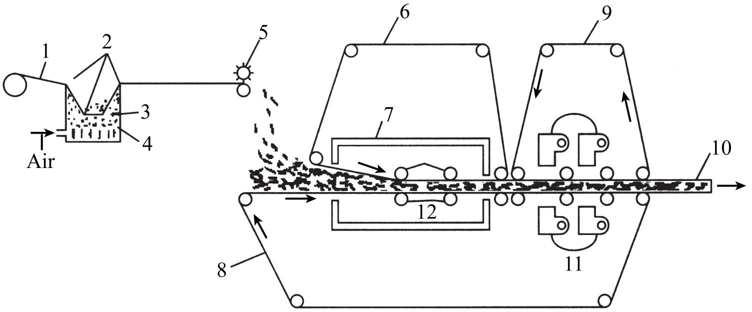
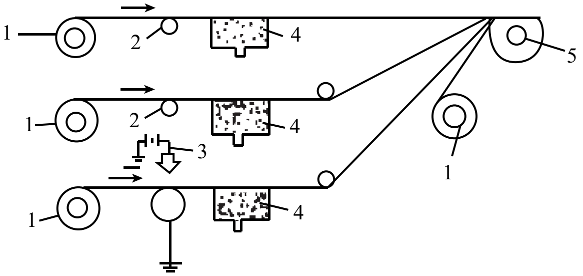


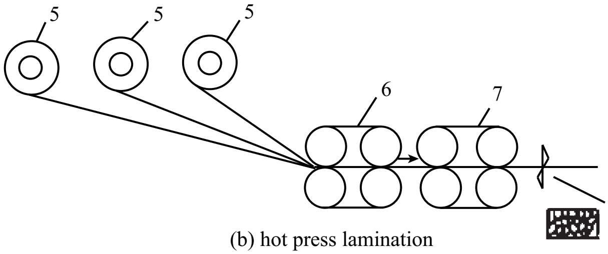
Fig. 5.26 The process of fluidized bed method for thermoplastic reinforced sheet: 1-fiber; 2-guide roll; 3-resin powder; 4-porous bed; 5-cutter; 6-hot rolling belt; 7-heating area; 8-conveyor belt; 9-cold rolling area; 10-sheet; 11-cooling area; 12-roll.

4) Electrostatic absorption

Firstly, the thermoplastic resin is made into film and charged with static electricity, so that when the film passes through the short fiber groove, it will adsorb fibers. Secondly, the above fibers were laminated and hot pressed into reinforced thermoplastic sheet (Fig. 5.27). The resin can be PA, PC, PE, ABS, AS, PET, and PBT, etc., with 0.01～1mm in thickness; the glass fiber is moderate long with length of 3～50mm.



(a) electrostatic absorption



(b) hot press lamination

Fig. 5.27 The process of electrostatic method for consolidated sheet:

1-thermoplastic resin film; 2-electrostatic friction roll; 3-high voltage electrostatic generator; 4-moderate long glass fiber; 5-coils of film absorbed glass fiber; 6-hot rolling area; 7-cooling area.

Exercises

1. Try to describe the technological process for preparing micro-particles reinforced thermoplastic granule. What's the key working procedure? And what influence does it have on the quality of granule?

2. Try to compare the advantages and disadvantages of long fiber reinforced pellet and short fiber reinforced pellet.

3. Try to describe the way of producing molding powder by dry method. What's the aim of hot rolling?

4. Try to describe the advantages and disadvantages of premixing and pre-impregnating method.

5. What's sheet molding compound? And what are its characteristics?

6. Briefly describe the constituents of SMC and point out the effect of each component.

7. What are mainly two kinds of prepregs of composites? What are their unique characters compared with other materials used for molding?

8. How many methods are there to prepare prepregs of composites? What's dry method or wet method? What conditions should high quality prepreg be consistent with?

9. How many main technical indices are there in prepregs for composites? How to determine them?

10. What's reinforced thermoplastic sheet GMT? How many kinds of GMT are there? How many main manufacturing method of GMT?

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6

Forming technology of polymer matrix composites

6.1 Overview

6.1.1 Main technique flow chart of preparing composites

As previously stated, composites products are prepared by processing and molding raw materials such as resins, fibers, etc. The typical technique flow chart of molding composites is shown in Fig. 6.1, which indicates that composites forming process includes three aspects: preparation of semi-product materials such as prepregs, preforming of reinforced materials which gets a preform or flan close to the shape of product and curing molding of composites. These three aspects can be done altogether or separately according to different technology methods, as long as compounding of resin and fiber, impregnation, curing and molding are well accomplished during the process. Moreover, the materials and products (or structure) of the composites are to be finished at one stroke in one molding process. The manufacturing process of semi-finished products has been discussed in Chapter 5 and we will proceed to the forming and curing technology of composites in this chapter.

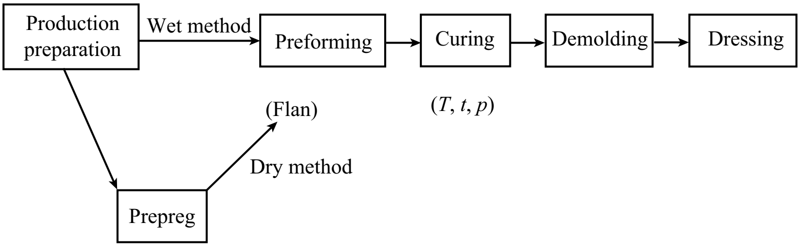


Fig. 6.1 Typical technique flow chart of composites processing.

6.1.2 Classification of composite processing

The composite processing technology is the basic and prerequisite of the development of composite industry. As the application field of composite broadens, composite industry is developing rapidly. The old processing technologies become more and more mature, and new methods emerge in large number. Until now, there have been more than twenty processing methods for preparing polymer matrix composites, which are suitable for processing of thermoplastic and thermosetting composites. Classification of these normal methods from different perspectives is shown in following.

1) Classification of preforming method

One character of composite process is the preforming of reinforcing materials before curing, i.e., the process to get flan with the similar shape and size to the product. Composites technologies can be classified into four kinds according to different preforming methods.

(1) Laminating method.

Laminating method is also called paperhanging method or manual lay-up/hand lay-up method, including wet method and dry method. The wet method refers to the adoption reinforcing materials such as clothes, belts or mats etc, the glue with low viscosity and the process of pasting the material manually, while the dry method refers to the process of pasting prepreg layer by layer. The wet method is most widely used for processing glass fiber reinforced composites. On the other hand, the dry method has become the main process method for advanced composites nowadays, which need to paste the prepregs and cure them in autoclave. Laminating method always uses the continuous fiber fabric as reinforced materials.

(2) Deposition method.

This method includes fiber spraying accumulation preforming and fiber suction accretion preforming. The former refers to the spraying of chopped fiber on mold surface by compressed air; the latter refers to the chopped fiber being absorbed onto net mold by vacuum. It should be noted that the reinforcing materials used in deposition can only be short fiber. Spray-up method is another molding method commonly used for preparing glass fiber reinforced composites. The fibers and glue are sprayed on mold simultaneously in this method, which grants it the advantage of high mechanization and production efficiency over wet method that adopts manual lay-up.

(3) Winding method.

In winding method, we wind the continuous long fiber yarns, cloth and belt after their impregnation in glue onto mandrel or inside lining that has the cavity size of corresponding product and then cure molding. This method is suitable for processing rotary products and is of high mechanization and production efficiency. If impregnated yarns or tape are adopted, the method is called dry winding. The reinforcing materials used must be continuous fiber in this method in which fibers can be arranged according to the stress state of product. The products have high fiber content and high strength.

(4) Weaving or braiding method.

It's a new preforming method of continuous fiber yarns developed in recent 20 years. With the development of fiber weaving technology, the reinforcing materials can be braided into three-dimensional fabric with almost the same shape as the product. The fabric will be impregnated and cured by RTM to form composite products with high strength in the normal direction to layer plane.

2) Classification by molding pressure

(1) Contact pressure molding. It refers to the pasting the reinforcing materials and resin by hand or simple tool and no pressure is given when molding. It includes wet manual lay-up method and spray-up method.

(2) Vacuum bag molding. We seal airtight the preform on the mold by vacuum bag and remove the air and volatile from vacuum bag outwards. In this way, a pressure will be exerted on the product below 0.1MPa (atmospheric pressure) to reduce the void fraction.

(3) Pressure chamber (pressure bag) molding. Airtight pressure chamber is made on the surface of the products, and then the air pressure of the chamber will be transferred to the surface of the products by compressing air with the help of vacuum bag or rubber bladder. The pressure in the chamber is generally 0.25∼0.5 MPa.

(4) Autoclave molding. Vacuum bag-autoclave molding refers to the method of curing the composite laminated flan sealed in vacuum bag under the pressure and heat generated by heating gas in autoclave. Autoclave is a general equipment used for air-heating and program-controlled temperature, with pressure of 0.5∼2.5MPa.

(5) Compression molding. Compression molding includes low-pressure molding of rubber plunger molding and high-pressure molding of metal match die method. Laminating molding for insulation composite laminates is a special compression molding under moderate-high pressure, which uses professional press and multiple plate molds.

(6) Resin transfer molding (RTM), resin film infiltration (RFI), glue absorption molding. These are kinds of liquid composite molding method: make the resin to flow into the mold to impregnate reinforced material preform by vacuum or pressure, then heat and cure to form the product.

(7) Reinforced reaction injection molding (RRIM). It is a manufacturing method combining polymerization and injection molding. It involves mixing the two kinds of reactive monomer liquids with chopped or milled fibers uniformly using special equipment, and then rapidly injecting the mixture into mold to cure.

(8) Pultrusion. In this method, fibers that impregnated with resin or yarns prepreg are to pass through a heated die with a fixed coross section, during which we extrude spare resin, and then cure the product under traction.

3) Classification by open mode or closed mold

The various processing technologies of composites can be classified into following kinds by open or closed mold.

(1) Closed mold forming. They are compression molding, RTM, injection molding and RRIM.

(2) Open mold forming or half mold forming. They are hand lay-up, spray-up, vacuum bag method, pressure bag method, autoclave molding, winding method, pultrusion and centrifugal casting molding (or rotational molding).

(3) Others. They are braiding, and suction accretion (glue absorption) molding.

6.1.3 Forming characteristics of composite products

Different from other materials, materials and products of composites are formed in the same process in one time.

Various technologies of composite adopt low-pressure molding, except for compression molding and injection method. The pressure adopted is below 2MPa. The low pressure molding is convenient for forming large products, and requires only low-level equipments. For instance, when making a product with an area of 1m^2 by compression molding, with unit pressure of 10MPa, the total load required is 1000t. So for the large products used in aircraft with size of several square meters even tens of square meters, it is hard to form them by high pressure molding. Low pressure molding can reduce investment cost of equipment because it needs no strong press and can use cheap and easily processed materials for mold.

The effect of adding pressure in general in the processing of plastic product is shown as follows.

(1) To make the plastic to flow, that is, to overcome the viscous flow resistance of plastic itself and friction generated by relative motion between plastics and mold (e.g., flowing through thin cast path, flow in the process of filling mold etc.).

(2) To remove small-molecule components and compact materials so that the materials will be inosculated with the mold to get dense and uniform products. For some thermosetting resin, there are amounts of volatiles components that escape during curing. So after mold closes, the additional pressure is needed to resist the pressure generated by volatile components and to ensure the compactness of product.

In the processing of fiber composites, several measures in the following are taken. That is the reason why fiber composites can be processed under low pressure.

(1) Preforming the fillers. The preforming method adopted in many technologies is to make the impregnated fillers into preform that has almost the same shape with the product or to make the fillers to preform and then impregnate and compact it. Using the methods above, the big relative flow of materials is avoided during the forming process of product. Consequently, frictional resistance in materials or be-

tween materials and mold is reduced and the amount of pressure is saved that is used to overcome the resistance.

(2) Adoption of resin formulations that can be processed under low pressure. The character of such resin system is that there are no or a little volatile components released per unit time when curing. So the pressure used to resist the pressure generated by volatiles can be reduced. The unsaturated polyester resin and epoxy resin with low viscosity are best among these kinds of resins since they need no solvent when impregnating fibers. All components reside in composites after curing. The curing of high-viscous epoxy resin is of addition polymerizing. Although the reaction itself does not generate any volatile components, the residual solvent in fillers will produce some of it during the molding. Modified phenolic resin is cured by condensation. However, thanks to the slow rate of condensation, the amount of side-product is small. Thus, the low-pressure molding can still be used, but certainly with a bigger pressure than the above cases.

(3) Transferring pressure by elastic medium (gas or liquid). The pressure at any place of the surface of products is vertically (Fig. 6.2) applied on, so the pressure exerted has its best possible effect.

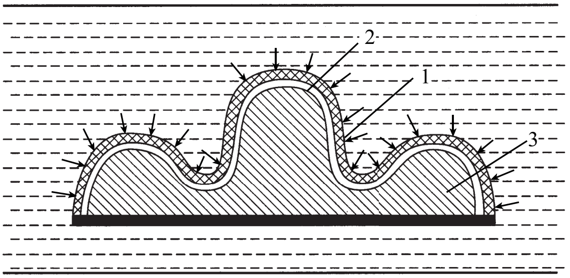


Fig. 6.2 The schematic about uniform pressure caused by elastic medium: 1-rubber cover; 2-flan; 3-model.

6.1.4 The main points must be followed in common in various technical processes

No matter which processing method is used, the main points are in common.

(1) Distributing the fibers uniformly in every part of product according to design requirements. This is because some properties of fiber composites mainly depend on the distribution state and the content of fibers. The inadequate content or uneven fiber distribution will lead to weak links in local places and affect the performances of product.

(2) Making sure that the resin can distribute in any part of product adequately and uniformly and cure appropriately. Too high or too low resin content is not suitable. Over-high or over-low resin content in local place will lead to weak links to reduce the performances of the whole product. Resin curing is a process

continuously changed in which the resin must achieve a certain curing degree, if not, the performances of product will be reduced heavily.

(3) Reducing the amount of air bubble as much as possible in processing, reducing the void ratio and improving the compactness of products. Generally speaking, the volatile gas cannot be removed completely during the preparation of fiber composites. So a certain pores are formed in product, some of which is visible and some invisible. The content of pores is presented by void ratio, i.e., the percentage of void accounting for the total volume of composite. The existence of voids will generate bad effect on the performance of composites, especially the long-term property. So, the amount of void must be reduced in the process as much as possible.

(4) Having a full grasp of processing performance of resin used so as to make a reasonable process rule. In the whole process, changes occur in resin instead of fibers. In primary period, the resin is low viscous liquid and can impregnate fibers to exclude bubbles. Its viscosity increases gradually in processing and then in gelation and even curing. Yes, some resins suffering gas generation, heat-release and volume shrinkage even during curing. The resin performances expressed in process are called processing performance. Only when the processing performance of the resin formulations used is fully grasped, can the reasonable process specification be prescribed and the products of good quality be produced.

6.1.5 The content of process designing of composite products

The main task of the technical staff's engagement into preparing of composite production is to search and adopt the best technologies and to prescribe the most reasonable process specification and furthermore to manufacture product with high quality. As we mentioned previously, the manufacturing of composite product is different from metals. The desired product is formed at the same time as the composite was made from raw materials. Therefore, there is no way we can isolate the design of the product itself from raw materials. The following shows the procedure of composite product design and fabrication.

Choose raw materials according to the required performance of products →ply design according to properties of unidirectional laminates→ choose molding method according to the processing properties of materials→ design tooling and assembling mould (mold line template method) → molding process test.

The designer must start with the selection of raw materials, according to the usage requirements of the products, choose appropriate reinforcing materials and resin glue. In choosing materials, its processing performance and resource must be considered besides the using properties. Once raw materials are determined, the performances of unidirectional laminate must be tested. Ply designing of products will have to base on these data.

The following requirements must be satisfied in ply designing: ① the materials chosen must be sufficiently supplied and cheap in price; its using property and processing performance must satisfy the technology requirement of products; ② the fiber strength must be used sufficiently to achieve equal strength design as much as possible to make the products light, strong and stiff; ③ other performance requirement can be satisfied such as dielectric, heat resistance, corrosion resistance etc.; ④ the products should be designed into integrated structure to reduce the number of parts and joints etc.; ⑤ the products must be able to be formed easily by simple equipment, and their processing procedures can be realized by mechanization and automation easily; ⑥ compensation process can achieve easily with no machining or simple machining when assembling.

In a project, the product designers and technology staff must work closely together. Product designer should be able to take into consideration of the feasibility of both using and processing performance in their product designing, while the technology staff must understand the technical requirements and construction characteristics of the product, before they can conduct the process design successfully.

Process design is the design of process procedure. The process procedure refers to the procedure that: manufacture the materials to parts and assemble the parts into assembly parts. The content of process design includes: ① examine the process of design drawing of products; ② determine technology methods and technology rules (molding and assemblage); ③ determine operation method, technology parameters and production notes of every procedure and compute the amount of every materials, the size of preform, procedure dimension, machining accurate degree and man-hour etc.; ④ determine checking system and raise safety matters in production; ⑤ choose instrument and process equipment (mold, fixture, templet) and tool (forming tool, cutter, measuring instrument, etc.), and determine construction program of process equipment; ⑥ write out process documents, such as process order, assembly graph and test norms etc.

According to the content of process design, besides satisfying design requirement, the economic effects, production cycle and production batch must be considered in studying out technology program. The contents of technology program include: ① choose raw materials accordant in quality according to the using requirement of product (in conjunction with design department); ② choose the most possible and best method by analysis and comparative study of various process according to structural design, usage requirement and production situation (materials, equipment and technical level of workers) of product; ③ choose equipments and instruments according to process method; ④ ensure reasonable technology parameters (such as parameters of processing–temperature, pressure and hold time) according to the use and design requirement of products, technology methods and process performance of raw materials by repeated testing; ⑤ plan out the whole operating rules of product manufacturing after the product is up to the standard by repeated process tests. The process document written is used to direct and organize the production.

6.1.6 Choice of processing technology for composites

How to choose molding method is the first and foremost problem for organizing production. Since the composites and their products are formed in one stroke, the choice of the process method must satisfy the basic requirements about many aspects simultaneously, such as material performance, production quality and economic effect. Specific base points on choosing include: ① performances of material and quality requirement of production; ② size of production batch and supply time; ③ target price and economic effect.

1) Three main points on processing

The whole process procedure of polymer matrix composite, from raw materials to products concerns three important aspects, they are figuration, impregnation and curing, which are also called three important factors of processing.

With respect to the three basic points such as performance, yield and price of the products, the ways to achieve the three important factors are evolving constantly.

(1) Figuration.

The basic problem of figuration is how to make the reinforcing material arranged uniformly, or how to ensure them in specified direction and to arrange them credibly. Preforming is the first step of figuration, where reinforcing materials form a preform which has a similar shape with the product. The find figuration is achieved in mold by pressure.

(2) Impregnation.

Impregnation means that the resin take the place of gas among reinforcing materials to form good interface bonding and low void ratio in composite. Impregnation mechanisms include defoaming and infiltration. The quality and difficulty of impregnation are affected by viscosity and type of resin, ratio between resin and reinforcing material, and the variety and patterns of reinforcing material etc. In preparing of prepreg of semi-finished products, the main impregnation procedure is already brought in advance, but in the heating process, the impregnation will proceed further.

(3) Curing.

The curing of thermosetting resin means the chemical reaction of matrix resin, i.e., molecular structure changed from linear to three-dimensional network by crosslinking. Curing requires initiator and accelerator and it needs heat to boost the progress of curing reaction sometimes. For thermoplastic resin, curing refers to the procedure of solidification cooling from viscous flow state or high elastomeric state.

Three factors of figuration, impregnation and curing influence each other. And the composite production can be manufactured economically by the well adjustment and combination of them. The relationship between three factors and raw materials are shown in Fig. 6.3.

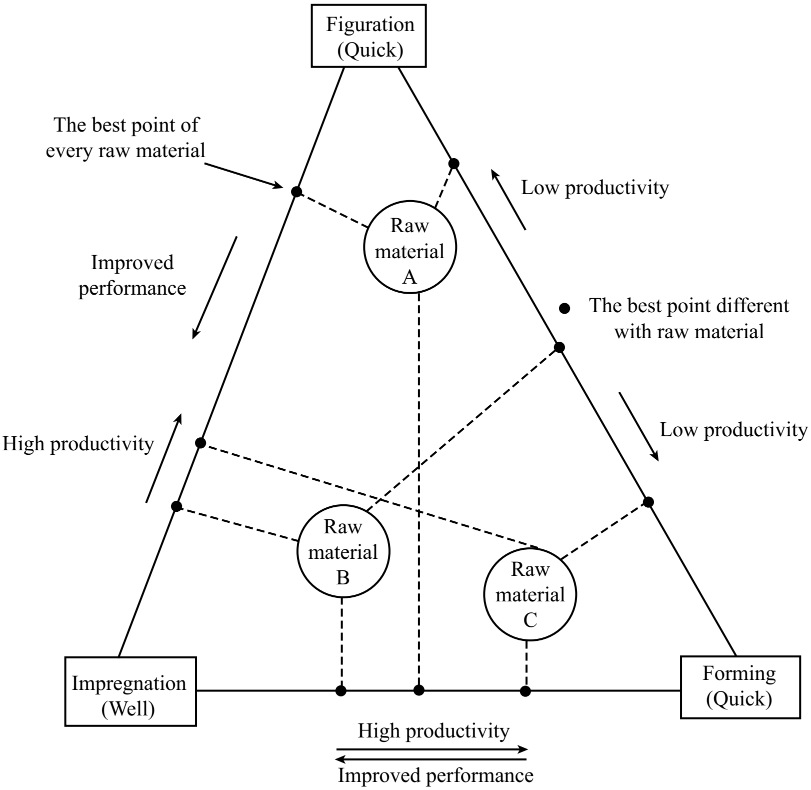


Fig. 6.3 The relationship between three main points and raw materials.

The quality of impregnation, speed of figuration and curing can affect the product properties and production efficiency simultaneously, which are usually trade-offs. If we emphasize economics and shorten the forming cycle, some performance will be lost; on the contrary, over-emphasizing performance will lead to a depreciation of the product's economic value. There exists an optimal combination of the different raw materials. The relational graph of three important factors of every process method must be drawn and studied so that most reasonable program can be chosen.

2) The choice of process technology

There are various methods for preparing resin matrix composites, according to performances of corresponding products, yield, cost of raw materials and combination of the three factors. The various process methods and the three factors are listed in Table 6.1.

Table 6.1 various molding methods and its three factors

Molding methods		Figuration			Impregnation			Curing				Production forms	
		Labor	Machinery		Pre-forming	Laminated impregnation	Overall impregnation	Room temperature		Heating		Batch	Continuous
		The same time at impregnation	The same time at impregnation	Preforming				Open	Closed	Open	Closed		
Hand lay-up		Fine				Fine		Excellent		Fine		Single-small quantity	
Spray-up		Fine				Fine		Excellent		Fine		Small-moderate quantity	
Cold compression molding			Fine			Fine	Excellent		Excellent		Fine	Moderate -quantity	
RTM			Fine	Fine		Fine	Excellent		Excellent		Fine	Small-moderate quantity	
Metal matcheddie method	Preforming		Fine	Fine		Fine	Excellent				Fine	Moderate -quantity	
	SMC				Fine		Fine				Fine	Large quantity	
	BMC				Fine		Fine				Fine	Large quantity	

(Continued)

Molding methods	Figuration			Impregnation			Curing				Production forms	
	Labor	Machinery		Pre-forming	Laminated impregnation	Overall impregnation	Room temperature		Heating		Batch	Continuous
	The same time at impregnation	The same time at impregnation	Preforming				Open	Closed	Open	Closed		
Pressure bag		Fine		Excellent	Fine			Excellent		Fine	Single-small quantity	
Pultrusion method		Fine				Fine				Excellent		Moderate-large quantity
Filamemt winding method		Fine		Fine	Fine						Single-moderate quantity	numerous
Continuous processing		Fine			Fine	Excellent				Fine		Large quantity
Centrifugal method		Fine			Excellent	Fine	Fine				Moderate quality	
Rotational method		Fine			Fine		Fine				Moderate quality	

The shape, structure and size of the product must also be considered in choosing process methods.

Generally speaking, mechanical forming methods such as compression molding are used in massive production of products with large number, small size and complex shape such as mechanical parts, electrical equipment, etc.; SMC compression molding with great table-board is suitable in production of products with big size and simple shape such as bathtub and auto parts, etc. Hand lay-up can also be used in small production. RTM can be used in manufacturing products with moderate size and quantity. Fiber winding method and centrifugal casting molding are used to make ratator products, such as pipe and vessel; hand lay-up and spraying are adopted in small production of products with big size such as ship shell and large tanks, etc,; when gel coat is needed on the product surface, hand lay-up or spray-up can be adopted, as well RTM; for board and linear products, continuous process can be used.

6.1.7 Concept of technological properties and evaluation basis

1) Concept of technological properties

The processablity of composites refers to the difficulty levels of operating and product quality guaranty when composites and their constituents are manufactured into specific products by specific process method.

For example, to prepare a pipe, hot extrusion method can be used for thermoplastics; cold extrusion method can be used for thermal-stable plastics such as polytetrafluoroethylene (PTFE); winding method can be used for glass fiber, clothes and long fibers reinforced composites. This shows that for the same product using three different materials each with its unique process methods and all the methods are easy to operate and to guarantee the quality.

Another example, to prepare a piece of rotor, the method used is hand lay-up and then compression molding, and it is easier for glass fibers and epoxy to guarantee the quality than carbon fibers and phenolic-based adhesives. This indicates that different materials will show different processability for the same product and processing method. Such character of materials is due to the result of different physical, mechanical, chemical actions of different materials shown in the process, which are further determined by the components of material and the structures of various components.

Therefore, components of materials and structure of each component are the foundation for showing some technological properties; but the specific structure of products and the manufacturing method are conditions of showing technological properties for materials.

It usually happens that some materials have good applicability but bad manufacturability, such as carbon fibers composites. In this condition, the manufacturability of such materials must be improved to expand its application range. There are three ways to do that; first, rehabilitate current process method or create new method and make it fit the well-known physical mechanical chemical performance of the material; second, change the performances of materials above to cater the current process method by certain means, such as adding new components or changing the components of material; third, develop new performance and create new processing method adapting to new performances.

What must be pointed out is that the study and discussion for materials' technological properties and using properties have equal importance.

2) The main foundation to assess technological properties of materials

Although the manufacturability of material should be related to process methods, it also can be generally assessed according to technology characteristics of production manufacture.

(1) Product quality is one of the main foundations to assess manufacturability of material. The way to assess material manufacturability is as followed. If the products are produced with the material under controllable condition and the products are of high quality and reliability, the manufacturability of this material is good. In other word, the fluctuation of performance indicators of the products must not be too large and the minimum value of the indicators should be in the range permitted by technology specification. Therefore, fluctuation of performance indicators can be used as one of the material indicator to assess materials' technological properties.

(2) Economy is also one of the main foundations to assess materials' manufacturability. The economy noted here includes the total cost in production procedure (the expense of technology equipment and instrument, the length of process routine, the requirement of staff technology level, management cost etc.) and the amount of materials consumed. For example, there are two kinds of materials which can be used to make various structure products by various technology methods. If the first one requires more expensive processing equipment and instrument, longer processing procedure, higher technology level, higher difficulty in management and more material in processing than the second one, then the second one will be considered better in its manufacturability. In this sense, the manufacturability of epoxy composites processed at room temperature will be considered better than that of phenolic composites processed at high temperature. Economic indicators depend on production level and batches and quality of products, so it's a relative indicator. For air products, the economic is improved just under the premise of ensuring the product quality.

(3) The harm to human should be one of main foundations to assess material manufacturability. Polymer matrix composites can often generate volatile harmful to human body during its processing. The more the hazardous substances are

emitted in material processing, the stronger the toxicity and the worse the material's manufacturability. This point is very important. Some materials have good applicability and economics but are toxic to people, then its usage and development is limited.

The first foundation plays a leading role in the three above. It is also the most important foundation of all problems considered in processing parts. That is to say "quality first" is the starting point to study and deal with all problems.

For specific structure parts and processing procedure, besides the general assessment of material, the manufacturability of the specific material shown in process should be studied, such as impregnation, bonding ability, fluidity, curing character of thermosetting resin; volatile content, resin content and tack of prepreg etc.

6.1.8 The roles of forming technology in composites structure

Forming technology is the only way to transform the raw materials into structure parts and become the design idea into objects. The important ways to expand the application range of composites include improving manufacturing level and lowering manufacturing cost.

Composites and metals are obvious disparate in their nature and processing technology. The uniqueness of composites and the significance of forming technology are shown in the following.

(1) Materials and structures are formed in one process.

(2) Structure design is closely related with manufacturing technology, i.e. the feasibility of manufacture technology must be considered in designing the composites structure.

(3) Designers have more freedom choosing process technology. There are trade-offs among operation, steady quality and low cost and designers can coordinate them according to needs.

(4) There are tens of thousands of fibers and interfaces with matrix. Controlling the reaction between fibers and resin is the foundation of getting good interfaces.

(5) Heat stress occurs when cooling because of the different heat expansion coefficient of fiber and resin. The value of heat stress is related to technology parameters.

(6) Distribution uniformity of fibers and resin has a big impact on the performances, especially in the normal direction. Uneven distribution will lead to deformation, so we must pay attention to avoid it.

(7) We often adopt various reinforcing materials to get structure done with the lowest weight and to realize some function. The compatibility among these materials is one of the difficult points in processing.

(8) The structures, performances and structure efficiency of product are different if we process the materials in different methods, such as integral cocured,

segment cocured and bonding connection. In the perspective of forming, the best process method will always be different for specific structures.

(9) The coupling effect exsits in composite material that common material does not have because of its anisotropy. In nonaxial tension of unidirectional composites, shear deformation will be caused since elastic modulus in axial is bigger than that in transverse; bending in nonaxial direction of unidirectional composites, rotational deformation will be caused; plying accuracy in processing has a big influence on the coupling effect.

(10) Integrated molding technology should be adopted as much as possible to avoid mechanical connection, so as to fully make use of the advantages of fibers bearing load and the reduction of stress concentration. Moreover, the number of connectors can be reduced to achieve the biggest loss of weight.

(11) Excellent composite structures are derived from the coordination of designers, technology staffs, chemists, mold designer, and reflect the synthesis of manufacturing technology.

(12) When manufacturing composite structures, the final test is merely the measure of the final performance. The process management in every step is the key to guarantee the standard products. It is important to implement quality control mechanism at every procedure in the process.

(13) Adoption of molding technology with high survival rate is one of important ways to get composite structures with high quality and low cost.

(14) Repair can't be avoided, and it is also an important aspect for expanding application of composites.

6.2 Brief introduction of various molding techniques

6.2.1 Hand lay-up process

Hand lay-up process (also known as paperhanging, layer-stacking) is a manual-based molding method of composite parts. Its primary feature is of course its manual operations, which is suitable for multi-product and small-scale production, as there are no limits in size and shape of products. However, this method is of low productivity, bad working conditions, and labor-intensive. It is difficult to control product quality, which often leads to poor performance stability and low strength compared to the other methods.

Hand lay-up process includes wet process and dry process. Wet process is directly to paste the reinforced materials (cloth, tape, felt) with resin solution or low viscosity glue without solvent. Its impregnation is achieved at the same time as preforming process. Dry process separates the impregnation and preforming process by using prepreg. It puts prepreg layer by layer for preforming process according to ply sequences. Then the preforming flan is cured by compression molding or vacuum bag-autoclave molding.

Wet process is: firstly a layer of release agent is coated on the mold. We evenly brush a layer of resin mixture with curing agent, and then lay reinforced fabric (cutting according to requirements of shape and size in advance) up on the glue layer directly. Afterwards, we use scraper, brush or roller pressure to force glue into fabric evenly and remove air bubble. After the reinforced materials are completely soaked by glue, we brush resin mixture and lay fabric. The procedures are repeated until the accomplishment of part pasting, and then we cure, demould and trim it. At present about 50% of glass fiber reinforced plastic products are manufactured by wet process.

1) Characteristics of hand lay-up process

Advantages: ① no need of complicated equipments, just a simple mold and tools, low investment, quick affection, fit for township enterprises; ② simple principles to teach, easy to master its production technology, production can be carried out just after short-term training; ③ FRP products are not limited by its size and shape; ④ it can be used to make composite with other materials, such as metal, wood, foam; ⑤ it may in site produce large products which is difficult to transport, such as large tanks, large roof.

Disadvantages: ① low productivity, slow and long cycle, not fit for large quantities of products; ② poor quality stability, and quality of product is impacted by operator skill and production environmental conditions; ③ poor production environment, smell, and large dust, need labor protection.

Hand lay-up process is particularly applicable to small-scale, multi-product production or the production of large or complex products.

2) Technique flow of hand lay-up process

Fig. 6.4 shows technique flow chart of hand lay-up process. The process flow is further summarized following three steps.

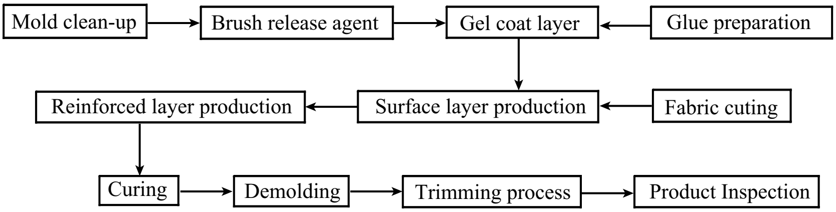


Fig. 6.4 Technological process of hand lay-up.

(1) Cut reinforced materials, prepare the glue.

(2) Mold clean-up.

(3) Brush release agent.

Release agent commonly used in hand lay-up process includes the following three categories: first, polyvinyl alcohol (PVA) release agent is water or alcohol solution with 5% of PVA; second, wax release agent is mostly the imported special demoulding wax; third, new liquid release agent is wax-free polymer solution. We can also use silicone grease, methyl silicone oil for metal mold and polyvinyl acetate cellulose and so on for wood mold.

(4) Gel coat layer preparation.

In order to solve the bad surface quality of FRP (wove pattern protrudes due to UP curing contraction), a special layer is usually designed on the surface of products, which is called surface layer. It can be prepared by glass fiber felt or gel coat resin with pigment (called gel coat layer). It is of high resin content, so it is also known as resin-rich layer. It can not only beautify the appearance of products, but also protect products from surrounding environment, medium erosion, improving their weatherability, water resistance, chemical resistance and wear-resistant performance, thus extending service life of products. Product quality and surface performance are directly influenced by gel coat layer, and therefore it is essential to choose high-quality gel coat resin and pigment paste, as well as correct brushing method. Gel coat layer should not be too thick or too thin. If too thin, products protection will not be achieved; if too thick, gel coat layer easily cracks. Its thickness is controlled at a range of 0.25∼0.5mm, or 300∼500g/m^{2}glue quantity per unit area.

Gel coat layer is usually applied by either brushing or spraying. Gel coat brushing is generally conducted twice. The second time should be carried out only upon the end of curing of the first. The brushing direction of the two should be perpendicular to each other. We should immediately lay-up a soft layer of reinforced material such as surface felt when resin begins to gel. This not only enhances the gel coat layer (to prevent cracking), but also contributes to the bonding of gel coat layer and the structure layer. The tools used are special brushes (short hair, soft texture, no losing hair). We should brush evenly and thoroughly and avoid introducing air into it.

Spraying can produce gel coat with even thickness, good cover rate, color uniformity and high surface quality. Usually, either gel coat machine or sprayer is used in operation. Gel coat machine pushes gel coat and curing agent through the pump straight into the tips and evenly spray the mixture onto the mould surface. It has high production efficiency, and is suitable for mass production.

UP gel coat resin contains many special types of resins that suit various uses. A typical gel coat formulation is given by:

Transparent gel coat resin	100
Methyl ethyl ketone peroxide	2 (initiator)
Cobalt naphthoate	1∼4 (accelerator)

Pigment paste	8∼10 (brushing), 4∼6 (spraying)
Diluent	2∼8 (spraying)

(5) Ply paste.

Molding operations include ply paste (surface layer fabrication, reinforced layer facture, stiffener fabrication) and curing.

Surface layer is produced by surface felt. It would prevent gel coat from wove exposure, forming resin-rich layer on the surface, thereby enhancing leakage and corrosion resistance of products. The surface felt with G_f of 30g/m^2 or 50g/m^2 is tailored according to the size of mold, paved on the surface of gel coat, glued with hair roller, and then defoamed with debubbling roller. After the process, the surface layer should have strictly no air bubble and glue content of surface layer is controlled at 90%.

Reinforced layer manufacture: reinforced layer is load-bearing layer of glass fiber reinforced plastics. Usually glass cloth or chopped mat is used as reinforced material. To implement the layer, we first cut and number the glass cloth and mix glue based on the amount of a paste, and then conduct ply paste.

Paste tools have a dedicated brush, special hair roller, and debubbling roller, scratch glue plate and so on. Pasting is a process that we should brush glue (or by glue roller) on the surface of the mold firstly, and then put the fabric layer (or felt) on the surface by hand, and then smooth and brush glue (or force back and forth with glue roller so that glue immerges into felt), and then scratch and defoam. Now we may paste the second layer, a layer of cloth again and brush glue. We repeat the process until the layer reaches the required thickness. We can cut cloth (or hand-torn felt) when encountering block corner or uneven pavement, and then compact smooth. Paste process should exclude bubbles as much as possible in order to control the glue content and its uniformity. We should also stagger the joints. The overlapping width should be 50mm. Furthermore, we should pay attention to the ply direction and stacking sequence.

(6) Cure.

FRP products generally cure at room temperature 15∼30°C for 8∼24h and can release after 8h. They can also cure at 60∼80°C for 1∼2h and demould if we want to increase production efficiency. After demoulding, an extra heating treatment at 60∼80°C for 1∼2h can improve the curing degree of products.

(7) Demould.

Demould is a key process for FRP hand lay-up. It is directly related to product quality and the efficient use of mold. Of course, it also depends on the quality of mold design, mold surface finish, release agent and brushing effect. Generally we use gas-off, eject-off, water-off, etc for hand lay-up products.

(8) Trim and mechining.

(9) Acceptance.

3) The raw materials of hand lay-up process

(1) Reinforced materials.

The reinforced materials of hand lay-up process should be susceptible to resin infiltration and have a certain capability of deformation. Commonly used materials are the following.

① Roving cloth (woven roving).

Roving cloth namely tartan cloth is the main reinforced material for hand lay-up process. It can improve impact properties of glass fiber reinforced plastics. The cloth has good deformation, high thickening efficiency, and is easy to soak by resin and easy to exclude air bubbles. Moreover, there are plenty of manufacturers in the market, thus enough supply. Roving cloth in the market covers a complete set of different specifications with low price. Its thickness is typically at 0.1∼0.8mm.

② Twisting cloth.

There are plain cloth, twill cloth, satin cloth, unidirectional cloth and so on. The thickness is 0.05mm, 0.1mm, and 0.2∼0.6mm respectively and they are generally waxy on the surface. The glass fiber reinforced plastics produced by twisting cloth have smooth surface and good air tightness. The drawbacks are that their price is high, difficult to soak by resin, and thickening effect is bad.

③ Glass cloth tape.

Use to strengthen the profiled and special parts.

④ Chopped fiber mat.

Chopped fiber mats have two kinds: E-glass fiber and medium-alkali glass fiber. It is the easiest to soak by resin, easy to exclude air bubbles and convenient to operate. It has good deformability and the products are with high resin content (60%∼80%). As a result, it has good anti-leakage property, and hence widely used in the waterproof products and corrosion-resistant products as anti-leakage layer. Commercial chopped fiber mats are available in many widths to 3000mm, and weights from 200g/m^2 to 1000g/m^2.

⑤ Staple fiber.

Used for filling the dead corner.

⑥ Surface felt.

Surface felt is used for resin-rich surface layer. It is produced by putting monofilaments with diameter of 10∼20 microns alternatively. It is very thin and generally has the single weight of 30g/m^2 or 50g/m^2.

(2) Resin.

FRP hand lay-up process has the following requirements for resin.

① It has a good wettability for glass fiber, suitable viscosity for hand lay-up process, that is 0.2∼0.8Pa·s.

② It can gel and cure at room temperature. There is no low-molecular compounds release in curing process, no need of pressure. It meets the requirements in use.

③ Non-toxic or low toxicity.

④ Cheap.

The most commonly used resin is unsaturated polyester resins (UP), followed by epoxy resin, and phenolic resin is less used in the hand lay-up process. UP is of more suitable properties and has the largest amount of resin in hand lay-up process. It is colorless and transparent, so it can match a variety of colors. It is of low prices and wide range of different specifications.

(3) Filler.

Adding fillers to the resin can not only reduce costs, increase stiffness, but also reduce shrinkage and increase flame-retardant effect. Some of them, such as calcium carbonate, talc, can reduce cost and shrinkage; glass powder, quartz powder can improve the strength of product; cast stone powder, ceramic powder can improve corrosion resistance; graphite powder, metal powder can increase conductivity; hollow glass beads can increase stiffness. In the hand lay-up process, adding fillers will affect the operations, and its content is generally controlled at 10% ~20%. Granularity of filler is larger than 300 meshes, and water content is below 0.5%.

(4) Others.

There are other raw materials in use, such as thixotropic agent (diatomite) and coloring agent (pigment paste, color). Coloring agent is got by adding titanium dioxide and a variety of pigments into carrier resin and grinding by the three rollers mill. It is added to gel coat resin so as to deploy the color of gel coat, typically adding at a range of 4%~8%.

6.2.2 Bag-pressurized molding, compression molding, laminating molding

The curing molding after dry hand-up preforming process, according to different pressure methods, mainly includes the following process: ① vacuum pressure bag molding; ② pressure chamber (pressure bag) molding; ③ vacuum bag - autoclave molding; ④ compression molding; ⑤ laminating molding.

Bag-pressurized molding includes vacuum bag, pressure bag and vacuum bag-autoclave molding. In pressure bag molding the negative pressure caused by the vacuum between molding bag and the mold or external load makes composites flan cling to the mold, then cure for final parts. Its biggest advantage is that it uses only one mold (male mold or female mold) while forming good quality parts with complex shape and big size, and it is also capable of manufacturing sandwiched structure. The process flow chart of pressure bag molding is as shown in Fig. 6.5. According to different pressure methods it can be divided into the vacuum bag molding, pressure bag molding and vacuum bag - autoclave molding.

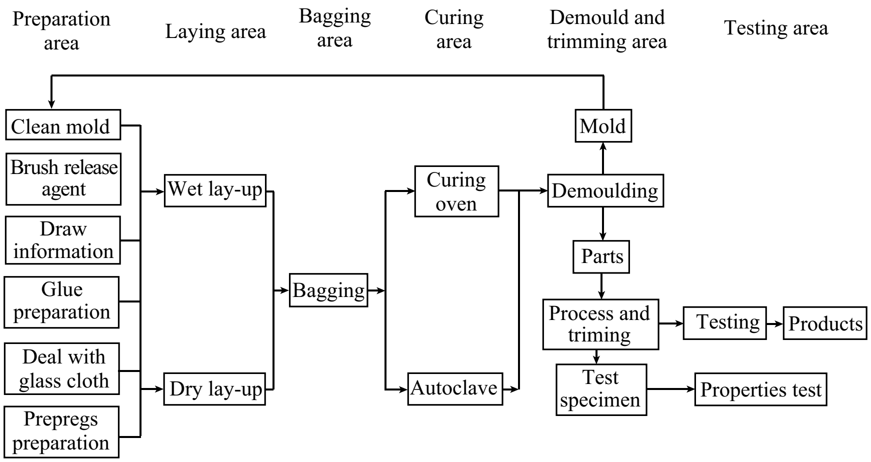


Fig. 6.5 Technique flow chart of pressure bag molding.

1) Vacuum bag molding

The working principle diagram of vacuum bag molding is shown in Fig. 6.6. Its main equipments are mold, vacuum system and an oven or other heating space to provide heat source. Vacuum bag molding is a forming method which makes use of the atmospheric negative pressure and its force on the products when vacuum is produced by pumping during curing process. It works in the following procedures. First we put the flan parts between the vacuum bag and mold. Then we start the vacuum pump to form negative pressure. Atmospheric pressure exerts force through the vacuum bag onto the flan parts. Vacuum bag should have ductibility, which is made from high-strength nylon film or similar materials. It is bonded together with the mold by sealant adhesive tape. Breathable felt is normally placed in the vacuum bag in order to keep the vacuum pathway unblocked. We demould to get the part after curing completely.

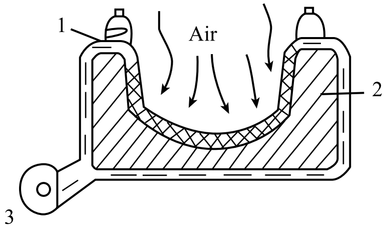


Fig. 6.6 The working principle diagram of vacuum bag molding: 1-vacuum bag; 2-mold; 3-vacuum pump.

The process is simple and does not require special equipments. It is often used to produce the parts that cure at room temperature and is also useful to produce the parts that cure at high, middle temperature in curing furnace.

It is suitable for molding large products, such as hull, bathtub and small aircraft components. As vacuum bag pressure is only up to 0.1MPa, the method can be applied only to composite plates below 1.5mm thick, as well as honeycomb sandwich structure. Composite plates with over 1.5mm thickness will require higher pressure, while honeycomb sandwich structure can only be produced under low pressure as a result of its own characteristics. Honeycomb core is likely to collapse under high pressure.

In low cost plan, decreasing material cost has become a key objective of research. The low-cost resin matrix material emerges as time requires. The so-called low-cost resin matrix material is the material that can cure at 130 ~ 150°C, and in particular, under 0.1MPa namely vacuum pressure. Such resin matrix material can significantly reduce manufacturing costs. LTM resin that was developed by the ACG in Britain is one of the examples. Large structure has been created with LTM, such as the X39 wing, DC-10 rudders. All of these are manufactured using vacuum bag method.

2) Pressure bag molding

Pressure bag molding is shown in Fig. 6.7. It is developed on the basis of the vacuum bag molding for some structure parts which need the molding pressure to be greater than 0.1MPa but not too much. It is mainly used to form thin skin and honeycomb sandwich structure. It places pressure on the flan parts by pumping compressed gas into air chamber made of rubber capsule (pressure bag), so the method is also called as pressure Chamber molding or pressure room molding. The pressure can be up to 0.25~0.5MPa. As a result of the high pressure, the mould should have high strength and rigidity, and at the same time thermal efficiency should be considered. Therefore, light metal mould is generally used and heating is accomplished within the mold. Similar to vacuum bag molding, this method is with simple equipments, easy operation and requires relatively small investment.

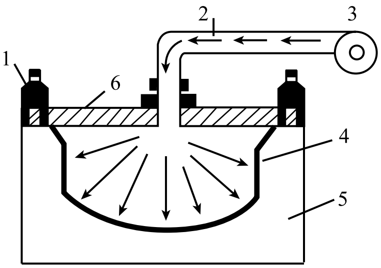


Fig. 6.7 The schematic of pressure bag molding:
1-sealant clamping device; 2-compressed air; 3-air compressor; 4-pressure bag; 5-mold; 6-cover.

3) Vacuum bag-autoclave molding

This method is widely used in forming advanced composite materials. Autoclave system is shown in Fig.6.8. The working principle is by means of the program -controlled temperature and static gas pressure in autoclave to make composite flan parts cure in a certain temperature and pressure. At present autoclave molding is still major manufacturing method for the vast majority of high load-bearing composite structure, as the product by this molding method has uniform resin content, compact internal structure and good internal quality. For thermosetting resin composites, the fiber as a reinforced agent does not incur any chemical reactions, while the resin has gone through complex chemical process, transforming from viscous flow state via high elastic state to glass state. These reactions need a certain temperature and a certain pressure.

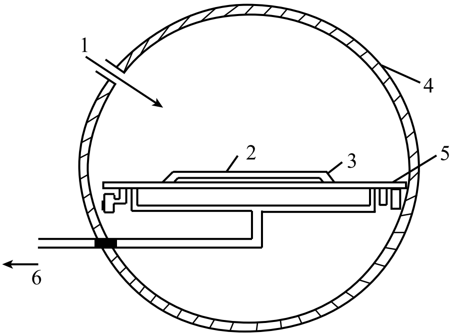


Fig. 6.8 The schematic of autoclave system:
1-compressed gas; 2-part; 3-vacuun bag; 4-autoclave vessel; 5-template; 6-vacuum port.

Autoclave is composed of tank, vacuum pump, compressor, gas storage tank, control cabinet and so on. Effect of vacuum pump is to form a low-pressure environment for pre-compaction absorbing glue after flan part is sealed packaging. Compressor and gas storage tank are responsible for pressurizing the autoclave. The gas within the tank is heated by the electrical heating devices, and pressure is produced by the compressor via gas storage tank and then the compressed hot gas is charged into the autoclave. Usually, plain air is adopted. Process of forming composite material parts is shown in the following: first we cut out prepregs and pave plies according to the drawing of parts, then repair and cut the edge profile by templet, and mark the coordinates of fiber orientation, at last seal and package. The objective of seal packaging is to form a vacuum system for the flan part, and then vacuum pumping is to discharge the air and volatiles in parts. We heat it to a certain temperature and pressure on the parts for pre-compaction (also known as pre-absorbing glue) and finally cure.

For autoclave molding, it is very important to form vacuum for the flan part and constitute an isolated, glue-permeable, glue-absorbing and breather system, so as to determine the resin flow in the flan part and its direction, outflow volume and its control as well as way-out of wrapped gas and the uniform distribution of external pressure. This is vacuum packaging system for autoclave. Ply sequence of seal packaging materials is shown in Fig. 6.9. This vacuum system is conducive to the extraction of low-molecular volatile compounds and the wrapped gas in prepreg. To obtain ideal uniform structure in the curing of polymer materials, applying pressure in a certain stage to build dense structure is a pre-requisite. The pressure must be imposed in the phase transition range from flow state to high-elastic state of the resin. A pressure too early will make a large amount of resin to lose, and a pressure too late will not work because the resin has become high-elastic state. Free high-elastic state will contain many air bubbles and pores, resulting in no dense structures. Uniform pressure in autoclave is a guarantee of good internal quality for composite materials. In order to control the changes of resin, many researchers have worked on the curing model, including flow model, thermo-chemical model, pore model and internal stress model, and established the expert system. Its key points are shown here: under a certain temperature and pressure the resin flows from bottom to top, we can determine its pressure point range by means of the changes of resin viscosity and dielectric properties. Once the resin enters high-elastic state, it has a sharp increase in the viscosity and its elastic modulus also increases, videlicet, the curing degree increases. The pore volume and internal thermal stress are related to the structure and density of the resin after curing, as well as the formed network structure of the resin. The incompact structure may wrap void. Dislocated structure or inappropriate rigid distribution may cause internal stress. Of course, bad control of heating or cooling, especially cooling too fast, will also lead to the formation of internal stress due to uncoordinated expansion and contraction.

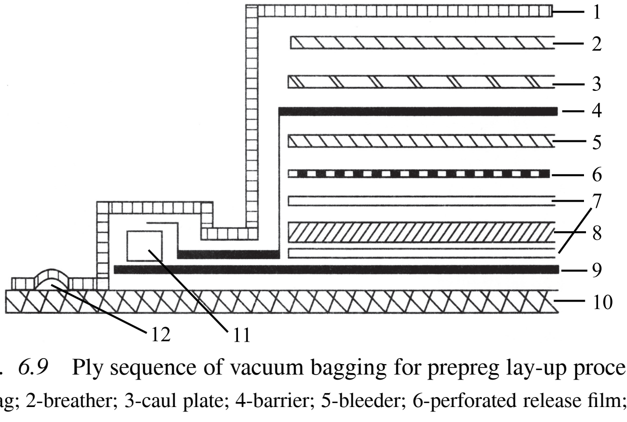


Fig. 6.9 Ply sequence of vacuum bagging for prepreg lay-up process:
1-vacuum bag; 2-breather; 3-caul plate; 4-barrier; 5-bleeder; 6-perforated release film; 7-peel ply; 8-prepreg lay-up; 9-non-perforated release film;10-mold; 11-metal dam; 12-sealant tape.

Although autoclave method has lower energy efficiency, high equipment investment, and must be accompanied with the air compressor and compressed air tank and security system itself, due to the inner uniform temperature and uniform pressure, the relatively simple mold, it is suitable for manufacturing complex large skin, wallboard and hull plate. As a result, aviation composite structures mostly utilize this method. However, from the perspective of lowering manufacturing costs, we should develop non-autoclave molding, such as winding method, pultrusion method, RTM, especially for fiber braiding/resin film infusion process, which draws many people's attention because of its low cost and applicability for large structure.

4) Compression molding

Compression molding is an approach that puts a certain amount of stacking flan or molding compound into metal mold, makes them plasticize, flow and fill the mold cavity at a certain temperature and pressurize, and then cure to products (see Fig. 6.10). Its main difference from autoclave forming is that the flan parts will not be put in a jar-like black box in molding process, and hence it has a good observability. Also, pressure can be adjusted in a wide range. Furthermore, compression molding features an ease of internal quality assurance and a precise geometric shape. Thus it is widely used in the manufacture of complex structures, such as aero-engine blades.

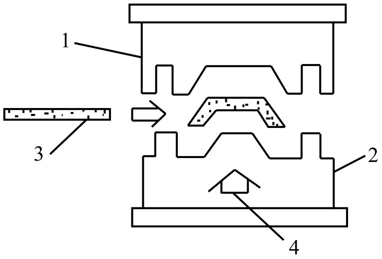


Fig. 6.10 Schematic of the compression molding process:
1-male mold; 2-female mold; 3-stacking flan; 4-temperature measurement point.

Thickness tolerances of the parts can be controlled within ±3%∼ ± 5%, deflection is less than 1mm (1m long). Difficulties of this forming method are the choice of the mold structure form, coordination of modules of mold and skills of part demoulding and taking out. As interlaminar shear strength of fiber composites is low, it suffers from easy delamination during demoulding. Most short fiber thermosetting molding compounds such as SMC use compression molding of matched die mold for various glass fibers reinforced plastic applications.

5) Laminating molding

Reinforced materials, such as glass fiber cloth, are wetted by resin in dipping machine, dried and made into prepreg (often referred to pre-impregnating adhesive cloth or varnished cloth). Then the prepregs are cut and stacked together. It follows that they are placed under a certain pressure and temperature by a dedicated multilayer tablet press for an appropriate time to form laminating molding products.

This is laminating molding process, also a kind of flat-panel compression molding. It can efficiently produce a variety of composite laminates, insulating boards, wave boards and copper foil coated laminates and so on.

6.2.3 Preforming method of short fiber deposition

This method is to make short fibers into felt-like flan similar to the shape of product, and then impregnate, compress and cure to get composite material products.

Preforming using short fiber usually has two methods: fiber suction accretion and fiber spray method.

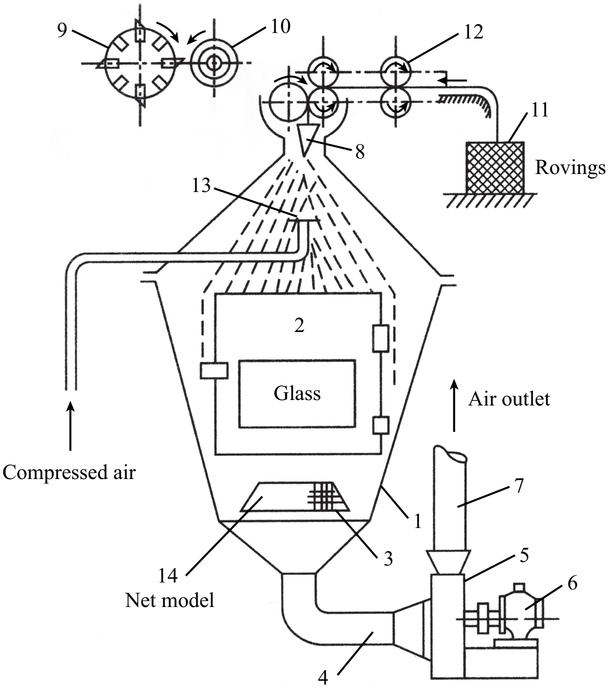


Fig. 6.11 Device of short fiber suction accretion performing:
1-outer shell; 2-glass window; 3-rotating table; 4-air path; 5-exhaust fan; 6-motor; 7-exhaust air tube; 8-bell mouth; 9-roll wheel with blades; 10-rubber roll; 11-roving bobbin; 12-guide wheel; 13-turbine with needle; 14-net model.

Fiber suction accretion method is shown in Fig. 6.11. The device includes an outer shell 1, rotating table 3, air path 4 and exhaust fan 5 which are linked with the middle of the table. Exhaust fan is driven by the motor 6. It pumps the air from the shell through the tube with a filter 7. Above outer shell there is a bell mouth 8, where is equipped with a cutter setup. Cutter setup includes roller wheel 9 with blade and roller 10 wrapped with elastic rubber, the blade contacts with rubber roller when rotating. The non-dipped glass roving wound on the bobbin 11 is guided by two guide wheel 12 into the rubber roller 10 when cutting fiber. Blade wheel rotates with the rubber roller at the same time, when the blade edge contacts with the rubber roller, the yarn will be cut off. The length of fibers depends on the distance between the two blades. In order to cut different length of fiber, the blades can be adjusted. In order to disperse the cut yarn into single fiber and drop evenly, below the bell mouth it is equipped with a high-speed rotation of turbine with needle 13. When the cut yarns drop on the turbine, they are dispersed into single fiber by its breaking up and centrifugal effect. The single fibers deposit on the net mold or perforation model 14, which is made with the needed shape of product and mounted on the rotating table. The pumping of air ensures the fiber's deposition on the net mold. Proper regulation of air flow and rotation model can help to construct fiber layer with uniform thickness. In the early deposition, more fibers accumulate in the front of model. With the increase of the thickness, the air is difficult to go through the top of model, and the air is easy to go through the side of model where fibers accumulate less. Therefore, more fibers accumulate at the side of the model at later stage, so that automatic adjustment of the fiber layer thickness is completed. For complex shape flan, in order to obtain the uniform thickness, we need more complicated models, with special shelter device built in model to change the air flow and falling direction of suspended fibers. In addition, there are many gates and gaps with switch on the device shell. Opening some gates and gaps can change the direction of fiber air flow, so that fibers layer evenly distributes on the model. Before demoulding, we need to spray the small amount of resin on the flan lightly, and dry it at 100∼120°C. Up to here, we have produced a mats-like preforming flan.

The suction accretion method can also carry out in liquid medium (such as water). The short fibers are dispersed in the liquid and we make it uniform by stirrer. At the same time liquid circulation is formed by pump. Then we use net mold for preforming flan and dry it for use. Thicker and heavier flans can be produced by this method than using air as medium and the production efficiency is higher (about 150kg/h). The method has a high degree of mechanization and more stable in quality.

Fiber spray method is to spray short chopped fibers or the pre-mixed fibers on the mold by compressed air flow to get the flan. Identical to fiber suction accretion method, cutter cuts continuous long yarns from the yarn creel into a certain length of short yarns. When the short yarns fall down, air swirl disperses it into single fibers and make them suspend in the air. We jet short fibers on net mold through the hose, and at the same time spray resin glue into the net mold so that it mixes with the fibers. This is precisely the spray-up forming process we will learn in the next section. Just a little forecast: the major feature of spray-up forming is to complete fiber spraying, resin spraying and impregnation at the same time.

Short fiber flan by suction or spray accretion method goes through further post-impregnated resin glue, pressure, and hot curing. Dipping may be conducted using vacuum resin infusion, RTM and spray method (i.e., spray-up molding: fibers and glue can be mixed within or outside the spray gun). For large-size products, we use vacuum bag, pressure bag, autoclave to apply pressure; for the small-size products, we use hot press instead.

6.2.4 Spray-up forming process

Spray-up forming process is to spray short fibers and atomized resin on the surface of the open mold through the spray gun at the same time, then roll and cure to get composite material parts. Preparation of the mold and the material is basically the same to hand lay-up process, and the main reform is the usage of spray equipment, transforming stacking process and manual paperhanging process to continuous operation of a machine gun. Spray-up forming process is shown in Fig. 6.12.

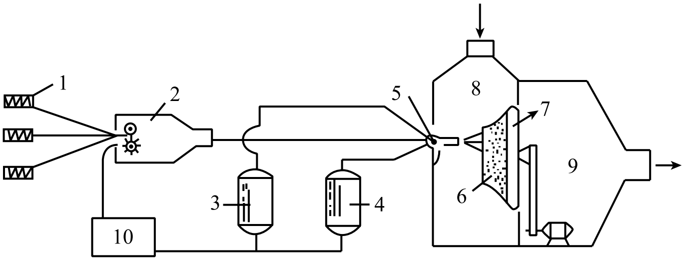


Fig. 6.12 Schematic of the spray-up process:
1-rovings; 2-glass fiber cutter; 3-resin A can; 4-resin B can; 5-spray-up gun; 6-sprayed product; 7-turntable; 8-isolation room; 9-ventilation hood; 10-compressed air.

In general, the resin with initiator and the resin with promoter will be put in two different cans, deliver them to the gun according to the proportion by the hydraulic pump or compressed air, and then spray-up in atomization from the two sides of gun (or mix within the gun). At the same time we will cut glass fiber roving by cutting machine and spray out the fibers from the center of the gun, depositing them together with the resin on the mold evenly. When the depositing layer reaches a certain thickness, we apply pressure to it by hand-roller so that resin impregnates fibers, making it compact with air bubbles removed. Then we continue to spray until the completion of flan and eventually conduct cure molding. Flow chart of spray-up forming process is shown in Fig. 6.13.

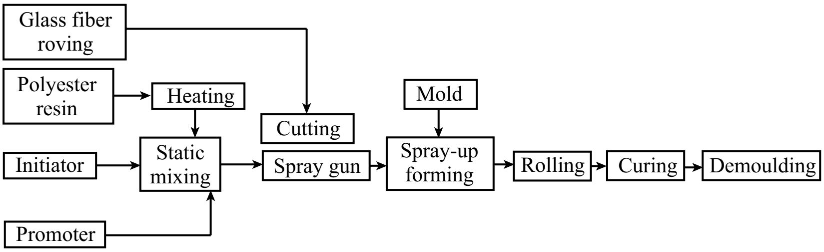


Fig. 6.13 Technique flow of spray-up forming.

Before spraying, we should check gel time of the resin, which can be determined by spraying a small amount of resin into the canister. We also must examine the ratio of the resin and glass fiber, which generally is 2.5:1∼3.5:1. We may start spray-up forming process as soon as gel coat resin gels (soften and anti-sticky hand). We should spray a layer of resin on the mold if there is not gel coat resin layer and then start the cutter, and spray the mixture of resin and fiber. The first layer should be sprayed very thinly (about 1mm), and rolled carefully. First of all, we use a short mohair roller, then a bristle roller or a spiral roller. This is to ensure that the resin and curing agent mix uniformly and glass fiber is infiltrated completely. We much operate carefully so that no air bubble in this layer and this layer is wetted by gel coat resin completely. When first layer gels completely we may proceed to the second layer. The second layer onwards should be approx. 2mm in thickness. If too thick, it is difficult to remove air bubble, thus not able to guarantee the quality of products. After spraying each layer air bubble must be removed carefully by rolling. The process repeats until it reaches its design thickness.

In order to obtain high strength products, roving fabric must be used too. Sufficient resin must have been sprayed on the mold before laying roving fabric. It follows with rolling and removing air bubble of course. For most spray equipments, the spraying rate is 2∼10kg/min. Similar to hand lay-up process, we can use surface felt in the final layer, and then we paint outer coat. Curing, finishing, post-curing and demolding process are the same as hand-up process.

The method has certain requirements for raw materials. The viscosity of resin system should be moderate (0.3∼0.8Pa·s), such that it is easy for atomized spray, air bubble removal and fibers wetting and meanwhile keeping it neither prone to flow away nor easy to induce static electricity. The most commonly used resin is unsaturated polyester that cures at room temperature or a slightly higher temperature under no pressure. Its glue content is about 60%. The fiber used is pretreatment untwisted rovings. In the final product, Fiber content is 28% ∼33% in products and fiber length is 25∼50mm.

Spray-up molding is a semi-mechanized molding technology for improving hand lay-up process. It was developed in the 1960s overseas and there are whole sets of spraying equipment for sale, supplied by companies such as the VENUS Company, CRAFT Company in the United States.

There are various types of spray-up forming methods (equipments). We now classify them using the spray power and mixing form of glue.

1) Pneumatic and hydraulic type of glue spraying power

(1) Pneumatic type (low pressure type).

Pneumatic type is air ejection spray system. It sprays the atomized glue and coats on the core mold by compressed air. Parts of resin and initiator smoke spread to the surrounding air by compressed air, so this form has been rarely used.

(2) Hydraulic type (high pressure type).

Hydraulic type is non-air hydraulic spray system. It squeezes the glue into droplets by the hydraulic pressure and sprays them on the mold. First pump the resin into the spray gun, jet by pump pressure; then pressurize resin can and curing agent can by air compressor, and under the pressure jet the resin and curing agent into the spray gun. There is no fluctuation caused by compressed air spraying and thus no smoke and the material waste is less.

2) According to mixing forms, there are: internal mixing type, external mixing type and pre-mixing type

(1) Internal mixing type.

Internal mixing type is to deliver the resin and initiator to the turbulent mixer of spray gun respectively for thorough mixing, namely mixing the curing agent within the spray gun before spraying. Because the initiator does not contact with the compressed air, the initiator does not vaporize. The disadvantage is that the spray gun can be easily blocked, which requires regular cleaning using solvent.

(2) External mixing type.

External mixing type is to spray the resin and initiator or the resins with promoter and curing agent respectively by the spray gun, so that they atomize in the air outside and mix. It includes two types, spray curing agent separately and spray the resin with curing agent. Due to the initiator's contact with the air before mixing with resin, and its volatile nature, this approach wastes material and causes environmental pollution.

(3) Pre-mixing type.

Pre-mixing type is to deliver the resin, initiator, and promoter in the static mixer firstly for fully mixing, and then send it to the spray gun to spray out.

It is generally believed that it is better to use low pressure, mix the resin and curing agent within the spray gun, and mix short fiber and resin in the air. This is named low pressure no-air spray forming process.

In addition to the spray gun a variety of spray forming equipments are mostly similar. They all consists of the following parts: pump for the transmission of the resin or curing agent; pressure tank for curing agent; pressure tank for washing solvent; reinforcement cutter; a variety of air conditioners and metering devices for control; a variety of hose for the transmission of materials; spray gun. There are many different types of spray gun. The most commonly used are as follows: external mixing type; no-air external mixing type; air-assisted internal mixing type; no-air internal mixing type; two-can system. Typical spray forming machine is double pressure tank glue-supplying type, pump glue-supplying type, as well pump cans glue-supplying type, etc.

For spray-up forming process, the productivity is 2∼4 times of that in hand lay-up process. The labor intensity is low. A relatively low equipment investment can reach medium-volume production; and glass fiber roving is used in place of fabric, lowering materials cost; good product integrity, and no lap joints; the shape and size of parts has no restrictions; we can freely adjust product thickness and the ratio of fiber and resin. The main disadvantage is big site pollution, and high resin content, low load-bearing capacity of parts. It is suitable for the manufacture of hull, bathtub, car shells, containers, plates and other large components.

6.2.5 Resin transfer molding (RTM), resin film infusion (RFI)

1) Resin transfer molding

Resin transfer molding (RTM in short) is a new forming process of composite materials evolved from the wet lay-up and the injection molding process. It is a low-cost technology suitable for more species, medium-volume production and high-quality composite material products.

It greatly reduces the manufacturing costs of composite materials as it requires no prepregs. The preparation of prepreg requires more expensive equipment investment, and very high operation technology; to prevent the reaction of resin prepreg, it often needs to be stored in low temperature conditions, so the cost is quite high. In resin transfer molding process, we only arrange the corresponding fibers to form the structure parts into preformed body in accordance with certain orientation, and then introduce the resin to the preform. After resin cures, the final structure of composite materials is made.

Resin transfer molding is also called pressure injection molding, in which the resin is injected into the sealed cavity by pressure. It infiltrates the fabric preform, and then cures. RTM is shown in the Fig. 6.14, its process is: mold preparation → gel coat coating →gel coat curing →manufacture of pre-forming flan and insert installation, etc. → mold clamping and sealing →resin injection → resin curing → open mold → demould → (secondary processing). It mainly includes the following:

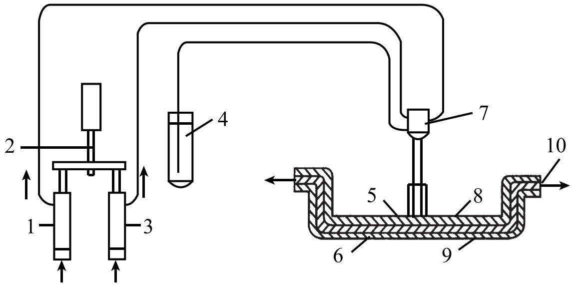


Fig. 6.14 Schematic diagram of RTM molding process:
1-ratio pump; 2-resin pump; 3-catalyst pump; 4-washing agent; 5-resin matrix;
6-dry fiber preform; 7-mixer; 8-male mold; 9-female mold; 10-exhaust vent.

(1) Manufacture of dry preform. Prepare the reinforced fibers into a certain shape in accordance with the requirements and put in the mold. The size of preform should not exceed the closed area of mold, thus convenient for close and seal. Reinforced fibers in the mold must to be uniform in density. In general, it is integral structure or three-dimensional braided structure. Mats accumulation and combination of sewing parts also will work.

(2) Filling mold. After the mold is closed, we inject resin into the mold under certain conditions. Resin impregnates fiber-reinforced preform and excludes the air at the same time. When the excess resin overflows from spill mouth, we stop injecting resin. In glue injection process, we may impose compressed air on the resin tank, vacuuming the mold to exclude air bubble as much as possible. The mold is usually warmed up or heated a little before filling in order to maintain a certain viscosity of the resin.

(3) Curing. After the mold was in full, we heat the resin so that they become crosslinked in the curing reaction. If the resin cures too early, it will impede the complete infiltration of resin to the fiber, resulting in void in the final parts and reducing its performance. The ideal starting time of the curing reaction is the time when the mold is just in full. Curing should be carried out under certain pressure. It can be done either at one stroke in the mold or in two stages. The second stage can be carried out in the curing oven after removing from the mold.

(4) Open mold. When curing is complete, we may open the mold and remove parts. For the parts curing completely post treatment can be given.

The main parameters of RTM process is injection pressure, injection speed, injection temperature and so on.

(1) Pressure. Pressure is one of the main parameters affecting the RTM process. High or low pressure depends on the mechanical requirement of the material and structural design of mold. High pressure needs high-strength and high-rigidity of mold and large clamp force. RTM process hopes to complete resin injection at a relatively low pressure. In order to lower the pressure, we take the following measures: reduce resin viscosity; appropriate design of injection mouth and exhaust port; appropriate design of the fiber arrangement; to reduce injection speed.

(2) Injection speed. Injection speed depends on the wettability of resin to fiber, surface tension and viscosity of the resin, and is also affected by the activity period of resin, the ability of pressure injection equipment, mold stiffness, the size of parts as well as fiber content. It is desirable to have high injection speed to enhance production efficiency. In order to exclude air bubble we should increase the flow rate of resin, but the increase of injection speed always accompanies with the increase in pressure. The speed of filling mold also has impact on the close combination of fiber and resin. The macro-flow can be used to predict the defects such as air bubbles, weld line and incomplete filling. The micro-flow can be used to

estimate the impregnation between the resin and fiber and the excluded volume of gases among the micro-fibers. As the complete resin impregnation to fibers needs a certain of time and pressure, slow filling pressure and certain filling anti-pressure can help to improve the micro-flow of RTM. However, the increase of filling time reduces the efficiency of RTM.

(3) Injection temperature. Injection temperature depends on the activity period and the temperature of the minimum viscosity of resin system. Without significantly decreasing the gel time of the resin and in order to enable the resin adequately infiltrating fiber under the minimum pressure the injection temperature should be as close as possible to the temperature of the minimum viscosity. Too high temperature will shorten the work life of resin. Too low temperature will increase the viscosity of resin and the injection pressure, and also hinder the resin infiltrating fiber. Higher temperature would reduce the surface tension of resin leading to the air rise in fiber bed, which is conducive to the discharge of air bubbles.

RTM machine generally includes hydraulic pump (such as resin pump, initiator pump), injection gun and mixer, cleaning devices, vacuum systems, air compressor systems and control systems. RTM machine has single-component type, two-component pressure type, two-component pump type, adding catalyst pump type, and so on (see Fig. 6.15). The simplest RTM machine has only one pressure pump, and it is applied to low reactive resin single-component injection system. Resin has to be heated to high temperature and cure, and it has long production cycle. Because it is one-component resin system, in order to prevent the resin gel from curing in the pressure system, cleaning must be done for every injection. We must choose two-pump pressure injection system for the high reactive resin system (such as composed of A and B). A, B is mixed by a mixing head, and are injected fast into the mold. Once high reactive resin is mixed, it begins to cure soon, the typical curing time is 1$\sim$5min. Therefore, when dealing with high reactive resin, there must be enough time to ensure that residual resin can be cleared from the mixing head before its curing. In the newly developed RTM equipments (such as Magaject-II) A and B are put in different resin tanks. They are pushed into injection pipe by pressure pump (gear pump or piston pump). When injecting, the flow resins mix fully in mixing head and inject the mold. When the mold is full and the pressure injection process is complete, A, B return to their pipe respectively. Meanwhile, the mixing head is dried by compressed air after the self-cleaning by the solvent. This automated RTM equipment allows the use of highly reactive resin system and is applicable to mass production. Under normal circumstances, we use hand-held injection gun or fixed injection nozzle to inject the resin through the mixing head into the mold. Combined hand-held gun with mixing head is generally used for relatively low pressure tank and dual-piston pump pressure injection system. Automatic fixed injection nozzle is fit for RTM pressure injection system of higher injection pressure. When using heated mold, the fixed injection nozzle must be cooled by liquid. In order the resin can expeditely be injected into mold, injection system should be cleaned with solvent after each injection, and then dry with air.

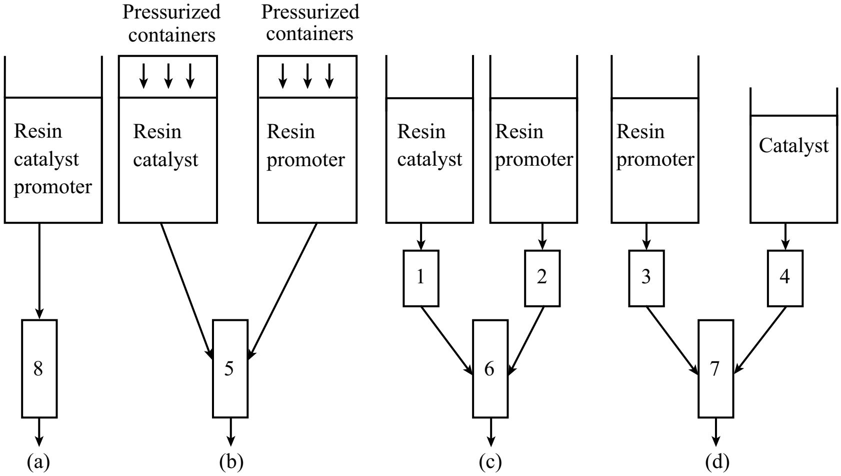


Fig. 6.15 The injection means of RTM:
(a) one-component type; (b) two-component pressure type;
(c) two-component pump group; (d) adding catalyst pump;
1,2,3,4-metering pump; 5,6,7-mixed into the machine; 8-injection machine.

RTM mold is a closed mold composed of the upper mold and bottom mold. Besides the need to ensure the shape, size and surface accuracy of products and other basic requirements, it should have no deformation and destruction under injection pressure. It should also be equipped with the devices of clamping and opening the upper and bottom mold, and also have appropriate injection nozzle, flow channel, exhaust port (spill mouth) and the seal. The mold can be generally electrified for heating. The commonly used materials for mold production are glass fiber reinforced epoxy or polyester resins and electroplating metals (such as aluminum, nickel) and so on.

In RTM process the requirements on the resin system can be summarized as follows: low viscosity (0.1$\sim$1Pa·s) at the room temperature or lower temperature and a certain work life (such as 48h); the resin has a good wettability, match and adhesion to reinforcing material; the resin does not contain solvents or volatiles and does not release small molecule during curing; the resin has a good reactivity at the curing temperature, and post-processing temperature should not be too high.

RTM is characterized by: the size of product is decided by the cavity, the product has high size precision, both sides of the component have a (smooth) moulded surface, no need supplementary processing, but the process is very difficult, injection cycle is long, injection quality is difficult to control, so a higher level of skill is required for the operators; products have high resin content and matched tooling is expensive and heavy in order to withstand pressures; good health and safety, and environment control due to closed mold process. It is suitable for the parts with a certain thickness and size requirements such as aircraft nose solid structure radome, auto composite materials bumper, A320 engine pylon rectifier tail fairing cone.

In order to improve the fluidity and impregnation of the resin in cavity, and to exclude air bubble more exhaustively, it is developed to pump vacuum in cavity, inject the resin by injection machine, or inject the resin only by the pressure difference between the outer and the inner due to vacuum. This is called vacuum-assisted RTM process. Terminologies include Vacuum-Assisted Resin Transfer Molding (VARTM), Vacuum-Assisted Resin Injection (VARI), Vacuum Resin Transfer Molding (VRTM) and so on. The use of vacuum reduces the pressure in the mold and makes it possible to use lighter mold. In addition, it also leads to the higher fiber content, the better resin impregnation to fiber.

American Seeman applied for the patent of combining RTM and vaccum bag molding process, i.e. SCRIMP (Seeman's Composite Resin Infusion Molding Process), which suits for the manufacture of composite structure with large size.

2) Resin film infusion

Resin film infusion (RFI) is a resin impregnation technology, combining resin film infusion with fiber pre-forming. It is the same to RTM as liquid molding process, and is also a low-cost technology to produce advanced composite materials structures due to its non-prepregs-free production. The process is: make the resin into resin film or resin block and place at the bottom of the mold; cover the top with fiber preform by suture or three-dimensional braided methods; seal and bag the cavity following the main points of the vacuum bag forming process. As temperature increases, under certain pressure (vacuum or pressure) the resin softens (melt) and moves upwards (flow). It impregnates the dry preform, and fills every empty space of the entire structure, achieving uniform distribution of resin and finally we proceed to the curing process.

RFI technology is developed from RTM technology, but there are significant differences between them. RTM can cure in the absence of pressure, while RFI usually need to be carried out under pressure from top to bottom. Fig.6.16 is schematic diagram of RFI technology. Compared with RTM technology, RFI technology has many advantages: it does not require special equipment like RTM process; simpler mold than RTM (we can use the mold in autoclave molding); it changes resin flow direction where resin flows through the thickness as opposed to along the part as with the other method such as RTM, which reduces the flow path of resin impregnating fiber so that fibers are more vulnerable to be infiltrated by resin; it does not require low viscosity for the resin, the resin can be high viscosity resin, semi-solid, solid or powder resin, as long as it can flow and infiltrate fibers under certain temperature, so ordinary resin of prepreg can meet the requirements of RFI. Compared with the autoclave technology, RFI technology does not require the preparation of prepreg, which shortens the process and improves the utilization of raw materials, thus reduces the cost of composite materials. However, for the same resin system, RFI technology needs higher molding pressure than autoclave molding.

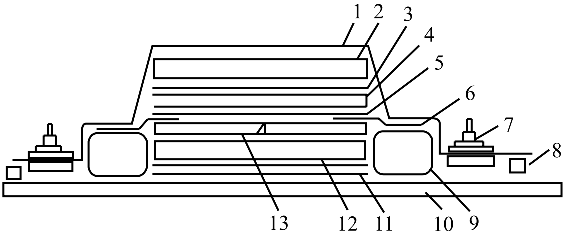


Fig. 6.16 Schematic of resin film (RFI) process:
1-vacuum bag; 2-breathable fabric; 3,5-perforated isolation film;
4-bleeder cloth; 6-edge sealant tape; 7-vacuum nozzle; 8-sealant tape;
9-metal dam;10-mold; 11-resin film;12-dry preform; 13-caul plate.

RFI technology usually associates with suture technology or three-dimensional braiding technology. In the application of RFI technology to make composite material parts, firstly we use the suture technology to make reinforced fabric into preform in accordance with design requirements, or use the three-dimensional braiding technology directly to weave the preform. In the RFI process, firstly we put resin film or resin block on the bottom mold coated with release agent, and then place preform, peel ply(optional), template with holes, perforated isolation film, bleeder material, breather material, etc. Finally, we seal vacuum bag and cure in autoclave.

RFI technology not only can reduce the molding cycle of composite materials, but also can greatly increase the damage tolerance. For example, compared with composite laminates, sewing / RFI composite materials drop by about 8% in tensile strength, drop by 5% in tensile modulus, 2% in compressive strength, about 3% in compression modulus, but their type-I interlaminar fracture toughness G_{IC} increases more than 10 times, type-II interlaminar fracture toughness G_{IIC} increases by 25%, compression strength after impact CAI is about 2 times of the original strength.

Boeing-McDonnell Douglas studied RFI technology under the support of the ACT (Advanced Composites Technology) program and produced a large wing component 12.19m in length, 2.44m in width. Its carbon fiber preform was manufactured by suture using advanced sewing machine (ASM), and the resin utilized 3501-6 epoxy resin film.

6.2.6 Injection molding and reinforcement reaction injection molding

Injection molding is to put the fiber-reinforced pellets into the hopper of injection machine, where the material is heated to the flow state, injected into the closed mold with a low temperature at high pressure and high speed, solidified for products. The process is mainly used to inject thermoplastics. Recently the new injection technology has been developed, such as reaction injection molding (RIM) and reinforced reaction injection molding (RRIM).

1) Reaction injection molding

Reaction injection molding (RIM) is a polymer processing method which combines polymerizing and processing. Its basic principle is: measure the two reactants (high reactive liquid monomer or oligomer) precisely, fill into the mold by high-pressure collision mixture, and rapidly cure and polymerize in the mold cavity. RIM molding process is shown in Fig. 6.17.

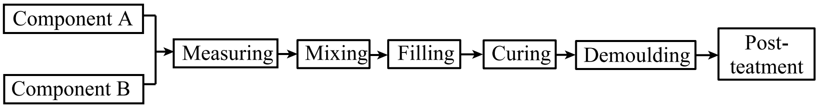


Fig. 6.17 RIM molding process.

RIM molding process is characterized by high productivity and low energy consumption. It began in the late 1960s, used for processing polyurethane at the first time. Ever since the United States start to produce polyurethane parts in large scale using RIM in 1974, RIM polyurethane chemical system has undergone following renovation: polyurethane→ polyurethane-urea → polyurea. With the development of RIM technology, it has been extended to other resins, such as nylon, polydicyclopentadiene, polycarbonate, unsaturated polyester, phenolic, epoxy, etc.

In general, RIM machine is composed of the following major components: they are feed systems, measurement and injection systems, mixing head and mold system. The most important requirements of RIM machine are: accurate chemical measurement, effective mixing and efficient production. Because of the extreme effect of chemical ratio on the properties of polymers, the measurement throughout the injection process must be highly accurate. React quickly and diffuse very slowly in the process, therefore the mixing must be short and efficient, which means that liquid flow rate is high through the metering and injection system. Feeding system is made from raw materials cans and heat exchanger.

In measurement and injection, in general, we can adopt spray devices, positive displacement piston pump or axial/radiation piston pump. Business RIM machine usually has servo mechanism to control measurement, which is achieved through the pressure or rotating speed of monitoring pump. Small RIM machine controls measurement by mechanical lever. The mixing head in RIM machine must be able to mix a large number of (3∼7kg) viscous liquid (about 1Pa·s) in a very short period of time (1∼3s) and maintain the mixing chamber clean, convenient for repeated cycle injection. Collision mixing is the only effective mixing method of industrial RIM machine. Before collision mixing, raw materials liquid passes the mixing head in low pressure and does not collide, maintaining uniform material temperature. When injection begins, the mixing head shifts from high-pressure cycle to injection state and opens the nozzle by the move of the center piston or hydraulic driving valve at the same time. In collision mixing process, the raw materials enter the limited mixing chamber, withstand intense indoor hybrid movement and become completely mixed by a strong shear and extend deformation. At the end of injection, the piston of the mixing head pushes out all the residual materials for self-cleaning of the mixing chamber, preparing for the next injection. Mold system includes flow channel and gate, and cavity and clamping mold plate.

Different from the injection molding of thermoplastics, RTM process is accompanied by chemical reaction. Reduce the clamp force and mold cost because the raw material is liquid and injection pressure is low; compared with the normal injection molding, reaction injection molding does not need plasticization and thus requires no plasticization set, and injection amount is limited less by equipment; low viscosity of raw material, low injection pressure and clamp force, so the clamp setup is simple. Because the liquid monomer is exothermic in the mold when the polymerization reaction occurs, heat for outside is no longer necessary, and energy consumption is less too. As the liquidity of materials is good, it can form the products with complex shape and changed wall thickness, as well high surface finish.

2) Reinforced reaction injection molding

Reinforced reaction injection molding (RRIM) is short fiber or flake reinforcement reinforced RIM, developed on the basis of reaction injection molding, in which reinforced materials are added to the monomer, namely monomers together with the reinforcing material through mixing head are injected into the mold (based on mixing head fibers should be short) for composite material products. Reinforced fiber mainly includes short fiber and grinding fiber. Short fiber is generally 1.5∼3mm in length, and its enhanced effect is better than grinding fiber.

Structural reaction injection molding (SRIM) or matting molding reaction injection molding (MMRIM) is usually to put long fiber-reinforced mat in the cavity, and then inject into the reaction materials, impregnate and cure.

Like the RTM, both RIM and RRIM are also liquid composite molding (LCM), but because of the high reactivity of RIM monomer, the mixed component must be injected cleanly every time.

6.2.7 Filament winding process

Filament winding is a process in which resin-impregnated fibers are wound under a certain tension over a rotating mandrel at the desired angle, and then cure at room or heated temperature into products. A typical filament winding process is shown in Fig. 6.18, in which a carriage unit moves back and forth and the mandrel rotates at a specified speed. By controlling the motion of the carriage unit and the mandrel, the desired fiber angle is generated.

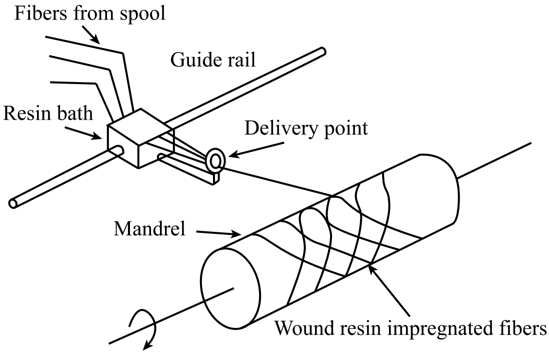


Fig. 6.18 Schematic of the filament winding process.

1) Classification

Winding process can be divided into dry, wet and semi-dry, in accordance with the different physical and chemical state of resin in the process.

Dry winding uses prepreg yarn (tape). Prepreg yarn (tape) is heated to soften state at the winding machine and then winded on the mandrel. It has high productivity and clean working environment, and its winding speed is up to 100 $\sim$ 200m/min. But it requires more complex winding equipment, high cost and its interlaminar shear strength of winding products is low.

Wet winding uses liquid resin system, the fibers are clustered and dipped, and then are directly wound on the mandrel under the control of tension, and then cure. Wet winding equipment is relatively simple, but because the dipped yarn (band) is immediately wound, it is difficult to control and examine the glue content of products. At the same time the solvent in glue is easy to reside in the products in the form of bubble, void and other defects. Moreover, fiber winding tension is not easy to control. Last but not least, the process introduces poor working conditions. It is labor-intensive and difficult to automate.

Semi-dry winding adds a drying process between fiber dipping and winding, we basically remove the solvent in the glue band. Like wet winding, it is difficult to accurately control the glue content of semi-dry products, but the bubble and void in products and other defects are substantially reduced.

In recent years, thermoplastic resin powder form is developed for thermoplastic resin. First of all, we coat thermoplastic resin powder on reinforced roving evenly by electrostatic powder method to form fiber bundle prepreg, and then heat it to soften and wind on the mandrel through payout eye, and then solidify into parts.

2) Winding rule

The winding rule is the relative motion law between the mandrel and the winding head, which is used to make sure the fiber wind on the mandrel uniform, stably and regularly. There are many specifications and forms of winding products, and winding form is ever-changing, but the winding rule can be attributed to three categories: hoop winding, polar winding and helical winding.

(1) Hoop (circumferential) winding.

Hoop winding is a winding method along the circumferential direction of the container. When winding, the mandrel rotates around its own axis uniformly, tow (delivery eye) moves around the cylindrical section parallel to the axial direction of mandrel evenly and slowly. Mandrel rotates each revolution, which corresponds that the tow advances one bandwidth of along the axial direction of mandrel. This continues until the surface of the cylindrical section is evenly covered with yarn, which is shown in Fig. 6.19. Hoop winding is characterized by: the winding can only be carried out around cylindrical section and not in the dome end. The neighboring yarn contacts with each other but does not overlap. The angle between the axis of mandrel and fiber tow that is called as winding angle, is usually 85°∼90°. Hoop winding layer is used to bear the radial load.

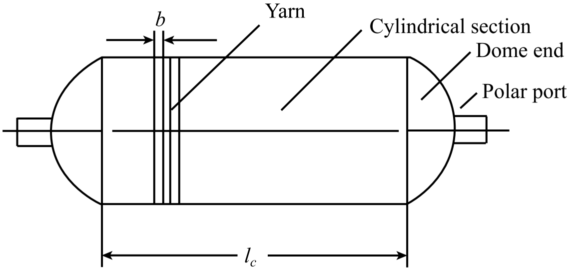


Fig. 6.19 Hoop winding.

(2) Polar (plane) winding.

In polar winding, winding head makes uniform circular motion in a fixed plane, and the mandrel does intermittent rotation slowly around its axis. One circle of winding head, the mandrel turns a small angle, corresponding to width of a yarn on the mandrel surface. The fiber turning each circle is in the same plane, so the polar winding is also called as plane winding. The fiber in polar winding is 0° ∼ 25° angle with the longitudinal axis of mandrel, and tangent with polar port of two dome ends. The fiber winds on the mandrel continuously and does not cross each other. The winding trajectory is a single-cycle plane closed curve. Polar winding layer is used to bear longitudinal load.

The speed ratio of plane winding is the revolution ratio between the mandrel and winding head per unit time. The angle between yarn and the longitudinal axis is winding angle (α), which is shown in Fig. 6.20.

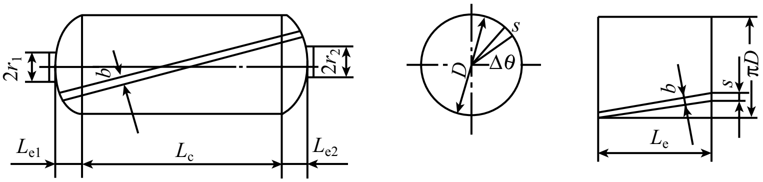


Fig. 6.20 Polar winding.

$$\tan\alpha = \frac{r_1 + r_2}{L_c + L_{e1} + L_{e2}} \tag{6.1}$$

Where, r_1, r_2 are the polar port radius on the two dome ends; L_c is the length of cylindrical section; L_{e1}, L_{e2} are the height of the two dome ends.

If the two polar ports are the same, and have the same dome end height, then we get:

$$\tan\alpha = \frac{2r}{L_c + 2L_e} \qquad \alpha = arc\tan\frac{2r}{L_c + 2L_e} \tag{6.2}$$

Yarn is b in width and α in winding angle, arc length in the parallel circle of mandrel $s = \dfrac{b}{\cos\alpha}$, the corresponding mandrel angle with arc length $\Delta\theta = \dfrac{s}{\pi D} \times 360°$. If the time for winding head rotating a cycle is t, then the speed ratio of polar winding is given by:

$$i = \frac{\dfrac{\Delta\theta}{360°} \times \dfrac{1}{t}}{\dfrac{1}{t}} = \frac{b}{\pi D \cos\alpha} \tag{6.3}$$

(3) Helical winding.

Helical winding is also called as spiral winding or geodesic winding. When winding, the mandrel revolves around its axis at a constant speed, while the winding head does reciprocating motion along the axial direction of mandrel at a certain speed, realizing the spiral winding in the cylindrical section and the dome end of mandrel. And its winding angle is approximately 12° ~70°. See Fig. 6.21. The rotation speed of mandrel is in proportion to the speed of winding head (here the speed ratio is the ratio of the revolution of the main axis of mandrel and the number of winding head reciprocating per unit time). Different speed ratio haves different winding pattern.

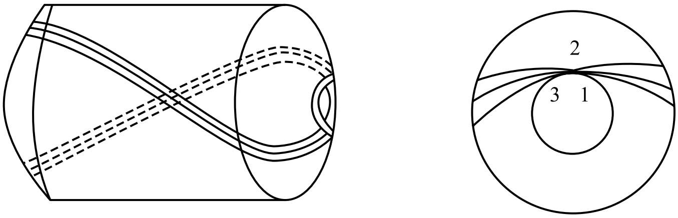


Fig. 6.21 Helical winding.

During helical winding, fibers are not only wound on the cylindrical section, but also on the dome end. Its process is: fibers firstly start from a point in the polar circle of one end, wind via the dome end along the curve in the curved surface of dome end which is tangential to the cycle of polar hole, then pass the cylindrical section according to the spiral line to the other dome end, then return again to the cylindrical section, finally to the initial dome end, repeat this cycle until the surface of mandrel is entirely covered with fibers evenly. Obviously, the spiral winding path consists of the spiral line of cylindrical section and the space curve in the dome end tangential to the polar hole, namely in winding process, if the yarn is winded on the mandrel by right screw, and then it returns by left screw.

The characteristics of helical winding are given: each bundle of fiber corresponds to a tangential point in the circumference of polar hole; the adjacent yarn in the same direction contacts with each other, but not intersect, but in different direction they intersect. Thus, double fibrous layer is formed when fibers entangle fully on the mandrel evenly.

3) Technological process

Its technological process is as follows: glue preparation, fiber drying and heat treatment, mandrel or lining manufacture, glue dipping, winding, curing, examination, trimming, and product. The main technological parameters which should be regulated include: fiber drying and heat treatment, dipping glue content of fibers, winding tension, width of yarn and winding position, winding speed, curing technology, ambient temperature, and so on.

The raw materials utilized during winding process mainly include continuous fiber yarn or band and glue. We use prepreg yarn (band) in dry winding. There are certain requirements for the viscosity and process performance of resin and its work life during winding process. The glue content is controlled in impregnation process. Impregnation glue is completed usually by dip and roller contacting methods, as shown in Fig. 6.22. The dip method controls the glue content by the pressure of extruding glue roller; with regard to glue roller contacting method, it is achieved through controlling the distance between doctor blade and glue roller to change the thickness of glue pickup on the roller surface.

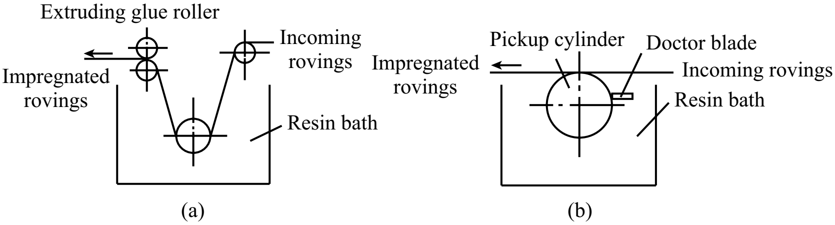


Fig. 6.22 Impregnation methods:
(a) dip impregnation; (b) roller contacting impregnation.

Lining and mandrel. In order to enable internal pressure vessel to have good gas tightness and not to seep, or possess certain corrosion resistance and high temperature resistance, lining is generally applied. Lining materials contain metal, rubber, plastic and so on. Convenient for demolding, the mandrel could be designed as dismountable (combination mold), fragile (broken mold), soluble (dissolved mold) and other forms. Metal mandrels are always designed as dismountable combination ones. For small batch or piecework products, the skeleton is generally made of metal and the molding surface is made of gypsum to reduce cost.

The winding tension influences the mechanical property of products, compactness, glue content, and so on. In order to avoid the phenomenon of loose inner and tight outer among in winding layers, which is caused by winding tension, we should reduce the tension regularly layer by layer and make the initial stress of outer and inner is equal, to achieve the purpose that they could bear load at the same time after the container is pressurized.

After winding, the preforming flan may cure in autoclave, drying oven or special curing oven. The parts should be rotated continuously until gelation to prevent uneven distribution of the resin caused by its outflow. For relatively thick product, stratified curing process should be taken into consideration.

4) Winding equipment

The main winding equipment is fiber winding machine; auxiliary equipments include bobbin and creel, fiber dipping bath and drying device, tension generator and measuring device, heating curing installment and control system. According to the main axial position of mandrel, fiber winding machine is divided into horizontal, vertical, and inclined winding machine, and so on.

The basic horizontal (chain type) winder mainly consists of three parts: main axis transmission mechanism driving the rotation of mandrel, hoop winding mechanism and spiral winding mechanism which drive the winding head to do reciprocating motion parallel to the main axis of mandrel, thus to realize two relative motions, mandrel rotation and winding head move. In main axis transmission mechanism, the main axis is motivated by an electric motor through a turbine wheel and a gear retardment mechanism, and the mandrel is directly linked in the main axis. The horizontal winder is commonly used for wet process of spiral winding and hoop winding. The hoop winding mechanism includes a guide screw parallel to the main axis, a slider in the guide screw (equip a winding head in the slider) and a commutator. When the spiral winding mechanism is at work, the electric motor drives the chain driver using retarder, then the chain driver makes the chain to turn around and drive a four wheel carriage reciprocating motion parallel to the mandrel by a pin set fixed in the chain. The winding head is installed on the carriage. The spiral winding is accomplished by the rotation of the main axis of mandrel and the reciprocating motion of the winding head driven by the closed chain. The hoop winding is accomplished by the rotation of the main axis of mandrel and the motion of the winding head driven by the guide screw parallel to the main axis. According to certain linear principle, the length of chain and its arrangement, speed ratio and its calculation, are the key points to utilize and design the winding machine. A well designed winding machine covers fibers evenly on the entire mandrel surface.

5) Characteristics of winding process

The main characteristics of fiber winding process are shown: fibers can keep continuous and intact; the part linearity can be designed according to the stress requirement of products, namely choosing reinforced materials depending on properties; high structure efficiency, high strength of products; continuous and mechanized production, short production cycle, low labor intensity; products do not need mechanical processing. The drawbacks are that the equipment is complex, the technical difficulty is great, the process quality is not easy to control and only limited to convex shaped components.

Winding process is primarily used for large hollow, generally circular or oval sectioned rotator components, such as pipes and tanks, which deserve a widespread application in chemical industry, food brews industry, shipping industry and aerospace, and so on. Typical applications include pressure vessel standing intrinsic and external pressure like air bottle, torpedo shell, chemical pipeline for transporting petroleum, water, natural gas and other fluid, chemical storage tank or railroad tank for storing acid, alkali, salt and oil medium, rocket motor casing, rocket launch tube, fuel tank and cone-shape radome and other military products. It can also be used to produce irregular and variable cross-section profiles.

6.2.8 Pultrusion

Pultrusion is used to fabricate a wide range of solid and hollow components with constant or near constant cross-section. The typical pultrusion process includes sending yarn, dipping, pre-molding, curing, traction and cutting, which is shown in Fig. 6.23. The continuous fibers are pulled from a creel through a resin bath and then through a heated die. The die completes the impregnation of the fiber, controls the resin content and cures the material into its final shape as it passes through the die. This cured profile is then automatically cut to required length. Fabrics may also be introduced into the die to provide fiber direction other than at 0°.

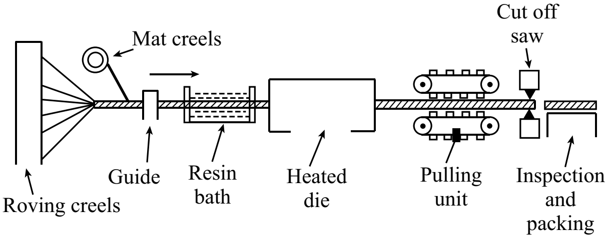


Fig. 6.23 Illustration of a pultrusion process.

Pultrusion machine is composed of creel, yarn collector, dipping device, molding cavity, pulling unit, cutting mechanism and operational control system.

The main reinforced materials of pultrusion are glass fiber rovings, continuous fiber felt, polyester fiber felt, carbon fiber, aramid fiber and hybrid fiber. It can also be two-directional fabric, weaving, or a whole three-dimensional braiding forms, and so on, which enhanced horizontal or interlaminar mechanical properties. Both thermosetting and thermoplastic matrix can be used in pultrusion. For thermosetting resins, the resin should have low viscosity, good wettability, long pot life and fast-curing, so unsaturated polyester resins, vinyl resins and epoxy resins are usually used. Internal release agent can be added into resin, automatically migrated to the surface of parts to reduce traction resistance. Dry pultrusion using prepreg yarn or fabric does not need the dipping process. Curing can be carried out incrementally, first cure to certain degree in the mold cavity, and then cure in the furnace completely. The cross-section of die can be designed into a variety of forms, such as I-shaped, angle, groove, profiled form or their combinations. Pultrusion of thermoplastic composite materials has entered practical stage, its main matrix have ABS, PA, PC, PES, PPS and PEEK, etc.

The most important features of pultrusion process are: this can be a very fast automated, and therefore economic, way of impregnating and curing materials. Structural properties of laminates can be very good since profiles can have very straight fibers and high fiber contents. Resin content can be controlled. Fiber cost minimized since it is taken from a creel. Resin impregnation area can be enclosed thus limiting volatile emissions. Unrestricted length of products, high utilization of raw materials, and no need use of accessorial materials.

It is an important method to manufacture high-performance and low-cost composite materials with high fiber content. The most common applications are in making beams, channels, tubes, grating systems, flooring and equipment support, walkways and bridges, handrails, ladders, light poles, electrical enclosures, etc. Therefore, pultruded composite materials can replace metal, plastics, wood, ceramics and other materials, and are used widely in oil, construction, electricity, transportation, sports goods, aerospace and other industrial fields.

6.2.9 Centrifugal casting molding

Centrifugal casting molding (also called rotational molding) is to put fiber and resin in the mold, which is then compressed tightly by the centrifugal force of rotating mold, and then the air is removed and cured into parts. It can also put braided cover, fiber felt or fabric inside the tube-shaped mold and then spray resin to form the flan. We can use braided cover for small tube, use fiber felt or fabric for medium-sized tank and groove parts, and use simultaneously spray short fibers and resin for large tank and groove parts. The method is characterized by uniform thickness, smooth and clean appearance.

6.3 Mold and auxiliary materials

6.3.1 Mold

1) Relationship between the mold and composite material parts

Composite material parts are produced with mold, different forming processes with different requirements on the mold. The mold gives the geometric boundary of components and specifies its coordinating relationship with other components. The materials choice and design of mold largely affect the internal quality and the surface state of composite components.

The selection of forming mold and mold structure depend on the structure form of composite materials, so is the types of mold. Given the complex process in building a structure, besides forming mold, we also need blanking die, pre-assembly mold, location mold and so forth. For advanced composite materials, common structural forms and manufacture technical units are as follows.

(1) Structure form of composite materials.

It includes: ① plate and shell structure; ② stiffened panel structure; ③ multiple wall structure; ④ honeycomb sandwich structure, foam sandwich structure, corrugated sandwich structure; ⑤ wall, rib, stringer structure; ⑥ bonding structure; ⑦ integral cured structure (such as rectangular box); ⑧ co-cured structure (such as grid structure).

(2) Technical unit of composite materials.

① Spreading unit. For structural composites by prepreg lay-up with profiled structure or curved surface structure, spreading of every layer is different. So a set of cutting and lay-up templates are often required for each layers. High-precision templates are the basis of high-quality composite materials. Computer-aided design is often needed in order to obtain high-precision templates.

② Locating technology. Namely, the plies are placed on the tool in the correct location and fiber orientation as specified by the engineering drawing or shop work order. Recently, besides hand-location lay-up by using Mylar templates, the laser ply projection has been developed to meet the higher location accuracy requirements.

③ Pre-absorbing glue technology. Namely, we eliminate excessive resin through glue-absorbing system, drive out the volatile and solvent within resin at the same time, hence obtaining the structure in which the resin content is in line with the structural design requirements.

④ Pre-compaction technology. Namely, we compact the flan to a certain size so as to precisely control the thickness deviation of composite structures. It is particularly important for parts with changing profile and complex shape. The process also coordinates mold assembly.

⑤ Forming B stage technology. Controlling the fluidity of resin is particularly important for high-quality composite structures. At B stage the resin could flow but its fluidity is not big, so it is the basic of technology. B stage is usually determined according to the physical and chemical changes of resin.

⑥ Soft mold forming technology. Rubber expansion mold and rubber pressure transfer mold technology are particularly important for co-curing and overall co-curing. But we should make a strict calculation and experimental verification on the expansion volume of rubber and its temperature in advance, before we can put it into engineering applications.

⑦ Pre-assembly technology. Before forming, we preassemble the flans through pre-absorbing glue, pre-compaction and B stage, observe and adjust the fitting state at each point, in order to ensure the good loop of vacuum system.

2) Basic requirements on the mold

The basic requirements of composite mold are as follows: ① meet the requirements of accuracy, size and appearance; ② sufficient stiffness and strength which ensure the molding contour surface unchanged and the products in original shape when curing; ③ smaller heat capacity to make effective use of energy; ④ light in weight, easy to transport and demould; ⑤ low cost, easy to get raw materials and easy to manufacture; ⑥ simple to maintain, long service life; ⑦ materials should be selected that match (close) the parts in the thermal expansion coefficient in order to reduce the deformation; ⑧ sufficient thermal stability for resisting thermal shock.

3) Mold materials

The materials of mold which are used to make composite materials should have good thermal conductivity and thermal stability, thermal expansion coefficient matching with components, easy to mold and process, low density, and low cost. It can maintain smooth demolding surface, is not subject to erosion of glue and auxiliary materials, and has no adverse effect on glue curing. There are varieties of mold materials, and we should choose the materials based on products' size, shape, using frequency, molding and curing process.

(1) Wood mold.

The life span is medium. There are micropores on the surface of wood, plaster, cement and etc., and there is water inside. They should be dried until moisture content is less than 10% before using, so as to reduce the deformation or cracking of mold in process. Micropores should be sealed at the same time.

Wood mold can be used as the mother mold (sampling mold) for reproducing FRP mold, and as the skeleton of frame mold. It is easy to process, light, and suitable for the products with the complex and large-size shape at room temperature curing.

(2) Plaster mold.

The life span is 1∼5 times. Plaster mold is easy to produce and costless, but it can't bear thermal shock and is easy to deform: it needs drying, surface processing and sealing pore, and it is suitable to make some large-scale products with simple shape and small products with complex shape.

(3) Cement mold.

The life span is medium. Cement mold is easy to produce and almost costless. It has good rigidity, hard to deform and could be used repeatedly, but it's difficult to correct the molding surface; it is applied to make large, medium-sized regular products with non-complex shape and smooth line.

(4) Wax mold.

Wax mold is disposable. It is reproduced by mother mold, demould by heat flow; convenient production, no release agent, wax can be used repeatedly, but it is easy to deform and the accuracy is poor; it is fit for the small profiled products with complex shape and demould difficultly.

(5) Foam.

It is used as the inner core of non-demould.

(6) Metal mold.

Frame mold: we use angle iron, groovy steel as skeleton, and sheet metal as molding surface.

(7) Epoxy adhesive sand, FRP, carbon fiber composite materials.

They can be used to produce the molding surface of frame mold.

The advantages and disadvantages of main mold materials and the application can be seen in Table 6.2. Different forming method needs different mold materials. See Table 6.3.

Table 6.2 Advantages and disadvantages of main mold materials

Materials	Advantages	Disadvantages	Application
Aluminum	Good manufacturing process and thermal conductivity, light weight	Low heat resistance, large thermal expansion coefficient	Low coordination precision
Steel	Small thermal expansion coefficient, large rigidity, and high using temperature	Heavy, limited size and high cost	High precision, thermoplastic resin molding
Inflatable rubber	Plastic molding, inflation control, can be used for pressure transmission	Expensive material, difficult to control inflation	Overall co-curing molding; complex profile surface molding
Carbon fiber composites	Light, and thermal expansion coefficient is the same as the molding parts	High cost, low thermal conductivity	Large-scale high-precision structure
FRP	Cheap	Low accuracy	Complex structure and simple profile surface molding
Wax, wood, plaster	Plastic molding, low cost	One-time or multiple use	Filament winding parts
Electrodeposition Ni, nickel steel	Small thermal expansion coefficient, multiple use	High cost	Precious complicated structure

Table 6.3 Mold materials of different forming method

Forming method	Materials	Forming method	Materials
Autoclave molding	Aluminum, steel, electrodeposition nickel, carbon fiber composite materials	Soft mold forming	Inflatable rubber, vulcanized rubber, non-vulcanized rubber
Vacuum bag molding	Aluminum, wood	Pultrusion	Wear-resistant steel
Pressure bag molding	Aluminum	Winding process	Steel, wood, wax, low melting point alloy
Compression molding	Steel	RTM molding	Steel, glass fiber composite materials

4) Mold structure

According to its structure, the mold for producing composite material parts are concave mold, convex mold, matched die mold and combination mold.

(1) Concave mold (female mold).

It is applied to the products that have high requirements of appearance and size; however, the female mold that is too deep and too large is not convenient for operation, it's not easy to exhaust bubbles and control quality, in addition, it difficult to produce and its price is high.

(2) Convex mold (male mold).

It's easy to operate, ventilate, and to control the quality. Inner surface of products is smooth and inner size is accurate. However, external surfaces are rough and with inaccurate size, usually used to produce the parts which require less strict shape.

(3) Matched die mold.

Matched die mold includes a female and a male mold, which is assembled together by a locating pin. It is used to produce the part which has high requirements of surface precision and thickness. The quality is good and the cost is high. Because it must be moved in the molding process, it's not suitable to produce large size products.

(4) Combination mold (assembled mold).

The combination mold is often assembled from a few parts for the complex structure products or facilitating mold release, which is called combination mold (assembled mold). Single mold (female or male mold) and matched die mold both have types of assembled mold.

5) Mold structure forms for aircraft structural parts

The aircraft structural parts have three forms; they are thin-walled wing structure, sandwich structure and pipe, tube-shaped and stringer-shaped structure. The mold used generally includes the following four structures in order to produce these structure components.

(1) Framework structure.

It consists of aluminum plate or steel plate and support frame (Fig. 6.24). The metal plate is usually 3~5mm thick, which is made into the molding surface by roll-bending or stretching and is corrected by a section template for many times. The support frame generally consists of metal pipe, angle iron or plate for supporting or fixing the upper mold plate. The support frame can also be made of wood. The molding surface is made of epoxy adhesive sand, FRP, or carbon fiber composite materials. Frame structure is hollow, so its heat capacity is small and hot air can flow smoothly in the internal and external surface of template, making it easy to reach uniformity in temperature. Moreover, and the weight is small, thus easy to transport. This structure is commonly used in autoclave molding and vacuum bag molding, pressure bag molding of large products.

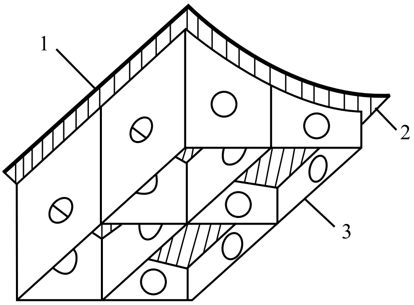


Fig. 6.24 Framework mold structure:
1-model surface; 2-back; 3-support.

(2) Carbon fiber composite mold structure.

Carbon fiber prepregs are used to produce the model surface and glass fiber profiled bars are used to produce the frame. The model surface can be repaired arbitrarily according to the template, which enhances the precision of the mold. Because the mold material and formed material are the same on the whole, thus we ought to solve effectively the matching problems of thermal expansion coefficient between mold surface and composite material components. It has been successfully used in making composite material products with high dimension accuracy and highly precise location.

(3) Rubber mold structure.

The plasticity of rubber is desirable in the forming of a variety of molding surfaces, such as the sine wave beam of complex molding surface. It uses the expansion of rubber and its controllability in the heating process. The expansion supplies a required curing pressure and sometimes it is used as the transmitting medium. When using rubber mold, it is usually designed as the internal cavity of mold and the external cavity generally adopts a closed steel structure with a self-heating system. The rubber mold materials are mainly silicon or non-silicon rubber block, as well non-vulcanization rubber.

(4) Steel matched die mold structure.

The steel matched die mold is mostly used in compression molding, pultrusion and injection process, which is usually composed of the upper mold and the bottom mold. The upper and the bottom should be assorted precisely, so a high accuracy is required.

6.3.2 Auxiliary materials

In composite material component molding, in particular in vacuum bag molding and autoclave molding, auxiliary materials are indispensable, which play an important role in getting good interfacial adhesion, uniform resin distribution, low void content and precise geometry size, and so on. Auxiliary materials primarily include release material, bleeder material, breather material, vacuum bagging film, sealing tacky tape, non-vulcanized rubber and pressure-sensitive adhesive tape, and so on. With regard to different molding process, different resin system and curing condition, the auxiliary materials are also different.

1) Release agent

Release agent can ensure that the products are successfully taken down from the mold. Its main forms are shown in follow.

(1) Oil release agent.

Ointment, wax such as silicon oil, silicon ester, Vaseline, butter, 201 ointment, polishing wax for car, can be directly coated on mold surface. This kind of release agent is easy to use, effective, non-toxic, and non-corrosion effect. But they will contaminate the surface of products, making them not smooth and also bring certain difficulties to the next painting process.

(2) Film release agent.

All kinds of plastic films such as PVC film, PE film, PA film, cellophane, and even typing wax paper can be used as a mold release in hand lay-up process. This kind of release agent also includes the release film and fabric usually used in autoclave molding. The advantage of film release agent is: they can be acquired easily and used easily and the effect is good. Disadvantage: poor deformation, only suitable to the products with simple shape; most of them have poor heat resistance. PVC film is not applicable to FRP polyester, as styrene can swell PVC.

(3) Solution release agent.

This kind of release agents is coated on the mold surface, and made into a layer of uniform film by volatilizing the solvent in polymer solution, such as alcohol-aqueous solution of polyvinyl alcohol, perchloroethylene solution, toluene solution of polystyrene, toluene solution of methyl silicone rubber, polytrifluorochloroethylene suspension, and so on. Some new are developed, such as the Air Tech's liquid release agent Release All 100, 150 (silicone resin), Release All 300, 13, 25 (non-silicone resin), etc. This type of release agents is used rather popularly and widely, but the solvents used are generally toxic except for those in alcohol-aqueous solution of polyvinyl alcohol. The 5%∼8% ethanol-aqueous solution of polyvinyl alcohol is commonly used in hand-up process of FRP domestically, which is inexpensive, non-toxic, available easily, good in performance (150°C or less), and can directly touch the products; its disadvantages include slow drying, long production cycle, which undermines production efficiency. Silicone rubber and polytrifluorochloroethylene have effective demoulding effect. They form thin film and have high temperature resistance, which is often used at high temperature above 150°C, even more than 200°C. Furthermore, they may be used several times each layer is brushed. Polytrifluorochloroethylene can be used for a long time, but after coating it must be roasted respectively at 200°C and 300∼350°C for 1∼2 hours, so it is generally used on metal mold for preparing the cured products at high temperature.

2) Isolation (release) materials

Isolation materials can detach composite materials from other materials or pollution, providing surface protection for the next bonding process, which can be divided into two kinds: non-porous and porous, such as PVC film, PA film, PTFE glass cloth.

Isolation material produced by Air Tech Company in United States (the letter P shows the film with pore, but only one-way pore about 0.045mm in diameter): A4000R, A4000RP3, A4000RPS, A4000RP4, red; A4000, A4000P3, A4000P4, A4000P5, colorless; Wrightlon 4500, used for the planar structure; Wrightlon 4600, using temperature is 202°C, used to demould in compression molding; Wrightlon 5900, fluorocarbon, used at 285°C, white transparent and easily distinguishable.

There are three types of release fabric in Air Tech of the United States.

(1) Breathable and perforated. Release Ease 234 TFP, glass cloth coated with PTFE; Release Ease 234 TFP-1, soft thin-film, suitable for curved surface; Bleeder Lease C, glass cloth coated with Release All 100.

(2) Peel-ply. Bleeder Lease A, Bleeder Lease B, peelable nylon cloth coated with Release All 100; Bleeder Lease E, peelable glass cloth coated with Release All 100; Release Ply A, Release Ply B, peelable nylon cloth with non-coated layer; Release Ply C, peelable cloth (polyester) with non-coated release layer by the electric treatment; Release Ply F, peelable cloth with non-coated release layer by the electric treatment.

(3) Non-porous release fabric. Release Ease 234 TFNP, glass cloth coated with PTFE; Release Ease 236 TFNP, glass cloth coated with extra-thick PTFE used for the mark; Tooltec, glass cloth coated with PTFE, and coated with pressure-sensitive adhesive on one side used for permanent protection and demould.

3) Glue-absorbing materials and breathable materials

Glass cloth, glue-absorbing paper, glue-absorbing felt (Airweave FR) can be used to adsorb excessive resin in prepreg, and by bleeding the wrapped air and volatile are taken out. The amount of bleeder materials (layer number) can be calculated in accordance with the saturated absorption content.

In vacuum bag-autoclave molding, except for glue-absorbing materials, in order to keep the vacuum bag ventilation and reasonable path, breathable materials must also be used. For example, Airweave S, a soft lightweight synthetic fiber, is used as breather, and it can also be used as glue-absorbing material. Airweave SS FR, Airweave N-10, are extendible breathable materials, replacing breathable glass fabric, can avoid air entrainment because of bridging.

4) Vacuum bag materials

For example, balloon cloth (cotton cloth coated with silicone rubber), rubber bag, nylon film, and so on, are used to form a vacuum system.

Nylon vacuum bagging film by Air Tech Company in United States; Wrightlon 8400, the using temperature is 230°C, green; Wrightlon 7400, the using temperature is 204°C, blue; BW900, the using temperature is 176°C, 10h, peachblow; DP900, the using temperature is 204°C, 12h, orange; WN1500, the using temperature is 230°C, blue; Wrightcast 8500Y, the using temperature is 230°C, 16h,yellow; Wrightcast 7500R, the using temperature is 204°C, 12h, red; Wrightcast 5550, the using temperature is 285°C, 15h, applicable to every kind of molding surface.

5) Others

For example, we have sealing tape (No. 88 glue, sealing putty, solid adhesive clay), pressure-sensitive adhesive tape, expansion rubber (non-vulcanized silicone rubber, acrylonitrile-butadiene rubber), etc.

Pressure-sensitive adhesive tape in the United States Air Tech Companies has no free silicon. Its carrier materials are nylon, polyester, glass cloth, PTFE, and polyimide Kapton. It is used to locate the parts, including inter-location of parts and location between parts and molds, as well as fixing the vacuum bag and the mold. The main varieties are: Flashbreaker 1 and Flashbreaker 1R (light green), 25.4μm polyester in thickness, general type; Flashbreaker 3 (dark blue) and Flashbreaker 2R (light green), 50.8μm polyester in thickness, have a high tensile strength, the using temperature is 200 °C; Tooltec, glass fabric coated with PTFE, can work at 316 °C; Airhold 10 CBS, double-sided tape with high temperature resistance, used to fix the workpiece during honeycomb processing; Flashguard, glass fiber fabric of 0.1μm in thickness coated with non-silicon adhesive, white, applied to 176 °C; Flashbreaker, polyester film of 0.14μm in thickness coated with silicon adhesive of 38.1μm in thickness. The silicone is completely cured, and therefore no pollution problem is caused by the transfer of silicon; Flashlease 2, 50.8μm fluorocarbons film in thickness coated with silicone adhesive which has been fully cured. White, the largest extension is 275 %, the using temperature is 202 °C; Teflease MG2 and MG2R, red sauce, used for demoulding of the Airpad, the using temperature is 285 °C; Tooltec CS5 and Tooltec CR5, are suitable for curved surface, and can work at 285 °C; its elongation at break is 300%, taupe; Airkap I, saffron, used to pack polyimide laminated board, the maximum using temperature is 368 °C, and its elongation at break is 20%.

6.4 Curing process of composite materials

6.4.1 The effect of curing process parameters on properties of composite materials

There are many factors to impact the properties of composite materials, such as fiber, matrix, interface, and so on. However, when other factors are fixed, whether the molding process is reasonable or not is the key factor. It has an impact on dipping process, performance of cured resin, glue content and resin distribution, residual stress, and porosity, etc.

The curing process parameters include temperature, time, and pressure.

1) Temperature: curing at several steps

The curing temperature affects the reaction activity of resins and curing agents. For thermosetting resins such as epoxy resin, curing reaction is generally centered on curing agents, and radiates from the center to the surrounding, forming two-phase spherules network structure (around curing agent center the cross-linking density is big, called as glue particle, and in other parts the cross-linking density is small, called as glue floc). If firstly pre-cure at a low temperature (then cure at a high temperature), the curing reaction is slow, macromolecules can move and the curing agent can fully react with the surrounding resin to form more reaction centers, forming uniform structure and more uniform cross-linking density. If directly cure at high temperature, the reaction speed is high and the curing agent has been encapsulated and is unable to react with more distant macromolecules, leading to structural heterogeneity, largely different crosslinking density and large internal stress. Therefore, advanced composite material components, autoclave process in particular, often use stepped-curing from low to high temperature.

In low-temperature step, the reaction is slow and the resin is cured partly, which is conducive to form uniform curing network. The internal stress is small, and resin performance is good. High temperature curing reaction can enhance the mechanical properties and heat resistance of matrix. Stepped-curing system is conducive to full impregnation. It further completes the impregnation process and eliminates air bubble in interface. In low-temperature step, the reaction is slow and easy to control the pressure point. For multi-component reaction system, stepped-curing is also the need of molecular design.

2) Pressure: pressure point

Pressure can make parts dense and remove low-molecular materials (such as residual solvents, water and other substances from outside, air bubble, as well small molecules released in curing reaction), accelerate and improve the impregnation, and control the glue content of products.

For forming composite materials, it is important to control pressure point when a pressure is imposed on parts. If too early, the resin has large mobility so that more resin will loss and the products will lack glue and have large void fraction (on the one hand residual room due to resin loss, on the other hand pressure can make the boiling point of volatile heighten, thus make it difficult to drain away); if too late, at this time the resin has already gelled, the pressure does not exclude air bubble, resulting in not compact, low interlayer adhesion, large porosity, and ultra thickness tolerance in composites. In general, the pressure should be imposed when the resin does not gel but almost gel, taking air bubble away using a small amount of glue flow.

The range or width of pressure point of composite materials is an important indicator to value the manufacturability of resins. In vacuum bag-autoclave molding process, pressure outside, pump vacuum inside and liquid delivery are very effective ways for pressure.

6.4.2 Determination of curing process parameters

The molding process of composite components is just the curing process of resin, so we must firstly understand the change of resin's physical state in the curing process. The curing process of thermosetting resins is a process that low molecular weight resins become cross-linked network structure. During this process, the thermal properties, electrical properties and mechanical properties of thermosetting resins have corresponding changes.

For mechanical properties, thermosetting resins may experience four mechanical states in curing process: they are ungelled glass state, viscous flow state, high elastic state, and gelled glass state. The corresponding curing reaction has four stages, they are: ① form ungelled glass state to viscous flow state; ② from viscous flow state to the gel point; ③ from the gel point to glass state through high-elastic state; ④ solid-phase reaction within glass state.

In the four stages above, the second and the third stages are the main stages to determine the properties of cured materials. During these periods there will be two changes. One is from viscous flow state to the gel point. At this point the system starts to become a huge branch network, but it does not fully crosslink. In molecular scale, the entire molecular chain can slip before the change, but only segment can move afterwards. The other is from high elastic state to glass state. This is when the system has formed three-dimensional structure, and segment movement is frozen and cross-linking reaction become difficult.

Table 6.4 Characterization of the four curing stages by a few analytical instruments

Analytical instruments	Indicator	①	②	③	④
DSC	dH/dt	Endothermic-Melting	Get to the peak value	Exothermic slowly	No significant changes
DDA	Dynamic η-t	Gradually get to the lowest point	Go up rapidly	Go up slowly	No significant changes
	Capacitance C-t	Gradually get to the level step	Get down rapidly	Get down slowly	No significant changes
	tanδ-t	Melting flow peak	Gel peak	Get down slowly	No significant changes
IR	Concentration of functional groups	A little change	A big change	No significant changes	No significant changes
Viscometer	η-T	Get down to the lowest point	Go up rapidly	Go up	Difficult to determination

We can study the structural change and state change in curing process of thermosetting resin, check them by infrared spectroscopy (IR), differential scanning calorimetry (DSC), dynamic dielectric analysis (DDA), viscosity analysis (viscosity-temperature curve), dynamic mechanical analysis (DMA), torsional braid analysis (TBA). The result can provide a reference to make reasonable curing system. Table 6.4 lists the characterization of the curing stage mentioned above by a few analytical instruments.

1) From ungelled glass state to viscous flow state

Early in curing process, as the temperature increases, the resin gradually softens and flows and curing agent melts. The system absorbs heat and the low-temperature area in DSC curve shows endothermic peak (Fig. 6.25).

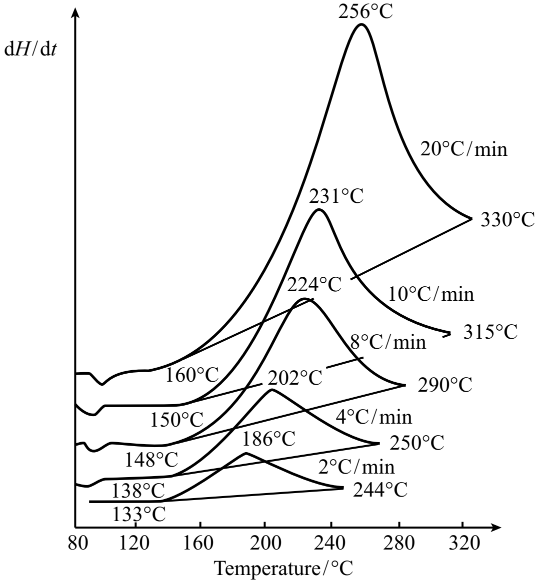


Fig. 6.25 DSC curve of thermosetting resin system.

When measure by DDA, with the viscosity decreasing, the activity of polar group gradually increases in alternating electric field, the capacitance will also increase accordingly. The low temperature area in dielectric loss-time curve appears the "flow peak"(Fig. 6.26). When the viscosity has a further reduction, the dielectric loss reduces to the minimum value.

2) From viscous flow state to the gel point

As the temperature continues to rise, the resin system polymerizes with heat release. In the DSC curve, as the temperature gradually increases, heat release rate ($\mathrm{d}H/\mathrm{d}t$) reaches to the maximum value (the exothermic peak in Fig. 6.25). Then it further cures, with the concentration of active groups decreasing $\mathrm{d}H/\mathrm{d}t$ declines

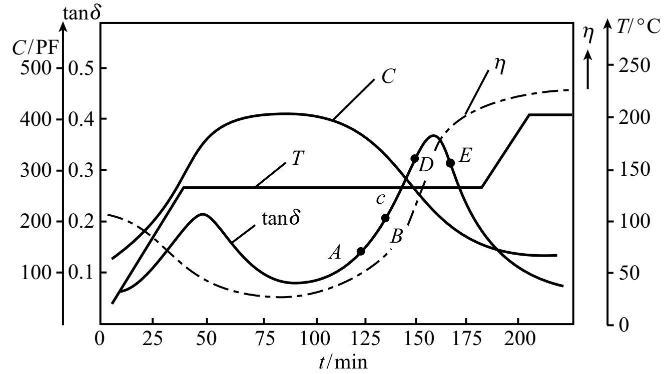


Fig. 6.26 The viscosity-dielectric loss curve of typical thermosetting resin in curing process.

and tends to a constant. In the DDA curve, the viscosity increases gradually with polymerization, which will hinder the orientation of dipole moment along the electric direction, so that the capacitance declines and lead to a further increase in the dielectric loss. With further curing, the viscosity increases rapidly due to cross-linking reaction and the orientation of dipole moment along the electric direction is more difficult. Dielectric loss decreases to a constant and at this time the curing is basically "complete". This process is reflected in the DDA on the dielectric loss curve that is appears the second dielectric peak in high temperature zone, which is called gel peak. It reflects the resin system gel in this temperature range and then achieves "complete" curing with a subsequent occurrence in dielectric loss.

According to Flory's gel theory, for any cross-linking reaction system, the reaction degree (curing degree) is a constant at the gel point, and it has nothing to do with the reaction temperature and experimental conditions. Accordingly, L.J. Gaugh deals with the curing dynamic equations by mathematical methods and establishes the following relation:

$$k = \beta \frac{1}{t_g} \tag{6.4}$$

Where k is the curing rate constant; t_g is the time of curing reaction to the gel point; β is a constant.

See equation (6.4), t_g can be used as curing kinetics parameters to characterize the speed of curing reaction. As the curing rate constant has the Arrhenius relationship with temperature:

$$k = A\mathrm{e}^{-\frac{\Delta E}{RT}} \tag{6.5}$$

Where R is a gas constant; T is the absolute temperature; ΔE is the activation energy; A is the frequency factor.

Substitute equation (6.5) into (6.4), we get:

$$\ln t_g = \frac{\Delta E}{RT} + \ln \frac{\beta}{A} \tag{6.6}$$

Fig. 6.27 can be got by graphing between lnt_g and $1/T$. We see that gel time decreases monotonously with the temperature increasing. The higher the temperature is, the faster the reaction is. ΔE can be obtained from the slope.

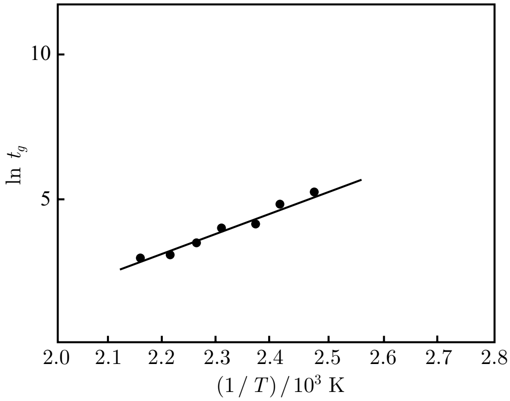


Fig. 6.27 The relationship of lnt_g and $1/T$ from liquid to gel point.

The characteristic temperatures of exothermic peak in DSC curve at different heating rate (initial temperature T_i, peak temperature T_p, final temperature T_f) are extrapolated to the exothermic peak T_i, T_p, T_f with a heating rate of 0 to determine the curing step temperature. Tanδ-t curve, η-T curve, t_{gel}-T curve are the reference to determine the pressure point (usually the pressure is imposed at the beginning of gelation).

DDA and other analytical techniques are used to monitor the curing process of composite materials. When the temperature is given, the pressure point is a key. In the tanδ-t curve (Fig. 6.26) selecting A, B, C, D, E as the pressure point to manufacture composite material and measure its short-beam shear strength (SBSS) and void fraction (V_V, %), Fig. 6.28 shows the results. From it we know that there exist the pressure point range of the maximum value of short beam shear strength and the minimum void fraction (B, C, D point where the viscosity increases to a certain value), which are the best pressure zone. But for A and E, composite materials will be of high void fraction, and low short-beam shear strength. Accordingly, we can adjust T, t, p process parameters in real time by dielectric characteristic curve of the best pressure zone.

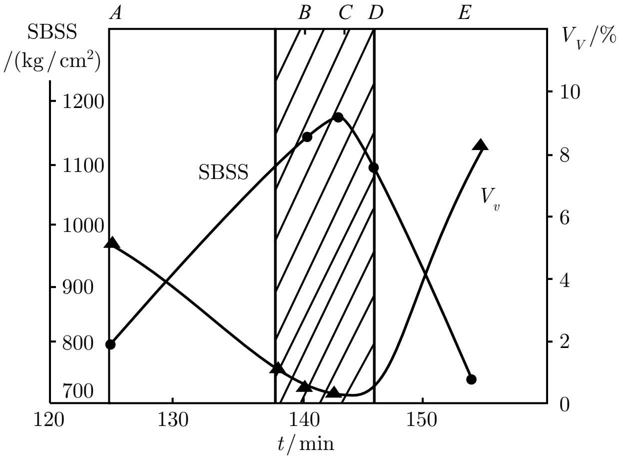


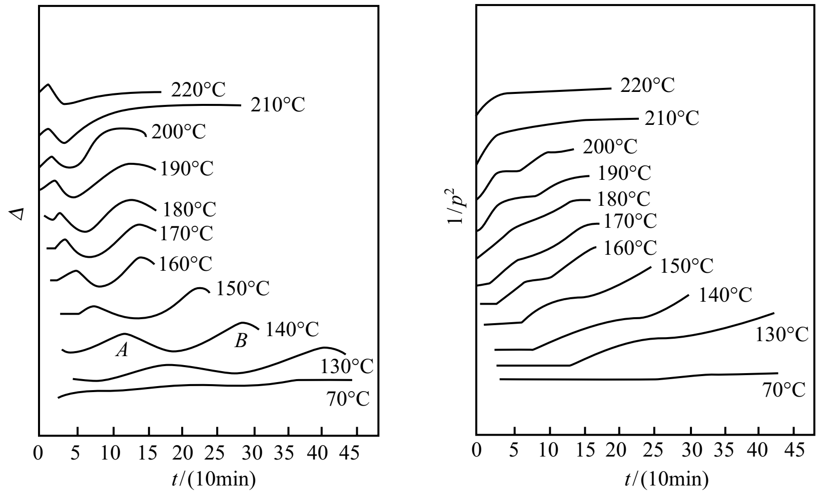
Fig. 6.28 The effect of different pressure time on composite performance.

3) From the gel point to glass state through high elastic state

At this stage, as a result of the rapid increase in viscosity, the reduction in the concentration of the reaction functional groups is not obvious. Thus it is not sensitive to determine the curing degree by the conversion rate of the reaction functional groups or by the ratio of the reaction heat under a certain temperature and the total curing reaction heat. Even if we apply the DDA dielectric loss curve, we still cannot determine the exact time of glass transition. Despite the difficulty, this curing stage is crucial. It largely determines the upper bound of the product performance. Because the curing is always related to mechanical properties, it can be thought that the curing process is a gradual increase in the modulus of resin system. For the final curing stage where the sensitivity of other analytical techniques is in sharp decline, it should have a good reflection on the mechanical properties, namely different curing degree can be reflected by the change in modulus. Therefore, we may wish to study the third and fourth stage of curing resin by using dynamic mechanical analysis (DMA) techniques such as dynamic torsional vibration analysis, TBA (torsional braid analysis).

Dynamic mechanical analysis is a test to measure the response or deformation of materials to cyclical force. The imposed force and generated deformation are changing according to the sine wave. From this test, elastic modulus and mechanical damping can be achieved at the same time. With different equipment, the shear modulus or Young's modulus is measured; the given mechanical damping is the energy loss in the form of heat when the material is deformed.

In TBA (torsional braid analysis) process, we take the glass fiber braid coated with polymer sample as a specimen and the inertia plate at its bottom swings back and forth in torsion. Because the structural units of polymers go through molecular motion and absorb the energy of the inertia plate, its amplitude becomes smaller and its cycle changes. The damping curve appears high peak at the transition point and the modulus decreases fiercely. Isothermal TBA analysis is to measure isothermal curing time-mechanic spectra of glass fiber braid impregnated with resin by dynamic torsion under different temperatures (Fig. 6.29). Fig. 6.29(b) shows stiffness curve, $1/p^2$ is the relative stiffness of the system. Fig. 6.29(a) shows damping curve, Δ is logarithmic decrement. At 130$\sim$220°C, the damping curve (Δ-t curve) has A, B peak and the relative stiffness curve ($1/p^2$-t curve) has two corresponding steps. A peak is the contribution of the gel effect to damping and B peak is the contribution of the glass transition effect to damping. Therefore, from isothermal curing time-mechanic spectra we can know the gel time (showing that the resin has entered high elastic state) and the glass transition time (indicating that the resin has entered glass state) under different curing temperature. Similar to other tests, the negative trend of gel peak A's occurring time with respect to the increase of curing temperature is in line with the equation (6.6). Likewise, the occurring time of glass transition peak B is also brought earlier at the beginning of the increase of curing temperature, but at a certain temperature it reaches the minimum value and then rises. This is because the mutual growth and decline of curing speed and curing degree in the process. Temperature increases, reaction speed becomes fast, glass transition time reduces; but at the same time, the glass transition requires a higher cross-linked system, which in turn requires a longer reaction time. Before the lowest point, the former plays a dominant role and then the latter. In this temperature range, glass transition temperature T_g of curing products is often close to curing temperature. However, as shown in the figure the damping



(a) (b)

Fig. 6.29 The time-mechanic spectra of isothermal curing at different temperature: (a) logarithmic decrement-time (Δ-t); (b) relative stiffness-time ($1/p^2$-t).

curve under 220 °C only appears a gel peak A (from liquid to rubber state), there is no glass transition peak B. This shows that at higher curing temperature (higher than 220 °C) the chain segment moves more actively so that the liquid resin only gets into rubbery elastomer rather than glass transition.

According to the gel time and the glass transition time under different curing temperature obtained from isothermal curing time-mechanic spectra by TBA analysis, we can draw three-T state diagram of resin curing (Fig. 6.30). The three-T are respectively curing temperature as Y-coordinate, time as abscissa and the gelation or glass transition curve. Moreover, the graph shows a variety of state regions of curing resin such as ungelled glass state, liquid, gelled glass state, rubber state and degradation area and therefore the word "state" in its name. Three-T state diagram fully demonstrates the characteristics of curing, based on which we may design a reasonable process for composite materials. In the figure, the intersection point of the gel curve and glass transition curve is the curing temperature with the gelation and glass transition occurring simultaneously, which is recorded as T_{gg}. The highest glass transition temperature when resin completely cured is recorded as $T_{g\infty}$. When $T_{cure} < T_{gg}$, only glass transition occurs, that is from liquid to ungelled glass state directly; $T_{gg} < T_{cure} < T_{g\infty}$, both gelation and glass transitions occur, with the reaction continuing, resin goes through liquid $\rightarrow$ high elastic state $\rightarrow$ glass state; $T_{cure} > T_{g\infty}$, only gelation occurs, resin is from liquid into high elastic state, no glass transition occurs even last for a long time.

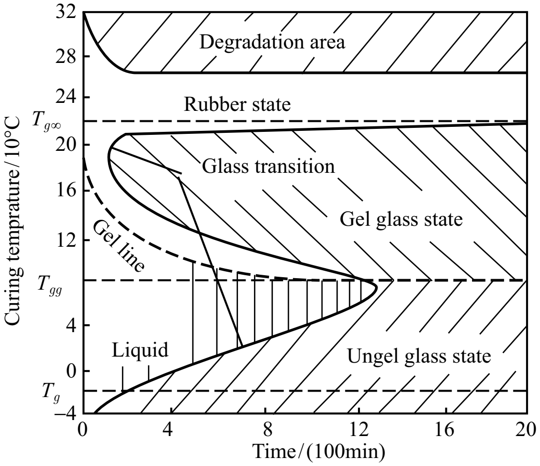


Fig. 6.30 Three-T state diagram of resin.

The gel time is given under different curing temperature in Fig. 6.30, which can be a basis for determining the low step temperature and the time point of applying pressure. The glass transition time under different curing temperature can be used as the basis for the determination of curing temperature and time.

The post-processing temperature should be close to $T_{g\infty}$; and T_{gg} can be used to determine the storage temperature of prepreg and forecast its storage period.

4) Solid-phase reaction in glass state

Through the third stage of curing reaction, the curing system has formed three-dimensional structure into glass state, but its cross-linking density is not necessarily very high and is constrained by curing temperature. In general, increasing curing temperature can make the cross-linking density higher. The glass state with low cross-linking density can be improved by raising post-processing temperature, thus increases glass transition temperature T_g and correspondingly improves the physical and mechanical properties of products. Post-processing at a temperature close to $T_{g\infty}$ can play roles of postcure (further improve curing cross-linking degree so that heat resistance, modulus and other performance increase) and relaxing internal stress at the same time. Dynamic mechanical analysis can also be used to study the secondary changes of curing system (such as β, γ relaxation), providing a basis for determining a reasonable post-processing.

To sum up, the stepped curing can be determined according to the exothermic peak temperatureT_i, T_p in DSC curve and TBA analysis. The curing time can be based on TBA analysis, transformation degree of functional groups by IR, mechanical properties and thermal properties of curing materials under different curing time, and so on. The pressure point can be based on DDA analysis, TBA analysis or the gel time-temperature curve determined by the electric hot plate. Post-processing temperature and its time can be based on TBA analysis, or other dynamic mechanical analysis and the experiments on mechanical properties and thermal properties.

6.4.3 Curing shrinkage and internal stress

1) Curing shrinkage

In curing process, thermosetting resin systems shrink owing to cross-linking and temperature change so that their density increases. Taking epoxy resin system as an example, its volume change is shown in the specific volume-T curve in Fig. 6.31. The unreacted liquid epoxy resin system is heated from room temperature to curing temperature, and its volume expands from point X to point A and reaches gel point C due to curing shrinkage in curing temperature. As curing continues, its volume shrinks to point B. And then cooling from curing temperature to room temperature, it reaches point Y through point D (glass transition temperature T_g) due to cooling shrinkage. The cooling consists of two stages: high elastic state above glass transition temperature T_g, BD; glass state below T_g, DY. Thermal expansion coefficients in two stages are different as reflected on two different slopes of lines in Fig. 6.31.

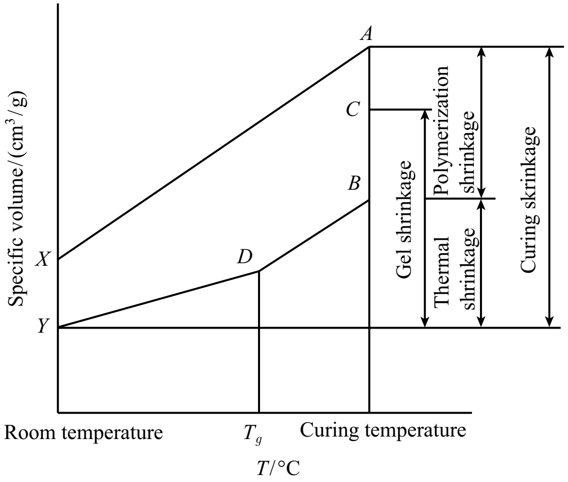


Fig. 6.31 The shrinkage of epoxy in curing process.

From point X to point A, it is the thermal expansion of non-curing system. From point A to point B, it is the shrinkage caused by curing reaction within given curing time at curing temperature, which is called polymerization shrinkage. From point B to point Y, it is the thermal shrinkage of cured system. The volume change between point A and point Y is the total curing shrinkage of system (curing shrinkage = polymerization shrinkage + thermal shrinkage). The volume change between point X and point Y is the volume change before and after curing, which is usually used to calculate the actual volume shrinkage after the system cured. We can compare the shrinkage size of different curing system, but it has little practical significance on the analysis of resin's curing shrinkage and its impact on product property. This is because only a part of curing shrinkage affects internal stress. When the resin system is still liquid (before the gel point), molecules are free and their relative position with mold or the surface of filler has not yet been fixed, and thus internal stress will not produce. So the post-gel shrinkage is more important, namely the volume change from point C to point Y, which is called gel shrinkage. The smaller the shrinkage, the lower the internal stress is.

2) Influencing factors on curing shrinkage

Resin type, nature and content of curing agent (or cross-linked agent), curing process specification, and so on, have a great impact on the curing shrinkage of thermosetting resin systems.

(1) Resin type.

Different types of resin have different curing processes and different curing shrinkages. For example, in phenolic resin there occurs polycondensation in curing process, and a large number of lowmolecule are released, so its curing shrinkage is large. For unsaturated polyester resin there occurs addition polymerization, although it is the same with epoxy resin without lowmolecules materials produced in curing process, it changes from inter-molecular van der Waals distance (0.340nm) to C—C covalent bond length (0.154nm), so its curing shrinkage is substantial. Curing reaction of epoxy resin is ring-opening polymerization of ternary ring. Ring-opening expansion will counteract partial shrinkage, so its shrinkage is the smallest.

(2) Type of curing agent.

Different types and different contents of curing agent form network with different crosslinking density and different tightness, so they have different curing shrinkages.

(3) Curing temperature.

In general, the higher the curing temperature is, the greater the shrinkage will be, and meanwhile the greater the internal stress will be. This is because the thermal shrinkage increases when temperature drops from curing temperature to room temperature. Of course, it is related to higher cross-linking density. There are also unusual cases sometimes. Too high a curing temperature may impede the transformation to the three-dimensional network with high cross-linking density, yielding a low shrinkage.

3) Internal stress in thermosetting resin

(1) Source of internal stress.

As discussed above, thermosetting resins will produce polymerization shrinkage in curing process. The higher the curing temperature is, the greater the shrinkage will be, and thus the greater the internal stress will be. Internal stress is not easy to relax when segment movement is frozen, which is relaxation characteristic of high elastic state. Moreover, the thermal conductivity of resin is poor, so the sooner the curing process, the higher the curing exothermic peak is. In the curing process, different heat radiation condition or cooling too fast will produce uneven temperature field in parts, especially for thick parts. It will also cause different curing temperatures and different shrinkages at different points, resulting in internal stress. Especially for the shrinkage after gelation, uneven temperature will lead to the different speeds of stress relaxation at different points, resulting in different stresses, which generates additional internal stress. Therefore, the greater the curing shrinkage of resin system occurs, the faster the reaction takes place, and the thicker the parts are, the greater the temperature gradient will be. With greater internal stress produced in the curing process, the parts will be proner to deform and warp.

(2) Measures to reduce internal stress.

To reduce the internal stress of thermosetting resins, we should take the following measures. ① Heat slowly and cure slowly at low temperature so that the curing and the shrinkage is more uniform; ② add powder filler or flexible resin to reduce curing speed or relax internal stress; ③ fully cure at the temperature close to T_g; ④ cool slowly, relax heat shrinkage; ⑤ post-treatment.

Exercises

1. How to classify the forming process of composites?

2. Which materials are made into the molds used in hand lay-up process, and what problem should be pay attention to when using the molds that are made of different materials?

3. What kinds of release agent are commonly used? What are the advantages and disadvantages of various types of release agent? Please give examples to illustrate.

4. What is the main effect of applying the pressure in making composites? Why is low-pressure used to form composites generally?

5. What are the three elements of forming composites? Illustrate their impact on product properties and production efficiency.

6. What is the processability of composites? What are the main criteria to assess the processability?

7. What is wet process? What is dry process?

8. How to choose forming methods for composites parts?

9. What is bag-pressurized molding? What forms does it mainly have?

10. What is the autoclave molding of composites? How to pave a variety of auxiliary materials when preparing parts?

11. What are the three winding rules in filament winding process? How to achieve?

12. What is RTM process? What are its requirements for resin system and fiber-reinforced materials?

13. Briefly describe the mechanism and characteristics of RFI process.

14. What structure forms do the molds have for forming composites? What is the frame mold? What are its advantages?

15. How to make reasonable curing process parameters of composites by experiment methods?

16. What is dynamic dielectric analysis DDA? How does it monitor the curing process?

17. What is the three-T state diagram? How to measure it by experiment?

18. Why do we need stepped-curing for composites?

19. Why is a good choice of pressure point the key to prepare high-quality composites? What is pressure zone?

20. Try to analyze the volume changes in curing process of thermosetting resin system.

21. Briefly describe the curing internal stress of composite materials and illuminate the measures to reduce internal stress.

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7

Molding technology of sandwich structure composites

Sandwich structure (or sandwich construction) is a structural form which is composed of high strength face sheet and light weight sandwich core. There are two different forms of sandwich core, according to different forms of core, which are honeycomb sandwich and foam plastics sandwich structure. The material for manufacturing sandwich structure is metal or non-metallic, or any combination of both. For example, face sheet can be a variety of composites (like GFCM, CFCM, KFCM, HFCM), metal (like aluminum alloy, titanium alloy, etc.); sandwich core can be honeycomb (like glass cloth, Nomex paper, cotton cloth, insulation paper, aluminum foil, etc.) and foam plastics (like PS, PVC, polyurethane, phenolic, epoxy, etc.).

The characteristics of the sandwich structure are: ① adiabatic, sound insulation, anti-vibration, and good high-frequency dielectric properties; ② weight reduction, high strength and stiffness. On the condition of such a structure without increasing weight and reducing strength, the stiffness can be reinforced largely. Therefore increasingly found on planes, such as wing (flap, aileron), radome, antenna cover, the posterior segment of rotary wing, siding, floor, and so on.

7.1 The molding technology for honeycomb sandwich structure

7.1.1 The size and shape of the honeycomb sandwich core

The plane (projection) shape of the honeycomb sandwich core are non-hexagonal (such as square, rhomboidal, rhombic, sine curved) and hexagonal (like enhanced hexagonal, diagonal hexagonal and ordinary hexagonal). Of all kinds of honeycomb shape, the hexagonal sandwich core has the highest stability. They can be made easily, so they are widely used.

The structure shape of the hexagonal honeycomb sandwich is similar to the natural structure of honeycomb. From a geometry viewpoint, it is the honeycomb vesicular structure shaped by an innumerable hexagonal in an orderly arrangement. The size of the honeycomb cell is usually indicated by side length a, wall thickness δ, and height h, while in England, America, France and some other countries it is indicated by the diameter D of its inscribed circle. $D = \sqrt{3}\,a$ in the hexagon. The side length a (mm) generally at 1.8, 2.7, 3.6, 5.5, etc., and corresponding D (mm) is 3.17, 3.76, 6.35, 9.52.

7.1.2 Preparation of the honeycomb sandwich core

There are two methods for manufacturing the honeycomb sandwich core, which are the ripple method (molding method) and the core strip expansion method (adhesive joint stretching method).

1) The ripple method

The corrugated plate of half hexagonal is made by hand lay-up molding or compression molding on the waveform mold, then we use glue to stick each other forming sandwich core. This method can make sandwich core into any size and the size is accurate, but this method is rarely used at present because of the low production efficiency, outmoded technology and also the need of molds.

2) The expansion method of honeycomb core strip

Fig. 7.1 shows honeycomb sandwich core made by the adhesive joint stretching method.

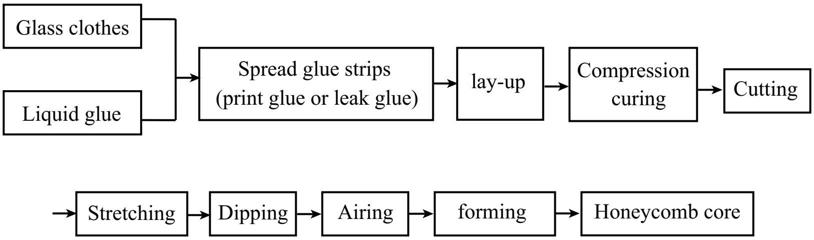


Fig 7.1 Technique flow chart of honeycomb core made by the adhesive joint stretching method.

(1) Spread glue strips and lay-up.

Glue strips are spreaded on glass cloth usually by mechanical gelatinizing technique with the gummer, or manual gelatinizing method.

There are two methods for gelatinizing, the glue-leaking type and the glue-printing type of spreadometer. See Fig. 7.2. The glue-leaking automatic spreadometer is mainly composed of the gelatinizing system, the transmission system and the heating drying system. Glass fabrics are wrapped on the drum first when gelatinizing, then they are connected to the impeller rotor through the leakage mouth, the drying plate and the guide wheel. Glue strips are spreaded mainly through the leakage mouth. The leakage mouth is made according to the principle of ball pen: there is a small spring holding up a steel ball in the mouth, so the liquid glue is not able to flow out because there is no gap between the ball and the side wall of glue mouth. We adjust the position of the leakage mouth up and down when spreading glue, then the steel ball and the cloth surface contact slightly. The round bead rolls continuously due to the cloth's friction when the cloth move forward, and the liquid glue spreads on the cloth when it flow out unceasing from the smooth surface of the steel ball. The size of the gap may be adjusted and determined by the glue's viscosity and the speed of the cloth moving. Glue strips are spread in the length direction when the glass cloth moves constantly.

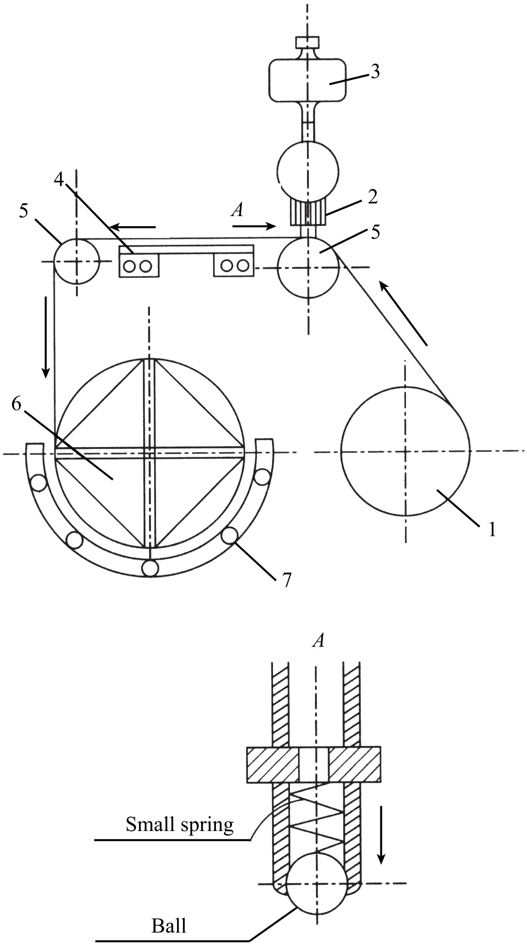


Fig 7.2 The schematic diagram of glue-leaking type of automatic spreadometer: 1-drum with glass cloth; 2-leakage mouth; 3-glue box; 4-drying plate; 5-guide wheel; 6-impeller rotor; 7-drying oven.

The glass cloth on which glue strips are spread is coiled on the impeller rotor after drying on the plate. Once the impeller rotor curls a cycle, the glue box may lift up (the glue mouth separates from the glass cloth) automatically and move towards left or right for a distance simultaneously. This distance is about one half of the distance between glue strips. Therefore, the glue strips on the glass cloth which is coiled on the impeller rotor stagger from the glue strips on neighbouring glass cloth, obtaining the honeycomb superposition. See Fig. 7.3, the lay-up is of A-B-A-B type and has a strict position. In a hexagonal honeycomb cell, the thickness of two side walls is equal to the thickness of two layers of glass clothes, and the thickness of nearby four walls is equal to the thickness of one layer of glass cloth.

This kind of spreadometer has very high production efficiency, but the structure is so complex that the gelatinizing is not easy to adjust and it is difficult to guarantee a good quality. Because there are dozens of mouths on a spreadometer and they are machined with a big tolerance, it is impossible to calibrate these glue mouths into uniform condition. It follows that the spreaded glue strips might be uneven in the width and must be regulated by hand. Therefore this kind of spreadometer is outmoded too and has been replaced with the glue-printing gummer.

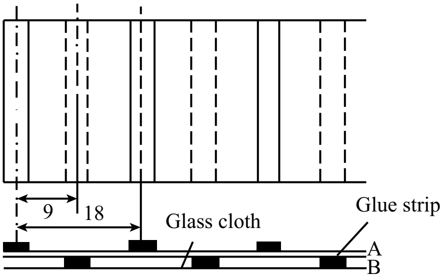


Fig 7.3 The schematic diagram of honeycomb superposition.

The structure of glue-printing type of automatic spreadometer is shown in Fig. 7.4. When printing glue, the cloth is rolled on the cloth roller 1, then it passes through guide wheel 6, two glue applicators 2 and the drying plate 7. Finally, we connect it to the impeller rotor 8 together with the glass cloth on another roller 1. The glass cloth moves towards the arrow when the spreadometer is started. At the same time, the liquid glue in the trough is carried on the convex ribs of the glue applicator through the glue carrier roll 4 and the glue transfer roll 3. The glass cloth happens to be on the tangential plane of the convex ribs and it moves straight. The glue applicator on the cloth rotates with the cloth in the same direction and prints the liquid glue strips continually on the glass cloth.

The equipment structure is not very complex by this method for printing glue, and the production efficiency is high, suitable for massive production. The equipment can be conveniently adjusted, which only need adjusting a suitable distance between the glue carrier roll or the glue transfer roll and the glue applicator in view of different viscosity of the liquid glue, then glue strips might be printed satisfactorily. But the viscosity of the liquid glue changes easily in printing because it is hard to seal the glue trough of this equipment, and the time for printing is long. Among other flaws, sometimes the glue is printed unevenly and the glue strips has cured on the glue applicator. This shortcoming may be avoided if raw materials are continuously fed into the glue trough.

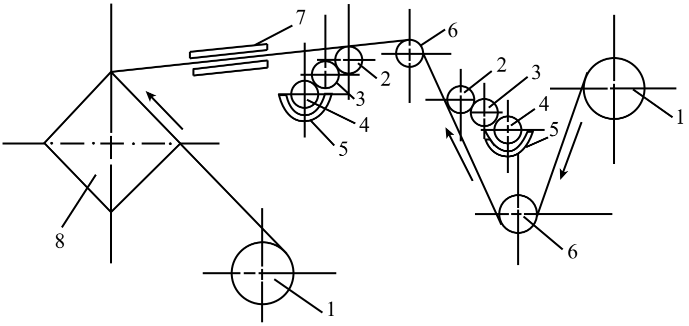


Fig 7.4 The schematic diagram of glue-printing type of automatic spreadometer: 1-cloth roller; 2-glue applicators; 3-glue carrier roll; 4-glue transfer roll; 5-glue trough; 6-guide wheel; 7-drying plate; 8-impeller rotor.

The key to make good honeycombs is to control the quantity of spread glue. We should prevent glue from missing or permeating and guarantee the size and width of glue strip. In the processing, the most important thing is the control of width, thickness, parallel level between glue strips as well as its degree of drying. The glue can only be coated on one side of the cloth, and cannot seep to the other side. As the designed width of the convex ribs of the glue applicator on the glue-printing spreadometer is 4.0mm, width of the glue strip is generally between 4mm and 4.5mm. Side length of the honeycomb cell made by the convex ribs seen in Fig. 7.5 is 4.5mm.

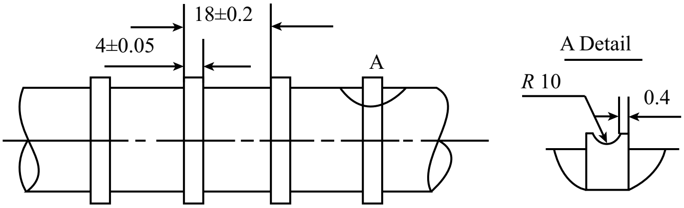


Fig 7.5 Convex ribs size of the glue applicator (side length of honeycomb cell is 4.5mm).

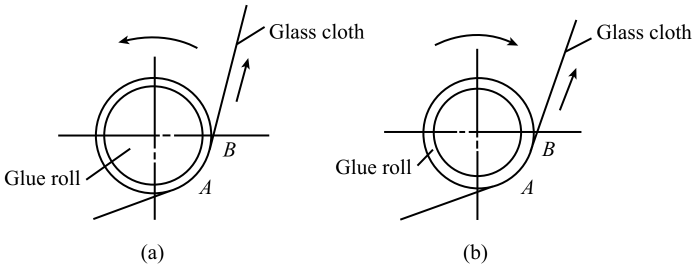
A lot of factors affect the glue penetration, such as fabric density and surface characters of the glass cloth, the viscosity of liquid glue, the condition of spreading, and so on.

If we use the glass cloth without any process to spreading glue strips, the wax sizing agent on it can prevent the liquid glue from penetrating to the other side.

The glue content of strips, the soakage and infiltration of the glass cloth in the liquid glue are influenced by the liquid glue viscosity. The viscosity of 100s to 120s (the 4th cup viscometer) is generally adopted for the X98-1 glue to print strips. Usually for high viscosity glue it is difficult for printing, and the glue layer is thick and easily permeates in compression curing. The glue with excessively low viscosity is so easy to diffuse that strips broaden quickly and shape of lattice is not regular after molding. It is also inclined to seep to the back side, thus cause difficulty in following stretching process. It is better with a higher viscosity of glue under the condition of spreading glue successfully.

The amount of liquid glue spread on the cloth should be suitably controlled by the distance between rolls or the contact pressure of leakage mouth. An excessive amount of glue will cause infiltration, while insufficient amount of glue might lead to low strength, making it debonded while it is stretched.

The contact pressure (the spreading pressure) between the cloth layer and the glue applicator or the glue leakage mouth should be reduced as far as possible. The bigger the contact pressure is, the bigger the friction force between them is. The liquid glue is even squeezed to the back side sometimes because of big extrusion, so it will not form in stretching. For the glue-printing spreadometer, the contact wrapping angle (the circle angle of arc length between the glass cloth and the glue applicator) of the glass cloth and the glue applicator has a great influence on infiltration. When it is oversized, the glue on one side of the cloth will penetrate to the back under the pressure of the convex ribs of the glue applicator. Therefore, the contact wrapping angle should be as small as possible under the condition of spreading evenly. In ideal configuration, there is only point contact between the glass cloth and the glue applicator. The concave arc slot with 10mm in radius notched on the convex ribs of the glue applicator (Fig.7.5) is designed to reduce the contact pressure between the cloth and the glue applicator and thus solve the problem of infiltration. In addition, we may tackle the problem differently by adopting glue-scratching instead of glue-printing. The only difference between printing and scratching is that: the glue applicator on the cloth surface turning in the same direction with the cloth for printing and it is in the reverse turning direction for scratching. See Fig. 7.6. The cloth and the roller contact at the area of A and B where there is the liquid glue in case of glue-printing. The liquid glue might penetrate because of the contact pressure between the cloth and the glue applicator. If by scratching, the contact area is still at A and B while the glue is only at point B. The glue is scratched to the cloth as soon as the cloth and the glue applicator contact at B. There is no pressure on the cloth because the cloth moves forward continually. It will not infiltrate as long as the liquid glue has a certain viscosity and the glue is not watery enough to infiltrate under no external force. As for the contact area of A and B, although a high contact pressure, there is no glue on the glue applicator in the second manner, hence no infiltration occurs. The



(a) (b)

Fig 7.6 Schematic diagrams of (a) glue-printing and (b) glue-scratching.

practice has proved that there is no infiltration even scratching with a low viscosity of liquid glue (60~80s, the 4th cup viscometer).

(2) Compression curing of honeycomb block.

After spreading, we take down honeycomb block from the rotor and press it on the hydraulic press which is preheated to (145±5) °C according to the glue (X98-1) curing standard. The stage lasts for 2h to 3h under 0.3MPa to 0.5MPa, then the pressure releases when it cools at temperature between 40 °C and 50°C. The guideline of choosing an appropriate pressure is that the liquid glue must not penetrate to the back and honeycomb sides must be joined well. If the pressure is too large, the side length (a) of the honeycomb cell could not be guaranteed because of infiltration and slippage. The holding time is determined by the thickness of the block.

The thickness of the honeycomb block, i.e., the number of cloth layer, is decided by the product size. It could be figured out by formula (7.1).

$$L = 0.866n(a + 1.15b) \quad \text{or} \quad n = \frac{L}{0.866(a + 1.15b)} \tag{7.1}$$

Where, L is length of the stretched honeycomb block, mm; n is number of cloth layer; a is width of honeycomb cell, mm; b is thickness of glass cloth, mm.

(3) Cutting, stretching and dipping.

The pressed honeycomb block is cut on the cutter machine according to the height h of the honeycomb (the cutting width), i.e., the distance between face sheets of sandwich panel. Then we stretch the honeycomb, and fix it on the hand tailored bracket in order to keep the mesh shape of the honeycomb. Then we plunge it into the liquid resin with certain viscosity prepared in advance. We take out the bracket slowly, and lay it horizontally for the solvent evaporation. The honeycomb core could be taken out from the bracket after 24h to 48h.

The quality of the honeycomb core is directly influenced by the procedure of dipping. The glass cloth honeycomb core can bear load only after the solidification of impregnated resin. Therefore we know that the glue content and the uniformity of the glue on the honeycomb cell foil is the key of honeycomb strength. The glue content is can be designed by controlling the viscosity, concentration or density of the liquid glue, among which its density is more convenient. High density glue is for high glue content in honeycomb, the strength may be increased but it is brittle, the honeycomb core is heavy and thus increasing the weight of the product. Otherwise, low density for low glue content, and strength and stiffness too low to satisfy the requirements.

If the glue content is uneven on the honeycomb cell foil, then the glue content is too much on one side and too little on the other side. The bearing honeycomb core would break even the integrated part lost stability because the side of the low strength firstly destroyed. In order to improve the uniformity of glue content, the bracket should better be dried in the revolving centrifugal dry equipment for 20min to 30min after it is took out from the liquid, then in room temperature.

(4) The curing of dipped honeycomb blocks.

The dipped honeycomb block cannot be used only after drying. It must be cured first. There are three types of curing for the honeycomb core.

① For the planar product, like the wall plate, the structural beam of honeycomb sandwich, and so on, the honeycomb core may cure on the planar template after it is taken out from the bracket, and then the product is made of the honeycomb core joint with the face sheet by adhesive.

② For products with simple shape, big radius curvature, like wing and all kinds of rudder-face, and so on, the honeycomb core can partly cure when it is heated on the planar template. The characteristics of this partly solidified honeycomb core are: it softens at some degree on heating, has certain distortion ability, and has certain stiffness at cooling, can withstand certain molding pressure. Using the partly solidified honeycomb core to make the sandwich structure with not big curvature may simplify the technology, lessen technical equipments, and suit for mass production.

③ For products with complex shape, small curvature radius of curved surface, for instance, all kinds of radome: firstly honeycombs are spliced to preform on the mold after drying; secondly by the curing of the honeycomb on the mold, the half finished good is made in the dimension coordinate according to the shape of the product; thirdly, the honeycomb joints with the face sheet by adhesive. There are several methods for edge splicing of honeycomb core, such as butting, scarfing, inserting, and squeezing. See Fig. 7.7.

7.1.3 Forming technique of the honeycomb sandwich structure

The sandwich product is composed of the core and the cover, which are jointed by the glue, so the sandwich product cannot escape from the glue bonding technology. Large-scale sandwich products on airplane like the wing, the antenna cover and so on are large structures. It is difficult to joint in such a big area. In addition, they are different kinds of materials. Contact area of honeycomb core and face sheet is very small, so the key of this processing is to ensure a good joint quality in a big area and a high enough joint strength.

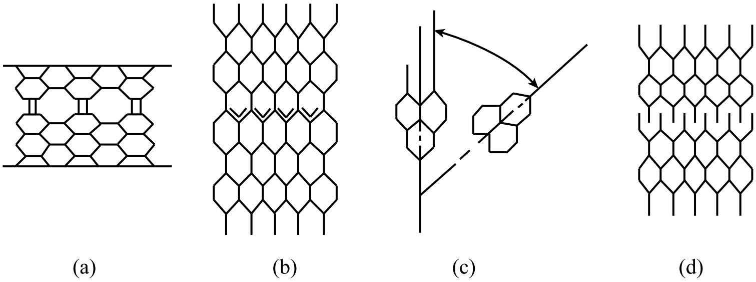


Fig 7.7 Connection manners of the honeycomb sandwich core:

(a) butting; (b) scarfing; (c) inserting; (d) squeezing.

The following procedures are the typical steps in manufacturing the honeycomb sandwich products: ① manufacturing of cover and skeleton parts; ② the forming and splicing of honeycomb sandwich core; ③ the adhesive bonding of the cover, the skeleton part and the honeycomb sandwich core; ④ machining (amending); ⑤ quality test. See Fig. 7.8.

1) Making covers and skeleton parts

The cover of sandwich product is largely determined by the pasting forming with the mold. Choosing concave mold or conrex mold mainly depend on structure, shape, dimension tolerance and surface smoothness of the product, and so on, but curing condition and compression forming of the end product are determined by the character of the liquid glue. As airplane parts, in order to make a smooth surface and to enhance the aerodynamic property, the outer cover is often made by the concave molding, and the inner cover is pasted on the honeycomb core.

The skeleton parts within product may be manufactured first on the forming mold of the sandwich structure or specially paste on the special mold, then process mechanically and repair rough edges after curing and demould, for bonding together with the honeycomb core and the outer cover.

2) The adhesive bonding of cover, skeleton parts and honeycomb core

There are three kinds of forming methods for joining honeycomb core and cover, one step forming method, the two steps forming method and three steps forming method.

The one step forming method is one that simultaneously solidifies, forms and bonds the inner cover, the outer cover and the core at one time. This method is the simplest, but it is not used commonly because the quality inspection is not easy. While two steps forming method or three steps forming method is commonly used.

The two steps forming method is that firstly solidify the outer cover (or the inner cover) which is pasted on the mold, load glue film and honeycomb core and paste the inner cover (or the outer cover) on the sandwich core, and then secondly solidify them; or firstly solidify the outer cover (or the inner cover) pasted on the mold and jointed honeycomb core, and secondly solidify the inner cover (or the outer cover) pasted on the honeycomb core.

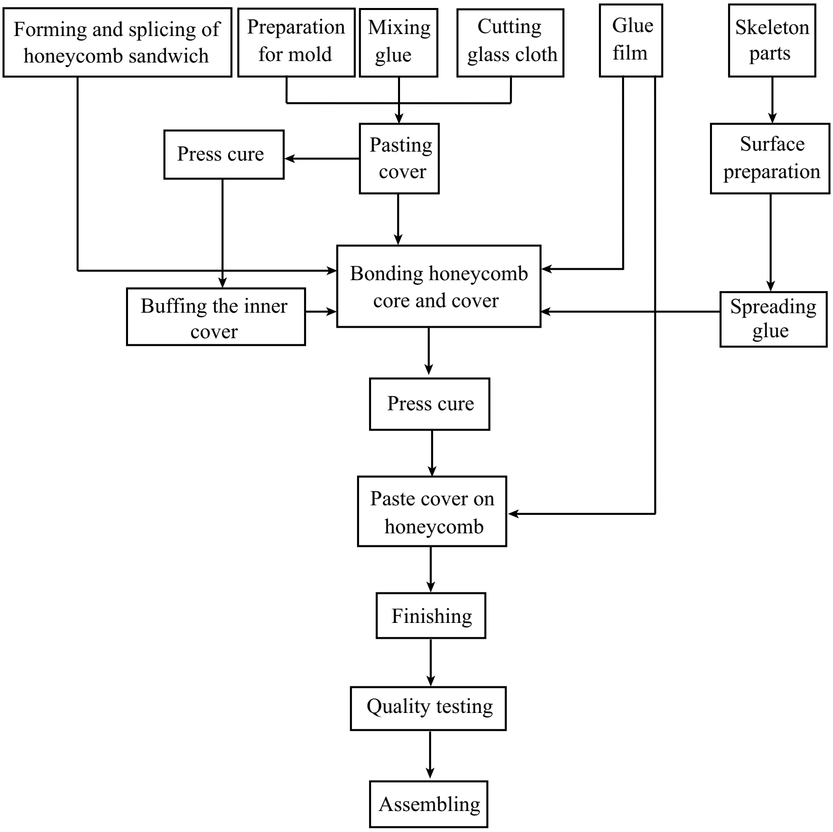


Fig 7.8 The technique flow chart for fabricating the honeycomb sandwich product.

The three steps forming method is the method that firstly solidify the outer cover after it is pasted in the concave mold, and then secondly solidify the sandwich core which is jointed with the outer cover, thirdly solidify the inner cover pasted on the sandwich honeycomb core in the end.

The practice has proved that, the two steps forming method might guarantee the product surface smoothness. But if we firstly solidify the outer cover in the concave mold and secondly solidify the honeycomb sandwich core and the inner cover, it is not easy to inspect the forming quality, for instance, the joint quality of honeycomb core and cover, the shrivelled phenomenon of the honeycomb, the delamination of cover and stressed belt, the bubble and the corrugation phenomenon, and so on. Despite the inferior surface quality, the other kind of the two steps forming method mentioned above is better in all issues, for instance, a better joint quality of honeycomb sandwich core and outer cover; low molecule released in curing can be eliminated more thoroughly than the former; the forming quality of the sandwich is easy to inspect and flaws be removed timely also. In the three steps forming method processing, the quality can be inspected gradually and the problem found during process can be solved timely since the outer cover solidifies in advance. The product surface is smooth and other qualities are all good. The shortcoming is the way of doing it step by step. It complicates the process and lengthens the duration.

It is convenient to preform and splice the honeycomb sandwich core on convex mold. We may splice the honeycomb core first on the epoxy plastic convex mold and cure in advance under low temperature, and then we put it in the aluminum concave mold to solidify under high temperature.

Honeycomb sandwich core joins the cover with glue. The glue can be either smeared on the edge surface of the core using brushes, rollers or scrapers, or attached to the sandwich core when we soak it in the liquid glue in depth of 2~3mm. The core taken out should be air or heat dried afterwards. The second way increases the joint area of the honeycomb. Certain gummosis is formed between the sandwich core and the cover, and glue fillets are formed on the edge surface of the honeycomb sandwich core, which guarantee the joint sturdiness. We usually use glue film for large-scale sandwich products. This is reasonable because it not only enlarges the joint area (making it more stable), but also ensures the glue's even distribution and sufficient amount of glue on the edge surface of the honeycomb sandwich core. It simplifies the operation too.

During solidification, design parameters such as temperature, pressure and holding time is related to the property of the liquid glue. Among them, the amount of pressure is also affected by the compression resistance of product structure and honeycomb core. It must be adjusted according to actual situation.

7.2 Molding process of foam sandwich structure

7.2.1 Introduction of foam and its sandwich structure

1) Variety of foam

(1) Type of material. Thermoplastic foam plastics, such as PS, PVC, PE, and so on; thermosetting foam plastics, such as phenol-formaldehyde, epoxy, polyurethane, and so on.

(2) Type of cell structure. Open-hole foam plastics (bubbles connect to each

other) and closed-hole foam plastics (sound insulating, adiabatic, low water absorption).

(3) Type of foam elasticity. Soft foam plastics, i.e., the sponge and rigid foam plastics (for structural materials such as being filled in sandwich). When foam samples are compressed to 50% of their thickness, after removing the pressure, the soft foam plastics have permanent deformation of $<2\%$, while the rigid foam plastics have permanent deformation of $> 10\%$. The foam hard plastics have high crossing linking density and high strength which suit for packing material as structures.

2) Components of foam plastics

Foam components include resin and foaming agent.

(1) Resin. There are two types of resin which are thermoplastics (thermoplastic resin, plasticizer, antioxidant, and so on) and thermoset (thermosetting resin, curing agent, toughener, and so on).

(2) Foaming agent. The foaming agent contains liquid foaming agent and solid foaming agent. Liquid foaming agent is solvents with low boiling point, like petroleum ether, freon, and so on. They gasify when heated, and retain in the foam. Solid foaming agents include AIBN (organic), NH_4CO_3 (inorganic), and so on. They decompose to gas when heated to certain temperature, and the gas retains in the foam.

3) Fabrication methods of foam

We've just seen the variety of foam plastics and naturally there are many fabrication methods to prepare them as well. Foams with different components demand different fabricating processes, but for simplicity we combine those similar in basic principles and classify the methods into the following three categories.

(1) Mechanical foaming method. This method is to mix the gas into liquid polymers with intense mechanical agitation, and then cure the resin to form the foam. For instance, the urea formaldehyde resin foam is prepared by this method.

(2) Physical foaming method. The low boiling point solvents dissolve in polymer at normal pressure or increased pressure. When foaming, solvents evaporate by heating and the gas produced scatters around the polymer in bubbles. Then the foam stabilized by cooling or curing to form the foam plastics. For instance, expandable polystyrene foam and polyurethane foam having fluorine hydrocarbon compounds (like F-113, F-11, F-12 and so on) are prepared with this method, etc.

(3) Chemical foaming method. There are two methods of chemical foaming: One method is by means of the reactions between compositions in foam plastics, which release gas to cause the polymer foaming. For instance, the polyurethane foam by adding water is foamed by this way. Another method is by means of the decompositon of solid foaming agent added in foam plastics when heating, which releases gas that causes the polymer foaming. Most of foam plastics are foamed

with this method, such as polyethylene, polyvinyl chloride, polystyrene, phenolic, epoxy, and so on.

4) Properties of foam plastics

Types and structures of the resin, types and amounts of the foaming agent, and density of the foam plastic all affect the mechanical properties, electrical properties, thermal properties of the foam plastics and technological properties for preparing foam plastics.

5) Preparation of foam plastics sandwich structure

Foam sandwich structures are used everywhere in applications such as radome (polyester FRP panel-polystyrene foam core or phenolic FRP or epoxy FRP panel - polyurethane foam core) and ventral fin (phenolic FRP panel-phenolic foam core). There are approximately two preparation methods.

(1) Prefabrication bonding formation. Firstly, we prepare foam plastics and process it into the core, and then bond it with face cover to get the sandwich structural products. For instance, polyester FRP is pasted on PS foam plastics (using methyl methacrylate esters as crosslinking agent, not using styrene which dissolves PS).

(2) Integrated part formation by in-situ filling. Firstly, we make sandwich structure skeleton-cover assembly, fill the half-finished foam products (liquid or solid) into the cavity, and then form integrated foam sandwich structural products by foaming.

7.2.2 Manufacture of PS and PVC foam products

According to different types of foaming agents, PS foam products are fabricated commonly by compression molding (use solid foaming agent) and grain-foaming (use liquid foaming agent); but PVC foam products are fabricated mostly by the compression molding.

1) Fabrication of PS foam by compression molding (or pre-pressing flan method)

(1) The foaming forming technological process.

See Fig. 7.9. The powdery polystyrene synthesized by emulsion polymerization is mixed and grinded with solid foaming agent AIBN according to certain proportion. Then we heat the blend under certain condition so that foaming agent decomposes into gas which disperses evenly in resin. Because polystyrene belongs to thermoplastics, its viscosity is low in melting state. Therefore the gas decomposed by the foaming agent escapes from the resin very easily, thus we use the pre-pressing flan by compression molding.

The pressing of flan is similar to the pressing of thermoplastics. The molding temperature is controlled around softening point of the material, and it is higher than the foaming agent's decomposition temperature. Then under high temperature and high pressure, the gas decomposed by the foaming agent within the material partly dissolves in polymers, and another parts of the foaming agent form very

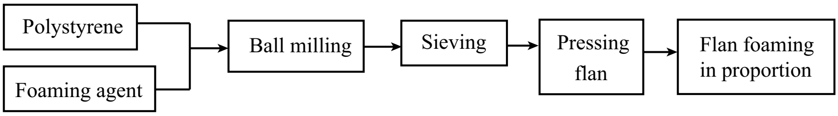


Fig 7.9 Technique flow chart of manufacturing PS foam by compression molding.

small air bubbles under the compression condition, therefore the pressure must be larger than the gas pressure of foaming in the material. The press mould must be closed, and the closed mold must be sealed so as to avoid escaping and redistributing of the gas. Otherwise it will foam unevenly and cause flaws such as different density and deformation of products and so on. The press mould heating must be even, otherwise the gas will distribute unevenly too. The pressing temperature of PS foam is 145°C and the pressure is between 12MPa and 15MPa. We need to apply the temperature and pressure for between 1.5min to 2min per millimeter thick in the product. When it cools to temperature between 30 °C and 40°C, we may release the pressure and demould.

The pressed flan is heated once more and the material softens. Gas will expand until the flan gets to equilibrium state under the temperature where the internal pressure of gas is balanced with the elastic stress of polymer thin film (foam wall). In order to prevent gas from breaking out of the material, it is only heated to the temperature of elastomeric state. For instance, the polystyrene flan can be heated to 100°C using steam, foamed for 60min to 120min, then cooled to temperature between 30 °C and 60°C, through which we get foam product with a size several times bigger than the flan it is made from. Sometimes in order to control shape, restricted mould will be used in foaming, the flan will foam to the end which cling to the mould and obtain accurate shapes.

(2) Estimate the amount of foaming agent.

The density of foam plastics mainly depends on the amount of foaming agent, and it also relates to the chosen molding parameters like foaming temperature, pressure and time, and so on. If we use the foaming agent AIBN, its decomposition temperature (a temperature range of maximum decomposition of the foaming agent) is between 90 °C to 100°C; the quantity of gas (the amount of gas decomposed from 1g of foaming agent) is 146.6mL/g under the standard condition. The amount of foaming agent in PS foam can be estimated with the following equation.

$$r = \frac{g+x}{V} = \frac{100+x}{\dfrac{100}{1.05} + 146.6x} \quad \text{or} \quad x = \frac{105 - 100r}{154r - 1.05} \tag{7.2}$$

Where, r is density requested of product, g/cm^3; g is shares by weight of resin, 100g; x is shares by weight of foaming agent, g/100g resin; V is theoretical volume of product, cm^3; 1.05 is density of polystyrene, g/cm^3; 146.6 is nitrogen theoretical content of AIBN under the standard condition, mL/g.

(3) Estimation of flan pressing pressure.

When pressing flan, the foaming agent decomposes and the gas produced causes a very big internal pressure. In order to make the compression mold closed, the compression pressure must be even bigger than the internal pressure. Generally, the compression pressure is 10% or 15% larger than the internal pressure.

The pressure size is related to such factors like property and amount of the foaming agent, molding temperature, and so on. The internal pressure could be calculated according to theoretical formula, and then the external pressure can be defined. A sample calculation of the internal pressure.

If the amount of pressing flan material W is 6300g, AIBN is 4.6 shares by weight, polystyrene density r at 1.05g/cm^3, flan density r_1 at 0.97g/cm^3, the molding temperature at 150°C, then the remained volume V of the compression molding cave should be:

$$V = \frac{W}{r_1} - \frac{W}{r} = \frac{6300}{0.97} - \frac{6300}{1.05} = 495(\text{cm}^3)$$

The volume V_{N_2} of nitrogen decomposed by foaming agent is given by:

$$V_{\text{N}_2} = 6300 \times \frac{4.6}{100 + 4.6} \times 146.6 = 40640(\text{cm}^3)$$

So the internal pressure P_1 of the compression mold is given by:

$$P_1 = \frac{P_0 V_0 T_1}{T_0 V_1} = \frac{1 \times 40640 \times (273 + 150)}{(273 + 20) \times 495} \approx 118(\text{kg/cm}^2)$$

In fact, the internal pressure decomposed by foaming agent is smaller than the calculated pressure, because a part of gas can be dissolved in the resin and some gas are lost (air leakage, material leakage) when the foaming agent and polystyrene mixed together; The closed mold compression should be carried out between 95°C and 115°C, then the foaming agent starts to decompose. A part of nitrogen escapes at that moment, therefore the compression pressure at 120kg/cm^2 is enough.

2) Manufacture of PVC foam by compression molding

PVC foam has two types: rigid and soft. Soft foam is soft because of the plasticizer in the components. It is commonly used as seat cushion on airplane. Contrarily, the rigid foam has high hardness and high strength because there is no plasticizer in the components, and it is commonly used as core material and liner for sandwich structure on airplane.

PVC has a bad plasticity in its viscous flow state, and in addition the decomposition temperature is close to its softening point. Therefore besides adding stabilizer, plasticizer must be used for improving processing property. Take pressing flan as an example, its fluidity may be improved, temperature and pressure be reduced.

When making the rigid PVC foam, there are two ways (Table 7.1) for improving liquidity of the resin. One method is that the monomer which can dissolve PVC is used in formula, like methyl methacrylate, the amount is 25% by weight. Therefore, at the initial stage of compression, methyl methacrylate can improve the liquidity of the polymer. At the end stage of compression, the monomer polymerizes by the function of initiator AIBN, and stops the plasticization. In the other method, the solvent like dichloroethane is used with the amount from 50% to 65% by weight (take 100 shares of resin as computations). After PVC is dissolved in dichloroethane, fluidity of the resin may be improved when pressing. But because of the solvent, the compression pressure must be enhanced in order to get homogeneous flan. Generally, the pressure is 20MPa. In the foaming formation of the flan, the solvent volatilizes when heating, so we get the rigid PVC foam.

Table 7.1 Formula of the rigid PVC foam

Raw materials	Formula 1	Formula 2
Polyvinyl chloride	100	100
Methyl methacrylate	25	—
Azobisisobutyronitrile	0.8∼1.1	12∼14
Ammonium carbonate	10	—
Sodium bicarbonate	8	—
Azobisformamide	—	7∼9
Tribasic lead sulfate	—	4∼6
Antimony trioxide	—	6
Tricresol phosphate	—	7
Dichloromethane	—	60∼65

The process of fabricating PVC foam by compression molding is essentially the same as that of fabricating PS foam. Grinding solid component in ball mill for 3h to 4h, then sift through 60-mesh screen, after liquid component be added and stirred for 30min to 50min, pressing in mould. The pressing temperature is between 160°C and 168°C; the pressure is between 15MPa and 20MPa; and the keeping time varies with different components. For example, the flan at a thickness of 20mm should be kept for 40min when monomer methyl methacrylate is used. The flan with thickness of 55mm should be heated for 30min to 50min when solvent dichloroethane is used. After finishing heating, we cool the flan for 30min to 40min, then release the pressure and demould.

The rigid foam flan is suitable for foaming in the saturated steam atmosphere between 95°C to 98°C. The soft foam is suitable for foaming in the hot water between 80°C to 85°C. In the process of fabricating the rigid PVC foam with solvent, after the flan foaming, it should be treated for 48h in heating oven [at (65±5)°C], so the solvent volatilizes effectively.

3) Fabricating expandable PS foam by grain-foaming method

There is quite a long history about fabricating PS foam with solid foaming agent and by compression molding. Because the manufacture process is complex, it needs heavy and very expensive mold and heavy press. PS foam product has high mechanical strength, but its high density, low production efficiency, high cost, and difficulty in forming into complex shapes has limited its application and development. In 1951, West Germany developed the manufacturing process of expandable PS, in which there is no need of heavy mold, high temperature and high pressure condition. Moreover, all kinds of foam products with complex shapes can be made by aluminum mold under low steam pressure or boiling water condition. The production thus developed very fast, it has been widely applied in industries such as refrigerating, construction, precision instrument, electronic as packing materials for heat insulation, sound insulation, shockproof and dampproof.

(1) Foaming mechanism of expandable PS foam.

For example, foaming agent is added to the suspended polystyrene particles to swell polystyrene. The agent chosen is gas or liquid under the normal state, such as petroleum ether, isopentane, pentane, butane, chlorination hydrocarbon compound, freon, and so on. These substances dissolve in PS under the condition of pressure and polystyrene swelling.

When foaming, expandable particles are firstly put in steam, hot water or hot air for pre-expansion, then foaming agent evaporates, polystyrene softens, pearls swell. The swelled particles can cool. Since the foaming agent condenses in the particles and dissolves in polystyrene again, a certain vacuum degree is formed in micropores, air will not infiltrate micropores through sidewall of the foam until internal and external pressure balance. This process is called ripening. When these ripened particles foam again, the expansive force is brought about by the mixing of gas and foaming agent.

The pre-expansion ripened particles are put in mold and are heated in steam, and these particles inflate again for filling the gap between each particle to form one body. Foam products in certain shapes will be obtained after cooling and demoulding.

(2) Preparation for expandable PS pearls.

There are many methods for preparing expandable polystyrene pearls. One method is that foaming agent like low boiling point hydrocarbons is added in the polymerization process of polystyrene. Another method is that foaming agent is soaked in the suspension polymerized PS grains under the condition of heating and pressure. At present in industry, polystyrene from extrusion pelleting and extrusion slicing is then infiltrated in foaming agent.

At present, one method has been adopted domestically: raw materials are put in reaction kettle according to the following formula, agitate and penetrate for 6 hours between 85°C and 95°C, and under 0.4∼0.5MPa. We discharge it after it cools to temperature between 35°C and 38°C, wash it with cold water and dry it, volatilize it slowly for 3∼5 days at 15°C, then dry it with hot air between 25°C and 35°C and pack it for sell.

Suspension polystyrene (10 to 20 mesh)	100
Petroleum ether (30∼45°C fractions)	15
Water	240
Sodium dodecyl benzene sulfonate	3

(3) Storage for expandable PS.

The foaming agent for expandable polystyrene is volatile component, therefore the lower the storage temperature is, the better it is. It can keep for three months being sealed in common plastic packing bags. If a long storage time is required, it must be immersed in water to avoid too much of foaming agent volatilizing.

(4) Forming process of expandable PS foam.

① Pre-foaming.

Expandable polystyrene is heated for pre-foaming. Heat to the temperature between 90°C and 105°C, and heating medium can be infrared ray, high frequency generator, hot air, hot water or steam, and so on. The experiment has proved that heating by hot water is better, for example, pellets volume may inflate 33 times when pre-foaming in hot water between 80°C and 85°C. At present, pre-foaming in hot water is widely used. Pre-foaming temperature is between 95 and 99°C, and pre-foaming time is 10∼15min, which is decided by molecular weight of polystyrene, amount of foaming agent and density of product.

② ripening.

The pre-foaming pellets need ripening. The ripening condition is: pellets are placed between 25°C and 30°C for 12h to 32h, or between 32°C to 38°C for 8h to 24h. The drier the pellets are, the more rapidly they absorb air, the more easily it balances internal and external pressure, and the faster the ripening is. The higher the temperature is, the more rapidly the air gets into microspores, and the faster the foaming agent escapes. Therefore, if pre-foaming pellets ripen over 5 days, they will not be able to form since too much of foaming agent has already lost then.

③ Forming.

The ripened pre-foaming pellets are fully filled in cavity of mold, heated to between 110°C and 120°C for 10min to 30min and these foam particles will further expand and fully fill the gaps among particles and melt polystyrene, they are adhered together to form foamed plastics. We also may use hot air, hot water or steam for heating. Heating by steam is the best choice because the steam can enhance foaming ability. After heating forming, surplus expansive force is still in the foam, if the foam is not cooled enough before demoulding, the foam will further, expand which cause the material to crack or distort.

New expandable PS foam that is just discharged from mold, displays a partial vacuum condition in micropore as it foams again. At the moment, the foam has very low strength and no elasticity (easy to be squashed), so it has to be ripened. The ripening time is proportional to its thickness, usually for 2 to 5 days, both of strength and elasticity of the ripened product will be enhanced.

There is usually a rigid shell on the surface of expandable PS foam product. The reason is a long heating time and big pressure in forming (the internal expansive force concentrates on the surface of foam product with metal mold). For packing material, the rigid shell will affect the anti-vibration performance of packing. If the cured product is treated in hot water or steam, i.e., heated at 90°C for 3min to 5min, then a few of foaming agents in this hard shell will foam slightly, making the hard shell thinner and softer.

④ Mold.

Since the internal pressure is not high in the formation of expandable PS foam, usually between 0.5kg/cm^2 and 3kg/cm^2, there is no need of high strength mold. The mold can be made using cast aluminum. Cast aluminum does not rust. It transfers heat quickly, has small thermal capacity, and is of light weight and low cost. Thereby, it has been widely used.

7.2.3 Forming process of phenolic foam and its sandwich structural products

1) Fabrication of phenolic foam

Phenolic foam the same as the pressing molding of PS foam is foamed by the gas which is from thermal decomposition of solid foaming agent. The difference is that phenolic resin belongs to thermosetting resin. During foaming, if decomposition of the foaming agent and growth of the resin viscosity are well controlled, we can avoid the gas escaping from the resin. Therefore phenolic foam can be directly formed by filling in structural cavity, not requiring the process of pre-pressing flan.

The usual phenolic foam includes pure phenolic foam and butadiene-acrylonitrile rubber (NBR-40) modified phenolic-nitrile foam. The production of half-finished foam products is illustrated briefly in Fig.7.10. All components are crushed and mixed in ball mill into the powdery half-finished products. When preparing phenolic-nitrile foam, firstly, rubber is plasticated for 15mins in rubber fining mixer. Secondly, the rubber and other components which has been crushed and mixed in the ball mill are mixed for 15min (feeding for 10min). The mixing temperature is below 50°C in order to avoid resin curing, rubber vulcanizing and foaming agent decomposing. Finally, the mixture is rolled for thin slices at a thickness of 3mm to 6mm. We crush the mixed slices to get the powdery half-finished products, and if the half-finished products are operated by extruder machine, we will get hollow or solid squeezed particles.

The half-finished products are put in cavitiy of relevant tools or structures, and are heated for foaming. The heating foaming process of phenolic-nitrile foam is like this: firstly, the half-finished products are heated to between 80°C and 90°C to soften a viscous matter, then its volume has a little reduction. Secondly, when we heat it up to between 90°C and 110°C, the foaming agent AIBN decomposes and emits massive gas; then the resin starts to crosslink and increase the viscosity, a stable foam material has formed for filling the entire mold cavity or structural cavity. Thirdly, we further heat it up to between 150°C and 200°C as heat treatment for resin curing and rubber vulcanizing, yielding a stable foam structure which has anticipated physical, chemical and mechanical properties. Finally, we cool the product and take it out (when mold release agent coated in mold or on structural cavity wall) or fill it in structural cavity (when adhesive coated on structural cavity wall).

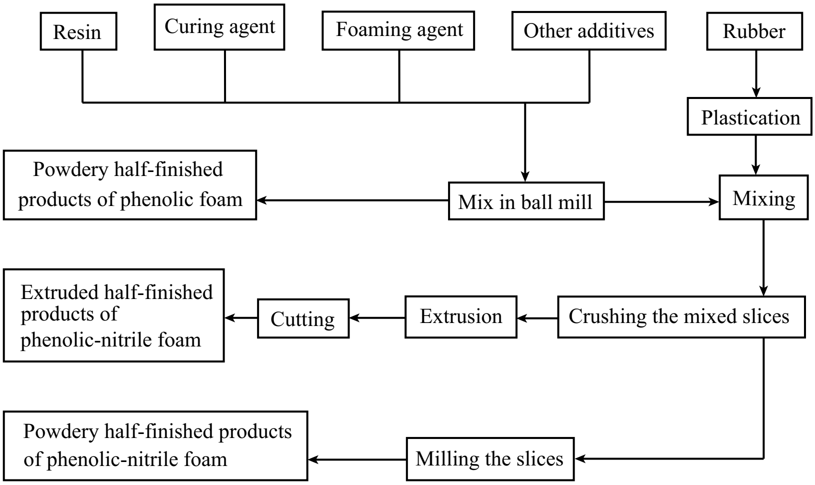


Fig 7.10 Fabrication process of phenolic foam half-finished products.

Temperature, heating rate and holding time have a big influence on size and structure of bubbles. During foaming, the decomposition rate of foaming agent, and the growth rate of air hole are required in accordance with the increase rate of resin viscosity during phenolic resin curing process. The foaming agent will easily decompose when resin is at low viscosity. This will break the air hole and make air escaped and result in coarse pore structure materials. On the contrary, if the foaming agent doesn't decompose until the polymer has very high viscosity, it will not foam. Reasonable parameters and compounds ratio must be confirmed by the experiments, so as to make the growth rate of resin viscosity in accordance with the decomposition rate of foaming agent.

2) Manufacture of phenolic foam sandwich structural products

Fabrication of this kind of products usually involves following procedures: preparing materials, surface treatment of filled part of products, feeding structural cavity, foaming and curing, mending and testing.

(1) Preparation of materials.

Half-finished products of phenolic foam (extruded bar or tube) must be cut or smashed before using, make their volume and gravity equal to or a bit smaller than the density of foam requested for product. Extruded half-finished product can be cut to cylinder with certain length, smashing must be done a few days ago before using in order to avoid adhering and needing re-treatment because of a long time storage.

(2) The surface treatment of product structural inner cavity.

In order for foam plastic to adhere the product structural inner cavity together firmly, each part which needs feeding foam must be cleaned with gasoline and acetone, and then we apply modified phenolic glue on it. The choice of glue is decided by the request of product heat resistance. It can be phenol-formaldehyde acetal glue, phenolic-nitrile glue, silicone modified phenolic butyral glue and so on. The glue content is between 150g/m^2 and 200g/m^2, the glue layer must be dried before feeding foam. Curing of glue bondline is carried out in the foaming process of foam.

During foaming, gas or volatiles in the structural cavity must be able to discharge smoothly; otherwise it will limit foaming, form porosities, sinkings, and so on. Generally, certain holes should be made on the structure (aperture is between 1 and 2mm).

(3) Stuffing the structural inner cavity.

Filling quality of phenolic foam sandwich structure is affected by cavity stuffing in a great extent. Since the semi-finished product has low fluidity when rolling or extruding, they merely fill the surrounding voids and bond together with each other during foaming. Therefore, the space must be stuffed with self-finished products evenly and closely during stuffing. The amount may be calculated according to the equation below.

$$G = \alpha r V \tag{7.3}$$

Where G is the amount of half-finished foam products, g; r is the density of foam products , g/cm^3; V is the volume of structural inner cavity, cm^3; α is the considered loss coefficient of material (1.02$\sim$1.05).

Variable profile products may be packed with semi-finished products in different granularity. For big size product with density varying with profile, semi-finished products in different volume weight may be used. Tiny semi-finished products with big volume weight are to be placed first, and then big semi-finished products with small volume weight are placed. In order to stuff the space consummately and closely, vibration table is usually used. The structure is put on the vibration table and we fill it while it is vibrating.

(4) Foaming and curing.

During the foaming process of phenolic foam, there is a high internal pressure (3∼5 times of atmospheric pressure), which often distorts thin-wall structure, thus foaming must be carried out in a restricted jig. Internal shape of the restricted jig complies with contour of the product, and the restricted jig should have high stiffness. This may prevent the structure distorting, and guarantee its requested accuracy. But structure of the restricted jig is different along with size, shape and request of the product. The entire block jig is often used for common small workpiece, and this kind of jig is equivalent to a big dismountable tool, which can grip entire outside surface of the workpiece. The skeleton jig (similar to assembly jig) is often used for big workpiece, and the corresponding contour surface part of the workpiece is made with metal plate. In order to install it conveniently, the contour plate is dismountable or rotatable.

After charge, the structure is sealed by closing the cover or blocking the charge orifice, and so on, then heating for foaming. Heating may be the contact heating which depends on heater element installed in jig, or heating the entire jig in drying oven. The workpiece should be guaranteed for temperature rising evenly and steadily. Since the foam has a low thermal conductivity, we adopt slow heating and stepped heating. For example, when heating in the oven, firstly, we put the restricted jig with product in the oven, slowly heat it up to between 90°C and 100°C, and hold the temperature for some time, so that the inner part of the product will also reach the same temperature. Secondly, we slowly heat up to between 150°C and 200°C (decided by curing request) and hold again until equilibrium. At the first temperature stage, the polymer must soften and the foaming agent starts decomposing. At the second holding temperature stage, the polymer must cure fully. After the polymer finishes curing, we cool it to between 20°C and 40°C and take out the product from the restricted jig.

7.2.4 Forming process of PU foam and its sandwich products

Main components of fabricating polyurethane foam are polyfunctional isocyanate (IC), polyhydroxy compounds, catalyst, surface-active agent, water or freon. These components can foam immediately when they are mixed evenly in proportions before using. To obtain high quality foam, the rate of gas production and foaming should be matched with the rate of polymer viscosity growth and curing. In order to keep the generated gas to stay in the polymer, the resin curing rate should be slow enough to enlarge foam and meanwhile rapid enough to prevent foam from breaking. At the end of gas generation, the polymer should have certain mechanical strength, maintain certain volume and it must neither collapse nor shrink heavily. So when fabricating PU foam, we must choose suitable formula and establish technical conditions according to the formula.

1) Constitution, foaming mechanism and properties of PU foam

(1) Constitution of PU foam.

The reaction of IC and polyhydroxy compounds produces polymers with urethane or carbaminate in its main chain, abbr. PU. With the difference between polyhydroxy compounds like polyester and polyether in raw materials, PU could be divided into polyester PU and polyether PU. Multi-hydroxyl polyether is prepared by the reaction of propylene oxide and polyols, and multi-hydroxyl polyester is prepared by the reaction of binary acid and polyols. The following are formulations and processes that are used to prepare rigid polyester PU foam and rigid polyether PU foam respectively.

Formula 1:

Constituent A

$76^{\#}$ Polyester	100g	Main constituent —OH
$3^{\#}$ Modified toluenediisocyanate	135g	Main constituent —NCO
Tween-80	0.5mL	Emulsifier

Constituent B

Triethylamine	0.3mL	Catalyst
Water	1mL	Foaming agent
F-113	17mL	Foaming agent

$76^{\#}$ polyester is the polycondensation product of 2 shares of decanedioic acid, 3.5 shares of glycerin, 0.5 share of phthalic anhydride and 0.5 share of glycol (mol ratio at 2 : 3.5 : 0.5 : 0.5), with viscosity between 18Pa·s and 20Pa·s, hydroxyl value at 480mg/g. $3^{\#}$ modified toluene diisocyanate is a kind of toluene diisocyanate modified by diethylene glycol (mol ratio at 1 : 4). The foam fabrication process of formula 1 is like this: firstly, mix constituent A evenly (stirring about 1min), then add constituent B and mix, and when the mixture becomes white after stirring for 1min, pour it into the pre-heated mold at 35°C, cure at 60°C for 30min and at 80°C for 6h.

Formula 2:

Xylitol polyether N-505	125g	Main constituent—OH
Polyaryl polyisocyanate PAPI	190g	Main constituent—NCO
DBP	15g	Plasticizer
380 silicon oil	0.7g	Surface-active agent

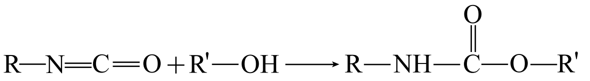
F-113		Foaming agent
Dibutyl tin laurate	0.05g	Catalyst
Triethylenediamine	0.2g	Catalyst

Xylitol polyether N-505 is a hydroxyl compounds with five functional hydroxyl groups, with relative molecular weight at 500 and hydroxyl value at 500mg/g. Foam preparing process of formula 2 is like this: firstly, add the first five raw materials together orderly and stir for 1min. Secondly, add catalyst to the mixture and stir for 1min. Finally, pour it into the pre-heated mold at 35°C, and cure at 80°C for 7h.

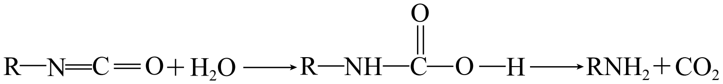
(2) Foaming mechanism.

① Analysis of formula 1.

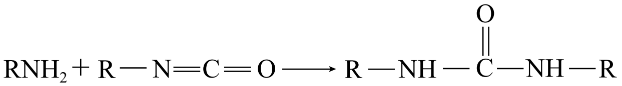
Chemical reactions in foaming process are shown in follows.



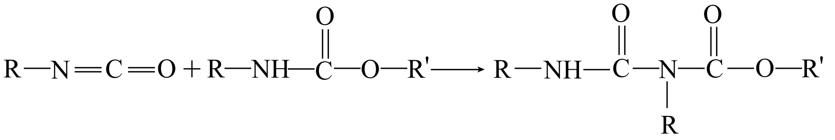
$$R—N{=}C{=}O + R'—OH \longrightarrow R—NH—\overset{\overset{O}{\|}}{C}—O—R' \tag{7.4}$$



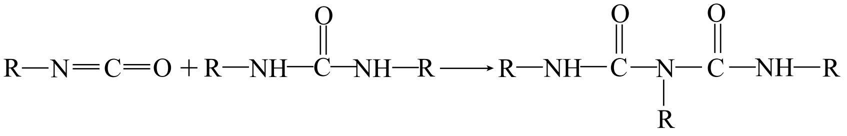
$$R—N{=}C{=}O + H_2O \longrightarrow R—NH—\overset{\overset{O}{\|}}{C}—O—H \longrightarrow RNH_2 + CO_2 \tag{7.5}$$



$$RNH_2 + R—N{=}C{=}O \longrightarrow R—NH—\overset{\overset{O}{\|}}{C}—NH—R \tag{7.6}$$



$$R—N{=}C{=}O + R—NH—\overset{\overset{O}{\|}}{C}—O—R' \longrightarrow R—NH—\overset{\overset{O}{\|}}{C}—\underset{\underset{R}{|}}{N}—\overset{\overset{O}{\|}}{C}—O—R' \tag{7.7}$$



$$R—N{=}C{=}O + R—NH—\overset{\overset{O}{\|}}{C}—NH—R \longrightarrow R—NH—\overset{\overset{O}{\|}}{C}—\underset{\underset{R}{|}}{N}—\overset{\overset{O}{\|}}{C}—NH—R \tag{7.8}$$

The equation (7.4) is the primary reaction of forming foam wall, and the viscosity growth of polymer is mainly caused by this reaction. The equation (7.5) is the main reaction that produces gas (CO_2), which serves as the main source of gas in foam. The equation (7.6) occurs simultaneously with the equation (7.5), so one water molecule can consume two isocyanate groups. Equation (7.7) and equation (7.8) are the secondary reactions of forming foam wall which occur at high temperature. Because urea structure is brittle, reactions of equations (7.7) and (7.8) occurring in large amount will result in poor toughness, but high strength.

If we only use volatile gas for foaming (like formula 2) and there is no water in polyhydroxy compounds, then no reaction equation (7.5) can occur, hence no equation (7.6) and equation (7.8) either. That means no structures of two-substituting urea and biuret, and thus the foam wall has small brittleness. Since these five reactions are all related to isocyanate, IC amount should be slightly more. All these five reactions are exothermic reactions, so we should control the reaction rate.

The viscosity increase rate and the curing rate of resin should be suitable with the producing rate of $CO_2$and the foaming rate. The emitted gas is required to stay in the polymer for successful foaming. These reaction equations of (7.4), (7.5) and (7.6) should be controlled strictly (at the initial foaming stage). They are related to species and amount of catalyst, raw materials and mold temperature. There are two kinds of extreme situation: (a) CO_2 increases rapidly while resin viscosity increases slowly. If raw materials have low initial viscosity, CO_2 will escape from the surface of liquid, then the plastic cannot foam. If raw materials have high initial viscosity, the plastic can foam, but if the producing rate of CO_2 is excessively high, the produced foam can collapse easily; or the foam holes are in different size, i.e., poor quality. (b) CO_2 increases slowly, resin viscosity increases rapidly. Due to the big resistance, it cannot foam, giving it a high density.

The goal of post-processing is to complete the reaction, i.e., to trigger reaction equations of (7.7) and (7.8) for the remaining —NCO. This is to enhance the crossing linking density of the foam, increasing strength and thermal stability, stabilizing size, making it less easy to shrink.

The reaction should not be too fierce. Since polymer has a poor thermal conductivity, if the reaction is too fierce, large amount of heat will release and air bubbles merge, which form big hole and burned yellowish parts in the middle of the foam plastics. We should therefore choose suitable formulas and technological conditions. For example in formula 1, F-113 does not participate in reaction, but it could take the place of water as foaming agent to absorb the heat produced in the system, thus reducing the temperature during foaming, making the reaction gentle. In this way, the emergence of hollow bubble is avoided.

② Analysis of formula 2.

Compared with the formula 1, the formula 2 has these characteristics. There is no water, so there are only reaction equations of (7.4) and (7.7). F-113 volatilizes by absorbing heat which causes the resin foaming (physical effect). The viscosity of xylitol polyether is lower than the $76^{\#}$ polyester, and secondary hydroxyl group has low activity. In order to enhance the reaction rate, two kinds of high efficiency catalysts are used such as bivalent tin salt and tertiary amine. The product from reaction of N-505 and PAPI has high crossing linking density, big hardness but brittle. Consequently, it is usually plasticized by dibutyl phthalate (DBP).

(3) The relationship between raw materials and properties of PU foam.

① Hydroxyl compounds.

The hydroxyl content of polyhydroxy compounds, the carbon chain length and the content of phenyl affect structure and properties of foam plastics. If hydroxyl value increases, crossing linking density, thermal stability and compressive strength all increases. If hydroxyl content oversized, however, the foam plastics will be brittle and cohering property declines. The activity of hydroxyl, viscosity and water content of polyhydroxy compounds affect formulas and processability of foam plastics.

② Isocyanate IC.

The commonly used isocyanate includes TDI (toluene diisocyanate), MDI (methylaniline diisocyanate) and PAPI (polyaryl polymethylene isocyanate), and so on. The sequence of activity: TDI $>$ MDI $>$ PAPI. The sequence of vapor pressure (toxicity): TDI $>$ MDI $>$ PAPI. The sequence of viscosity: TDI $<$ MDI $<$ PAPI. Using PAPI may cause the crosslinking density of the foam increased, the strength increased and the thermal stability increased.

③ Foaming agent.

Foaming agent of PU foam mainly include water and freon such as F-11 (Cl_3FC, boiling point at 23.8°C), F-113(CCl_2FCClF_2, boiling point at 45.57°C). The difference between water and freon as foaming agents is: (a) fluorocarbon compound volatilizes and takes the heat away it has good processing properties, thus not easy to burn within foam plastics. (b) Good toughness, low strength (because of no urea structure). (c) Reduction of reaction heat may result in closed cell structure, with ratio of closed cell increasing, hygroscopy declining, permeability declining and thermal insulation increasing. (d) Reduction of IC amount can reduce cost.

④ Catalyst.

In order to obtain foam plastics with high quality, we must adjust the reaction rate of —NCO with —OH and H_2O, the requirements are as below : (a) when gas production reaches the biggest amount, the foam does not break. (b) The foam wall has enough strength before the gas in the foam cools so that the foam is stable and will not shrink. Therefore the catalyst and its amount must be suitably chosen. The commonly used catalysts in polyurethane foam are tertiary amine such as triethylamine, triethanolamine, triethylenediamine, and organic tin salt such as tin dicaprylate, dibutyl tin laurate, and so on.

⑤ Surface-active agent (emulsifier and surface tension conditioner).

The emulsifier and the surface tension conditioner are both surface-active substance. They both contain polar group and non-polar group in the molecule. Therefore it can reduce surface tension in any liquid system. But in PU foam systems there are differences between functions of emulsifier and the surface tension conditioner.

Main function of emulsifier is to make hydrophilic polyhydroxy compounds, hydrophobic IC, water and catalyst to form mixture in homogeneous phase (be evenly mixed) and to guarantee even reaction in the entire foam system, while reduction of surface tension is merely a side product. The surface tension conditioner's primary role as the name suggests is to adjust surface tension, so that air bubbles are formed easily and are stable. It helps in producing tiny air bubbles and foaming under low gas density. Comparatively, its emulsification is small. The emulsifier and the surface tension conditioner are also nucleating agents, which promote the formation of tiny and uniform bubbles. Water soluble silicone oil and Twain-80 are normally used for the surface tension conditioner and the emulsifier respectively.

⑥ Flame retardant.

The addition of flame retardant such as low molecular compounds containing element P, Cl and N generally reduces the closed cell ratio, strength and thermal stability of foamed plastics, increases water absorption. For example, if we use multifunctional alcohol including P, Cl, the flame retardance will be enhanced while keeping other properties stable. This is the result of the compound participants in PU structure.

(4) Calculation of constituent amount.

① Calculation of IC amount.

It refers to calculation of IC amount needed for 100g polyester.

There are two ways for consuming IC: polyester (ether) and water. The hydroxyl value refers to weight (mg) of KOH which has equivalent amount to hydroxyl in 1g polyester; therefore the gram equivalent number of —NCO exhausted by 100g polyester is hydroxyl value × 100/(1000 × 56.1) and the IC amount needed by 100g polyester is hydroxyl value × AE/(10 × 56.1). AE refers to gram equivalent of IC, which is the weight (gram) of 1 gram equivalent of IC. Since one water molecule will consume two —NCO, and the gram equivalent of water is 9, then the IC amount consumed by w g water is $w \times AE/9$. So the total amount of IC is given by:

$$\mathrm{IC} = \left(\frac{\text{hydroxyl value}}{561} + \frac{w}{9}\right) \times AE \times a \div b \tag{7.9}$$

Where a is the excessive coefficient of IC (1.05∼1.1); b is the purity of IC (PAPI is between 85% and 90%, TDI is between 98% and 99%).

② Estimation of foaming agent amount.

It refers to the relationship between density (ρ) of foam plastic and amount (x) of foaming agent.

Suppose there are x g foaming agent in 100g foam plastics. 1mol water or 1mol volatile gas foaming agent produces 1mol gas. The volume of the gas produced by

x g foaming agent under the standard condition (0°C, 1atm) is $V = 22.4 \times 1000 \times x/M$, the volume $V' = V \times (273 + t)/2730p$ under the foaming condition ($t = 45°\text{C}, p = 0.105\text{MPa}$). Assume that the volume of foam wall can be neglected and the density of foam plastics (ρ) is given by:

$$\rho = \frac{100}{V'} = 0.004 \times \frac{M}{x} \tag{7.10}$$

In the equation, M is molecular weight of foaming agent; such as H_2O, $M = 18$, $\rho_{\text{water}} = 0.072/x$. F-113, $M = 117$, $\rho_{113} = 0.406/x$.

If for gas mixture (two kinds of foaming agents), then the density (ρ) of foam plastics is given by:

$$\rho = \frac{100}{V'} = \frac{100}{\dfrac{273+t}{273 \times p} \times 22.4 \times 1000 \times \left(\dfrac{x_1}{M_1} + \dfrac{x_2}{M_2}\right)} \tag{7.11}$$

2) Methods of fabricating PU foam

There are three methods for preparing PU foam, the one-step method, the pre-polymerization method and half pre-polymerization method.

(1) The one-step method.

See Fig. 7.11. During the process of one-step method, various components are mixed evenly by certain charge order under mechanical agitation, the reaction starts immediately. After mixing for a certain time, bubbles start to rise. Foaming will finish in a few minutes, and then the resin is heated for curing completely.

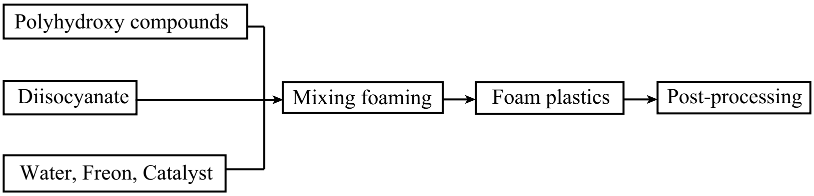


Fig 7.11 Fabricating polyurethane foam by the one-step method.

(2) The pre-polymerization method.

See Fig. 7.12. During the process of pre-polymerization method, firstly, diisocyanate and polyhydroxy compounds polymerize partly, and then they foam by adding freon or adding water. At the same time, the polymer viscosity rapidly increases and foam cures.

(3) The half pre-polymerization method.

In Fig. 7.13, during the process of half pre-polymerization method, part of polyhydroxy compounds and all diisocyanate react to produce pre-polymer with massive unreacted isocyanate groups. Then the pre-polymer, other polyhydroxy compounds and other components are mixed for foaming. The resin is heated and post-processed for full curing.

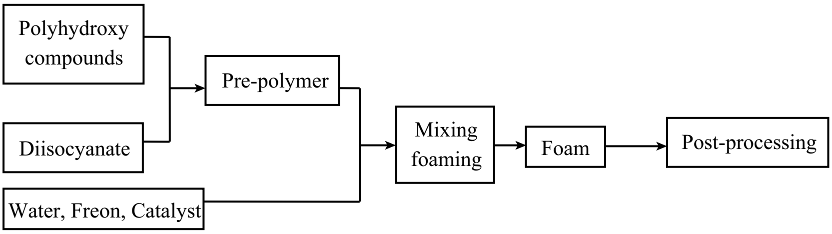


Fig 7.12 Fabricating PU foam by the pre-polymerization way.

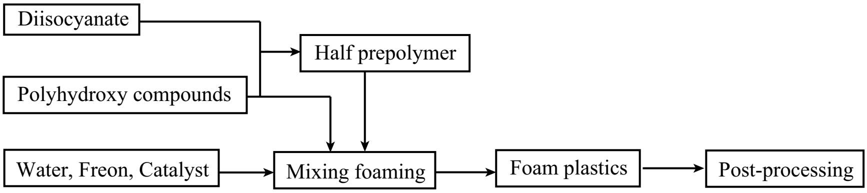


Fig 7.13 Fabricating polyurethane foam by the half pre-polymerization way.

The three methods have different scopes of usage. The soft foam are usually prepared by pre-polymerization, because multi-hydroxyl polyether prepared for the soft foam has low viscosity and low hydroxyl value. It follows that the polymer viscosity increases slowly when foaming and the gas escapes easily from the polymer. In order to enable the growth rate of polymer chain to adapt the generation speed of gas, the initial viscosity of components should be increased by pre-polymerization method. The rigid foam plastics usually use quasi-pre-polymer method or the one-step method. The choice varies according to different raw materials. When polyisocyanate PAPI is used, the one-step method is adopted for preparation foam because of its large viscosity, low reaction activity, low vapor pressure and low toxicity. When toluene diisocyanate is used, one-step method will not be appropriate because of its big reaction activity. Toluene diisocyanate reacts with polyester, polyether or water very fast, and give off massive heat. The production will be out of control if all the reactions happen simultaneously. This is especially true when casting bulk foam plastics. In that case, there is a danger of center scorch. Moreover, it has a high vapor pressure and a big volatility. Its toxicity is extremely harmful to people and we should avoid its vapor inhalation. Therefore the half pre-polymer method is often used in industry. It reacts with polyhydroxy compounds first to produce half pre-polymer so as to reduce its activity and the vapor pressure. Then the foaming process is easy to control and the toxicity is reduced too. In fact, for user convenience, modified isocyanate with high viscosity is available in the market. It is made by the reaction of toluene diisocyanate and polyol, so that the one-step method can be used for preparing foam.

3) Filling technics of PU foam

Mix each components of polyurethane foam according to the formula, fill them in corresponding molds or cavity structures, then they can foam and form.

Materials are mixed according to the formula, and the typical order is that polyester or polyether is generally mixed with water or freon and other components first, then isocyanate is added. Alternatively, polyester or polyether can be mixed with isocyanate and surface active agent first, and then water and other components are added. The goal is to avoid the uneven mixing and reacting when water and isocyanate are added simultaneously.

When materials are mixed, the stirrer agitation is used for mixing. Materials are preserved in thermostat between 28°C and 35°C before mixing. After continuous mixing for 0.5min to 2.5min, the mixture temperature will rise by 7°C to 10°C and the volume increases slightly. White color appears and the viscosity reduces. It follows with the phenomenon of big bubbles' breaking. When stirring again, the big bubbles disappear and white color appears again, it is the opportunity for foaming. The mold space should be filled immediately (mold temperature between 35°C and 45°C), and foam will form after 4min to 5min. Then the foam is heated to cure at 80∼150°C for 4h to 7h. The heating temperature is decided by requirement for heat resistance of products. If foam plastics have no requirement for heat resistance, they can even cure between 50°C and 60°C under the condition of extra catalyst in formula. The products obtained will be of low strength.

Usually polyester or polyether used for rigid polyurethane foam has high hydroxyl value, therefore it reacts with isocyanate fiercely, gives off massive heat. As a result, factors like quantity of material mixture, heat transfer ability of filled mold wall, rising speed of temperature when foam plastics curing, and heating uniformity when the mold are heated, and so on, all have a very big influence on qualities and properties of foam plastics. Therefore when formulating the filling technique of polyurethane foam, these factors must be considered. In addition, space size and shape of filled structures also make a difference.

There are four types of filled volume. ① The large scale product: volume is between $1.2\times10^4\text{cm}^3$ and $1.5\times10^4\text{cm}^3$; filling thickness is between 7mm and 10mm; those has a changeable thickness between 1.5mm to 45mm is belong to this type. ② The medium product: volume is between $1.5\times10^3\text{cm}^3$ and $2\times10^3\text{cm}^3$; filling thickness is between 5mm and 10mm. ③ The small scale product: volume is between 5cm^3 and 50cm^3; thickness changes from 0.5mm to 10mm. ④ Massive and plate product: volume is between $0.6\times10^4\text{cm}^3$ and $1.0\times10^4\text{cm}^3$, filling thickness at about 100mm.

When filling large-scale products (type ①), the amount of massive blends from 3kg to 3.5kg is used. During mixing, because of massive heat emitting, the reactive material is rapidly heated, which accelerates the reaction of polyester or polyether with isocyanate, reducing the life of blends greatly. When the products have very narrow gaps, it is hard to fill these gaps with the blends, which makes foaming formation very difficult. In order to increase the life of blends, we must slow down the reaction rate. Organic acid is added as a reactive decelerator. For example, catalyst-22 is a solution made with diethyl ethanolamine, oxalic acid and water. As a result of diethyl ethanolamine oxalate, the PH resides approximately at 9～10, which is lower than other catalysts like triethylenediamine. Catalyst-22 has low catalytic effect too. Its amount of usage is 2～3 times of other catalysts, in order that the curing time of foam plastics can be reduced after the blends foaming. With organic acid as reactive decelerator, the time for agitation in the foaming technical process is abundant. Thereby the end point of agitation can be easily controlled; good fluidity facilitates filling mold; foam rises steadily and tiny and even foam is formed. Nevertheless, during the first 1h of blends foaming, because of the low rate of polymer viscosity rising, the foam is not stable enough. To maintain the pore structure of foam plastics, we put the product under mold temperature between 35°C and 45°C for 1h to 2h, then heat up evenly for further curing.

For products of type ②, 300g to 700g blends are needed. It is inappropriate to add the reaction decelerator in formula at this time, because there is enough time for filling the mold cavity after these blends are agitated evenly. Since the blends have big reactivity, it is undesirable to prolong the holding time for the mold between 35°C and 45°C, generally within 1h, products can be heated up for curing.

When filling small products with thickness changeable walls or with components and small gaps nearby, it is another story. As the blends foam in these gaps, the mold will conduct massive heats, so the reaction rate will be slow down greatly. If the precipitation speed of gas is faster than the viscosity increasing rate of resin, the gas can escape from the blends very easily, so that it is hard for filling up the mold cavity. The amount of catalysts should be increased suitably to enhance the viscosity increasing rate of the blends.

When making foam plastics (type ④) with very big thickness (100mm), we should use the minimum amount of catalysts. With the increase of catalyst amount, a vertical bell-mouth will be formed on the bottom of products, which is related to the too fast reaction.

When the blends foam in closed vessels, it will cause a very big internal pressure, sometimes the pressure might be 2 to 5 times of atmospheric pressure. So in choosing restricted equipment structure for filling these products, such situation must be considered.

4) Fabrication of polyurethane foam sandwich structure products

Polyurethane foam has a simple foaming forming process and polyurethane resin has an outstanding adhesion property. Therefore, when preparing sandwich structures with it, its blends are often filled in structure cavity for directly foaming. When preparing sandwich structure products with this method, mechanical processing of the foam may reduce to minimum. Moreover, when filling internal skeleton products, the foam not only fills the entire cavity of products, but also joins together with the skeleton sturdily, forming a firm rigid structure.

In aviation industry, in order to decrease the structure weight, cover thickness of sandwich structure products are all generally designed to be very thin. When polyurethane foam foaming, its internal pressure may be up to 0.2MPa to 0.3 MPa. To cope with the pressure, we use restricted molds. That keeps the contour shape of the product undistorted during the foaming process.

The restricted mold is made with aluminum alloy, steel or other materials, and its structure is decided by the contour shape and the external dimension of the product. The heating may be conducted with steam or with electric heater to directly apply to the mold wall. Alternatively, we may heat the mold in oven. No matter which method is used, the key is to heat evenly, because quality of the foam has much to do with the heating temperature.

Taking aerial fairing as an example, we make a simple introduction and illustration of forming process of the sandwich structure.

For the structure of the aerial fairing, its outer layer is composed of polyester or other resin FRP formed at low pressure, and polyurethane foam is selected as its core. When making the product, there are basically two procedures: make the FRP shell; fill the cavity between inner and outer shell with foam. Technological equipments are mainly the male mold, the female mold, the demoulding equipment and so on. The detailed process operation is shown as follows.

Firstly, we spread silicone oil or release agent like polyvinyl alcohol on the mold. Secondly, we paste inner shell of the fairing by male mould, and outer shell by female mold. To paste the cover easily, the metal skeleton is used to hold up the rubber cover (the metal skeleton contour has a good fit with the female mold), on which glass cloth is pasted to a certain thickness. Then we remove the skeleton, put it in the female mould together with the rubber cover, and cure by compression molding. When fabricating the inner and the outer shells, the pressure generally is between 0.09MPa and 0.35MPa, the temperature is between 120°C and 170°C, the exact condition varies with the resin.

The inner and the outer shells after fabrication are still kept on the mold. The release agent contacted with the rubber cover is removed. Then we spread phenolic-acetal glue or polyurethane glue on the surface that has been gently polished by sandpaper. After drying at room temperature for 20min to 30min, we pour the quoted and evenly-agitated foam mixture on the outer shell of the female mold. We rapidly cover the male mold that has inner shell (see Fig. 7.14). The entire operation must be completed within 3min to 5min. The foam mixture is poured in mold which should be heated in advance between 35°C and 45°C, so the mixture will be evenly filled in the entire cavity between inner and outer shells. This may be observed through the hole on the male mold. After about 15min to 25min, when the foam gets out of the hole, we close the hole. Then we heat up to cure the polymer. The curing conditions must be decided according to foam formulas, thickness of filling layers, shape of workpiece and heating methods. The ordinary circumstance is that temperature rises from between 60°C and 80°C to between 120°C and 150°C gradually in 4h to 6h. It finally demoulds after it cools to between 20°C and 40°C. When demoulding, we must impose pulling force evenly along peripheral, so that the product can be guaranteed undamaged. For easy demoulding, a flange is generally made on the shell of the product, on which the demoulding force may be applied on. After demoulding, we cut the flange and process surplus with circular saw or band saw, and then decorate to get the product.

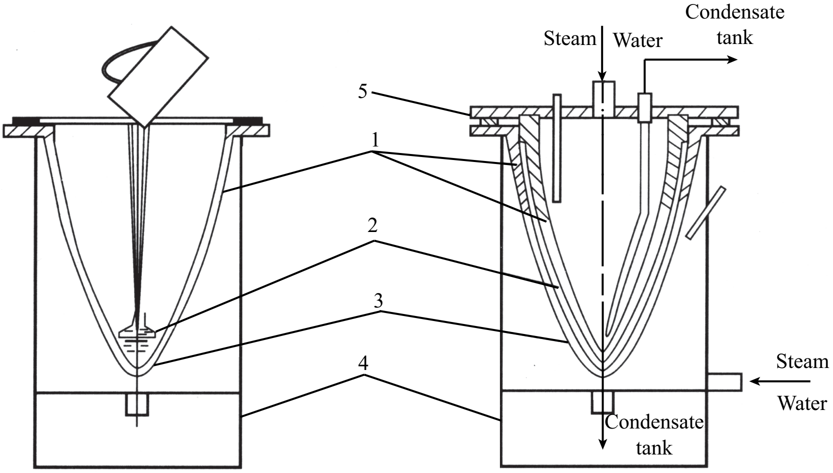


Fig 7.14 The schematic diagram of PU foam filled by three-layer structural aerial fairing:

1-GFRP shell; 2-foam plastic; 3-female mold; 4-heating chamber; 5-male mould.

Exercises

1. What is the sandwich structure? What is its performance characteristic?

2. What are the differences among properties of honeycomb sandwich core in direction of x, y and z?

3. Please make a simple summary about the main technological process of fabricating honeycomb sandwich core by core strip expansion method. How to control the technological process for fabricating the honeycomb core with good size and properties?

4. How to fabricate the honeycomb sandwich construction? Why do we use two steps forming method frequently?

5. How to classify the foam plastics? What are the main two fabrication methods for the foam sandwich structures?

6. What measures should be took in order to obtain the foam with a tiny and also stable structure?

7. What are the two main kinds of polystyrene foams? How to prepare them?

8. Please make a simple summary about fabrication of phenolic half-finished and foam product.

9. Estimate the density of a kind of foam and the amount of isocyanate PAPI according to the following formula, and point out the function of each component.

601 Fire retardant polyether	70
311 Glycerine polyether	24~26
411 Amidogen polyether	4~6
204 Silicone oil	2
3β Chlorine ethyl phosphate	10
Dibutyl tin dilaurate	0.1
Trichloro fluorine methane	2.5
PAPI	?
ρ	?

Known

	601 polyether	411 polyether	311 polyether
Hydroxyl value	350±30	750±50	630±30
Water content	< 0.1	< 0.5	< 0.2
PAPI molecular weight		383 $(n = 1)$	
Purity		90%	
Excessive coefficient		1.1	

10. If density of the foam is invariable (above problem 9), and we use water as the foaming agent in stead of freon, then how many grams of water will be needed for 100g foam? If still use this formula, how many PAPI will be increased?

11. Preparing for polyurethane foam with polyether and polyester, how to choose other components in designing the formula?

12. Compare PAPI to TDI, what are their using properties?

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8

Elementary mechanical properties of composite materials

8.1 Introduction

In engineering technology and everyday life, no matter what physical properties of solid material we use, it must have certain strength, modulus and other mechanical properties, otherwise it could not be used. Therefore, the mechanical properties are the basic service properties of materials. With the development of production and science and technology, the requirements for materials, especially for the mechanical properties of structural materials have become higher and higher. In order to understand the relationship of the composition and structure of materials and their mechanical properties, to gradually achieve the design of materials, we should conduct an in-depth study of the destruction process and enhancing mechanism.

Since the first man-made synthetic resin, phenolic resin, was introduced in 1872, there have come forth many types of thermosets and thermoplastic synthetic resins. Most of them have strength in a range of 40∼70MPa, few more than 90MPa; modulus is generally 2∼4GPa, few more than 6GPa. So it is difficult to be used as the structural materials. In order to improve their mechanical properties, in addition to continuing to improve its own performance of resin, the current attention focused on using composite methods to improve mechanical properties. Practice showed that the method of combining dispersed material with the high strength and high modulus (such as fiber) with resin to form polymer matrix composite materials, significantly improves the mechanical properties of materials. For example, the long fiber composites' tensile strength reached up to more than 1.2GPa, modulus is up to more than 50GPa. This unleashes the potential of synthetic resin in the structural materials field, for it has become comparable with metal in performance. Because of fiber composites' high specific modulus and specific strength, good fatigue performance and damage-resistant safety, as well as designable mechanical properties, they are used intensively as structural components in aerospace and aviation. In order for engineering professionals to correctly choose and use composite materials in mechanical point of view, this chapter focuses on analysis of the mechanical properties of composite materials. Examples and discussion will be given for continuous fiber and its fabric composite materials.

8.1.1 Mechanical classification of composite materials

In order to facilitate the analysis of the basic mechanical properties, the mechanic classification of composite materials is conducted.

The mechanical properties of composite materials, depends largely on the variety, performance, content and arrangement of the reinforcing fibers. Reinforcing fibers are arranged in different ways, so that the mechanical anisotropy of composite materials has a greater difference. Therefore, according to the arrangement of fibers, from the mechanical point of view, composite materials have the following five types.

1) Unidirectional (fiber reinforced) composite materials

Continuous fiber is used as reinforced material, and all the fibers are arranged in parallel in the same direction, the obtained composite material is called unidirectional (fiber) composite material, also known as a unidirectional laminate, often noted as [0]. Fibers in this composite material are more closely arranged; fiber volume fraction is up to 60%∼75%; higher strength appears along the fiber direction, in the other direction strength decreases significantly. When analyzing the basic mechanical properties of composite materials, in order to explain fiber arrangement, the direction of load and deformation, we usually set up rectangular coordinate system (Fig. 8.1), unidirectional fiber composite material in the direction of coordinate system is set as follows.

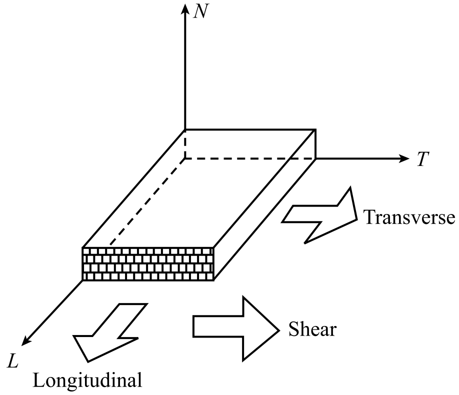


Fig. 8.1 Rectangular coordinates system of composite materials.

(1) Longitudinal: the direction parallel to fiber is called longitudinal, or L direction, 0° direction.

(2) Transverse: the direction perpendicular to fiber (in the L-T plane) is called transverse, or T direction, 90° direction.

(3) α direction: in the L-T plane, and the direction in the α° angle with longitudinal is said α° direction. The provisions of the positive and negative direction: clockwise rotation from the L direction to the +α° direction for positive + α°, on the contrary counter-clockwise rotation from the L direction to the -α° direction for negative -α°.

(4) Layer direction: the direction vertical to L-T plane is layer direction, or N direction, normal, $\perp$ direction.

Unidirectional fiber composite is the basic element of composite laminates in engineering structures, which has 11 parameters of the basic mechanical properties used in the ply stacking design of composite laminates, that is, longitudinal tensile modulus E_L and strength σ_{Lu}, longitudinal compression modulus E_{-L} and strength σ_{-Lu}, transverse tensile modulus E_T and strength σ_{Tu}, transverse compression modulus E_{-T} and strength σ_{-Tu}, longitudinal-transverse shear modulus G_{LT} and strength τ_{LTu}, and Poisson's ratio which reflects transverse deformation caused by the longitudinal stress μ_{LT} (called the main Poisson's ratio).

2) cross-ply (orthogonal fiber) composite material

Using orthogonal fabrics (cloth) or unidirectional ply as the reinforcing material with orthogonal stacking alternately in 90°, the obtained composite material is called cross-ply (orthogonal fiber reinforced) composite material, it is called cross-ply laminate in engineering, denoted as [0/90]. In the two orthogonal directions (L and T direction) it has high tensile strength and modulus, in the other direction of the L-T plane (α direction) low tensile strength and modulus; while the worst strength in the layer direction vertical to the orthogonal direction, due to no reinforcing fibers.

3) Multi-directional (fiber-reinforced) composite materials

In the L-T plane, in addition to 0° and 90° reinforcing fibers, there is $\pm\alpha^\circ$ fiber arrangement. Such composite material is called multi-directional (fiber reinforced) composites, recorded as [0/90/$\pm\alpha$]. Composite materials in all directions of L-T plane still have different strength, modulus, but the difference is reduced, and it is nearly isotropic in plane. Again, the worst strength occurs in layer direction due to no fiber arrangement.

4) Three dimensional fiber-reinforced composite materials

Using the fiber braiding fabrics along three orthogonal directions as reinforcement, this composite material is said three dimensional fiber-reinforced composite materials, also known as three dimensional fabric-reinforced composite materials. Since there are braided fibers in layer direction, the composites overcome the shortcomings of the lower strength and modulus of the unidirectional, cross-ply and multi-directional composite laminates in the N direction.

5) Short fiber (reinforced) composite materials

Short fiber composite materials, using chopped fibers as reinforcing material, according to the distribution of short fibers, it includes unidirectional short-fiber composite materials, planar random distribution short-fiber composite materials and space random distribution short-fiber composite material. Short-fiber composite material in space random distribution, also called chaos short-fiber composite material, is more common. Its mechanical properties at the macro level can be approximated as isotropic. Similar to homogeneous isotropic materials, it has the three elastic constants - Young's modulus E, shear modulus G, and Poisson's ratio μ, with relation of $E = G/2(1 + \mu)$.

In current research and application of composite structure, most of them are made of the former three types of composite materials, so we just discuss these three types of composite materials in this book.

8.1.2 Mechanical properties of composite materials

Mechanical properties of composites depend on properties of the reinforcing material and the matrix resin, as well "combination" situation between them. Under external load, the reinforcing material plays a primary role in bearing the load, while the matrix material in general acts only in transferring shear stress among fibers and preventing fibers from buckling. Usually in the right processing conditions and the same external factors, the mechanical properties of composite materials are related to the following three factors: ① performance, content and arrangement of fiber; ② performance and content of the matrix resin; ③ combination and interface situation of fiber and matrix.

According to the above reasons, we first discuss mechanical properties of constituent materials.

1) Mechanical properties of the main raw material of composites

(1) The mechanical properties of reinforcing material-fiber and fabrics.

① The concept of fiber-reinforced.

Pure resin matrix has lower strength, by adding reinforcing fibers we can improve strength. This phenomenon is called 'reinforcing'.

When adding reinforcing material into the matrix to form composite materials, there is a fundamental point of view, that is, in the formed composites the properties of the reinforcing material and the matrix can both be exerted fully. For example, glass fiber has a high axial load-bearing capacity, after being added into the matrix, the tensile strength of formed composite materials increases a lot comparing the original matrix. However, glass fibers themselves cannot be a "beam" because they do not bear the load, and only after combination with the matrix as a whole they can be used as a "beam". Therefore, in composite materials, fiber is the main load-bearing material, and matrix supports fiber, transfer load and bear load with fibers.

② Mechanical properties of glass fibers.

Mechanical properties of glass fiber has been introduced in the second chapter, here we make a brief summary and supplement.

A) Glass fiber has the characteristics of brittle materials, i.e., no apparent plastic stage before pulling breakage, the stress and strain accord with elasticity law until break.

B) Glass fiber in the composite materials play a major role in bearing load, but whether it is a simple glass fiber or glass fiber in fabric (more complicated due to the fiber bending and torsion in fabric), mechanical properties along the axial and other direction of fibers are different, this is the fundamental cause of the anisotropy in glass fiber composite materials.

C) Glass fiber has high strength, but low modulus.

D) Test the strength and elastic modulus of glass fiber and fabric, in order to facilitate comparison of test data, test conditions should be specified.

Glass fiber has different varieties, and its theoretical strength is 7∼14GPa, but the actual glass fiber has defects, lowering its strength to about 1∼3 GPa, far below the theoretical value. Limited by technological level, for the same composition and specifications of glass fiber, performance also has fluctuations, its strength accords to the Weibull distribution statistical law. A reasonable average can be obtained according to dispersion coefficient, confidence level and probability requirement.

E) The strength of glass fiber is controlled by the internal defects, and it has the size effect or volume effect, that is, when monofilament diameter d_f increases, and fiber strength decreases; when test length l_0 (standard distance or gauge length) increases, and the measured strength decreases. In addition, woven bending and fracture in batches make glass fiber monofilament's strength higher than yarn strength, and yarn strength higher than cloth.

F) The mechanical properties index of glass fiber: generally the design strength of E-glass fiber is set as 1GPa, which is conservative. The converted average fracture strength of 9 kinds of glass fiber yarns (standard distance 200mm), which were produced by Yaohua Glass Factory in 1971, is 1.11GPa at lowest, the highest is up to 1.53GPa, dispersion coefficient of 6.95%∼14%. For 10 kinds of different thickness of glass cloth's average fracture strength (effective length of testing segment of sample is 100mm, and width 25mm), the lowest is 1.12GPa, the highest is 1.89GPa, dispersion coefficient is 5.5%∼15.3%.

In general tensile elastic modulus E_f of E-glass fiber is about 70GPa; E_f of high modulus glass fiber is about 100GPa. E-glass fibers' fracture elongation $\varepsilon_{fu}$is about 2.6%; the Poisson's ratio μ_f measured by bulk glass is about 0.22.

③ Mechanical properties of carbon fibers.

Carbon fiber is similar to glass fiber in the characteristics of mechanical properties. Its stress-strain curves maintain a straight line before break, which accords with the elastic law; no obvious plastic deformation, with the characteristics of brittle materials.

For carbon fiber both tensile strength and tensile modulus are higher and with different carbonization temperature different strength and modulus of carbon fiber is available. For II-type or high-strength carbon fiber (HS) the strength is up to 3GPa, modulus 230$\sim$270GPa, elongation at break is 1%$\sim$1.5%. For I-type carbon-fiber or high modulus (HM) carbon fiber the modulus is 390$\sim$420GPa, strength about 2GPa, fracture elongation is $0.5\% \sim 1.0\%$. With improvement of raw materials and manufacturing process, internal defect reduces, performance has been improved, ultra-high strength (UHS) carbon fibers and ultra-high modulus (UHM) carbon fiber continue to emerge. For T1000 Toray introduced in 1986, the strength is 7.05GPa, E_f is 295GPa, ε_{fu} is 2.4%; for P-140 pitch-based carbon fiber the Union Carbide Compounds Company (now under the Amoco Performance Product Company) produced, modulus is as high as 966GPa, close to the theoretical modulus of ideal graphite crystal. But carbon fiber is more brittle than glass fiber, and lower interfacial bonding strength with the resin matrix than the glass fiber.

④ Mechanical properties of aramid.

Kevlar-49 as a representative of the aramid is a high modulus organic fibers, and has low density (ρ_f is 1.44g/cm^3, and E_{GF} is 2.54g/cm^3, T300 is 1.76g/cm^3), high strength (σ_{fu} is 3.62GPa), higher modulus (E_f is 125GPa) than glass fiber, good toughness (fracture elongation ε_{fu} is 2.5%). But Kevlar exhibits inert surface, and poor interfacial bonding with resin, bad compressive and torsional performance.

(2) Mechanical properties of synthetic resin adhesive-matrix material.

Resin matrix is an organic polymer material, and its mechanical properties depend on its own structure, such as the rigidity, cross-linking density, as well the environmental temperature and outside load. Low temperature and small load lead to change of bond length and bond angle, high temperature and large load result in high-elastic deformation and even plastic deformation until failure. Strength and modulus of matrix adhesive are lower than the reinforcing fibers, the strength is about 1/40 of glass fiber, and modulus is about 1/20, so reinforcing fibers in composite materials is the main bearing material. Fracture elongation ε_{mu} of resin cast is about 1%$\sim$ 3%, and density ρ_m is about 1.1$\sim$1.5g/cm^3.

(3) Effect of matrix material on mechanical properties of composite materials.

① Reasonable content of matrix in composite materials.

Since the strength and modulus of reinforcing material are greatly higher than the matrix material, the content of matrix has a great impact on the mechanical properties of composite materials, and therefore reasonably reducing content of matrix is one effective way to improve the mechanical properties of composite materials.

A) Theoretical content of matrix material. Assumed that the fiber is arranged closely and the matrix only fills the gap among the fiber, thus the theoretical content of the matrix can be estimated, which reflects the minimum content of the matrix in composite materials, by weight for unidirectional glass fiber reinforced plastics GFRP it is 5%, and for orthogonal composites from 1:1 plain weave cloth it is 12%.

B) The actual process content of matrix material. As a result of changes in the diameter of glass fibers, the different weaving, molding process and methods and conditions in curing process, the actual content of the matrix is often much higher than the theoretical content. The actual process content of matrix, by weight percentage, for GFRP it is 10%∼30%, for orthogonal glass fiber reinforced plastics it is 25%∼50%.

② In order to enhance the mechanical properties of composite materials, we should consider more in choosing the matrix material.

The principle of choosing the matrix has the following main points.

A) Mechanical properties of the matrix material are good itself to meet the performance requirements of the matrix in composite materials. This includes high cohesive strength, elastic modulus, the elongation at break matched to reinforcing fibers, heat resistance, and toughness.

B) There are good wetting and adhesion with reinforced materials to ensure a good adhesive interface.

C) Excellent technology. Methods and conditions of molding and curing are simple, and there are low curing shrinkage and small internal stress.

Moreover, in the choice of matrix materials, we should also consider the economics. Convenient sources of raw materials, low cost, low toxicity are all pluses.

③ Effect of the mechanical properties of matrix on mechanical properties of composite materials.

Effect of the mechanical properties of matrix adhesive on mechanical properties of composite materials can be summed up in Table 8.1, which depends mainly on the elastic modulus, fracture elongation, cohesive strength, fracture toughness, adhesion strength and curing shrinkage of matrix material. In composite materials, the matrix material exists in the state of film, film strength is higher than the cast, and usually the mechanical properties of the matrix is determined by the cast, so when selecting the matrix, the performance data of the cast can only be used as a contrast reference, but not the basis for design.

2) The mechanical anisotropy of composites

Directions of fiber in composite materials cause the anisotropy in mechanical properties of the composites. There is disciplinarian variation with the change along the loading direction. In the rectangular coordinate system, firstly determine the coordinates the performance of material along the certain axis as the original performance, and then analyze the relationship between the performance in different directions and the original performance in coordinate system, thus identify the change law of performance. Anisotropic materials along the three axial direction of rectangular coordinate system have different properties, which are called the orthotropy.

Table 8.1 Effect of matrix adhesive on mechanical properties of composite materials

Strength category	The influenced performance of adhesive	Effect sensitivity	Description	Recommended Test method
Longitudinal tensile strength σ_{Lu}	①Tensile modulus E_m ②Interface bond strength	Weak	①Weak resin sensitivity ②For composite materials with high interlaminar shear strength, very sensitive to gap	①Longitudinal tensile test ②Three-point bending test
Longitudinal compressive strength σ_{-Lu}	①Compressive strength σ_{-mu} ②Modulus E_m, G_m ③Interface strength	Strong	①Avoid whole buckling and cracking of the end ②For low modulus of the resin and the environment-sensitive resin, use bending samples	①Longitudinal compression test ②Three-point bending test
Transverse tensile strength σ_{Tu}	①Tensile modulus E_m ②Ultimate strain ε_{mu} ③Fracture toughness ④Interface strength	Strong	Very sensitive to gap	Transverse tensile test
Transverse compressive strength σ_{-Tu}	①Compression modulus E_{-m} ②Ultimate strain ③Fracture toughness	Weak	Very sensitive to gap	Transverse compression test
The edge shear strength τ_{LTu}	①Shear modulus G_m ②Ultimate strain	Strong	When the fiber parallel to the length direction of specimen, the destruction is longitudinal cracking	①Torsion test of bar or pipe ②±45° diagonal tensile test
Interlaminar shear strength τ_u	①Shear modulus G_m ②Ultimate strain ③Interface strength	Very strong	It is very convenient for the evaluation of materials, process and controlling performance	Short beam bending test
Flexural strength σ_{Fu}	Modulus E_m	Weak	Damage begins from the tensile surface	Three-point bending test
		Strong	Damage begins from the compression surface	

There are two commonly used methods to analyze the mechanical anisotropy, network analysis and orthotropic analysis. Network analysis only considers the load-bearing capacity of fiber, the matrix cannot bear load, and it only plays the role of fixing fiber. The composite structure is a bearing network, thus stress can be solved only by the balance of power. There is no need to obtain the deformation. Network analysis can be used for the design of the strength, winding law and process parameters of winding parts. Orthotropic analysis also takes the load-bearing capacity of the matrix into account, analyzing statically indeterminate structures. In stress analysis we must utilize the auxiliary equation of the deformation to derive strain equation, and then according to the elastic relationship to derive out stress equation. In the basic mechanical analysis behind, we focus on the orthotropic analysis.

8.1.3 The design steps of composite material component

Two types of composite material components are used in aircraft, one is load-bearing member, such as the tail, fuselage, etc., and the other is the radar antenna protection cover (radome) which is made of wave-transparent material. Design and manufacture of composite components are quite different from the traditional metal components. Metal materials, such as aluminum skin, were bought for sheet metal and joint manufacture. The raw materials of composite materials such as carbon fiber, resin curing agent however, are only ingredients before manufacture. The material is yet to produce. Therefore, production of composite materials requires materials technology staff to work closely with mechanical designer. Only in this way can we design and manufacture qualified composite materials products, its design procedure is shown in follows.

1) Material design of unidirectional laminate

Materials technology staff, based on the mechanical performance requirements of components, choose correct materials (including reinforcing fibers, the type of matrix material and its ratio), prepare unidirectional laminate and determine 11 engineering mechanics parameters of unidirectional laminate for ply stacking design (elasticity constant $E_L, E_T, G_{LT}, E_{-L}, E_{-T}$, μ_{LT} or μ_{TL}, strength σ_{Lu}, σ_{Tu}, σ_{-Lu}, σ_{-Tu}, τ_{LTu}). Unidirectional laminate design reflects the material design of composites. Design required performance of unidirectional laminate based on the performance of component materials and the ratio, and then verify by experiment.

2) Ply stacking design and structure design

Mechanical designer based on the mechanical properties of unidirectional laminate, designs a reasonable ply sequence that reflects the structure of composite materials. By changing the arrangement of unidirectional laminate and the relative proportions we can design required composite laminate. Materials technology staff prepares composite laminate and conducts performance testing to verify the performance of composite plate. Based on the ply design, we may design the structure, and finally decide the shape and size of the product. For example, helicopter rotor works under both torsional force and centrifugal force, so we choose 0°/90°/±45° ply, and ply proportion can be determined by stress state. It can be designed to the extent that upon damage, the product has no strength surplus in any direction, so as to realize the maximum weight saving. This is something isotropic materials cannot do.

3) Components trial-manufacture

Based on the result of stacking sequence and structure design, shape and complexity of size of component, material technology staff can determine an appropriate molding method, draw up process conditions, progress the design and manufacture of mold and work equipment, and finally trial-manufacture composite material products.

4) Test

Since the performance of composite materials is affected by a number of factors, and trial part can be finalized and produced in batch only after non-destructive testing (NDT) and destructive testing for eligible verification. Non-destructive testing such as ultrasonic flaw detection can measure manufacturing defects and porosity of composite components, etc., to verify product quality and manufacturing process. Static, fatigue and other destructive test verify the ply structure design.

The three levels of design, unidirectional laminate material design, ply design and structure design are prerequisite for each other. They have mutual influence and mutual dependence. Therefore, composite materials and its structure design break the traditional boundaries of materials and structure research. Designers must take the material properties and structure into consideration, in other words, material design and structure design must progress at the same time and be unified in the same design. This is why material technology staff should learn the mechanical properties of composite materials in this chapter.

8.1.4 Research area of composite material mechanics

Research field of composite material mechanics includes mesomechanics (often called as micromechanics), macromechanics, fracture mechanics and damage mechanics. The research subject, research method and purposes are presented in Table 8.2. The book focuses mainly on micromechanic properties of materials, namely use micromechanics approach to discuss tensile, compression, shear, bending and other basic mechanical properties of composite material under a single stress, as well as mechanical properties under simple complex stress conditions. This is to equip material technology staff with the following skills: ① understand the characteristics of basic mechanical properties under the simple stress; ② estimate the mechanical properties composite materials according to the properties of raw materials (fiber and matrix); ③ make reasonable choice of raw materials in accordance with the mechanical properties requirements of composite materials.

Table 8.2 Research field of composite material mechanics

	Mesomechanics (micromechanics)	Macromechanics	Fracture mechanics (damage mechanics)
Research object	Mechanical properties of unidirectional laminate (fiber, matrix as the basic unit)	Mechanical properties of composite plate (unidirectional laminate as the basic unit)	The mechanical properties of composite materials with hole, and notch
Research method	According to the structure characteristics of unidirectional laminate, choose a typical unit, and then simplified into mechanical model. Use material mechanics or elasticity mechanics method to derive out the formulae that estimate mechanical properties of unidirectional laminate (E, σ)	According to the mechanical properties of unidirectional laminate and its arrangement, using the elasticity mechanics method to estimate the mechanical properties of composite plate (such as stiffness, deformation, strength, etc.)	Use linear elastic fracture mechanics or damage mechanics method, to study the mechanical properties of composite materials with hole, notch or damage, understand the fracture mechanism, fracture toughness and damage tolerance of composite materials
Research purpose	Guide material design	Guide ply stacking design	Reliability design or the design of damage tolerance

8.1.5 The basic assumptions and the typical unit of micromechanics

1) The basic micromechanics assumptions to study the mechanical properties of composite materials

Composite material in reality is complex. For convenience of micromechanics analysis, we idealize and simplify the issue by making the following four basic assumptions.

(1) The equal initial stress assumption.

Matrix material and reinforcing material themselves are uniform, continuous, isotropic, no porosity, cracks and other defects. Fibers are arranged equidistantly in parallel, its nature and diameter are uniform. The initial stress of fiber and matrix is equal to 0, and we do not consider the thermal stress caused in manufacturing process.

(2) The consistent deformation assumption (integration assumption).

The bearing load by composite material is respectively shared by the reinforcing material and matrix material. Fiber is firmly bonded with matrix to form a whole, in load-bearing process, the interface between fiber and matrix does not slide, that is, they have the consistent deformation.

(3) Linear elastic assumption.

In the elastic range under load, the fiber, matrix and composite materials showed a linear relations of stress and strain, comply with Hooke's Law.

(4) Poisson's effect is not considered.

In the discussion of longitudinal loading, transverse deformation caused by different Poisson's ratio of fiber and matrix is not considered.

2) Typical unit cell

Based on the above assumptions, composite material is uniform in macroscopic view, and therefore a representative unit can be chosen to research into. It should be small enough to show composition of micro-structure of materials, and big enough to represent all the characteristics of composite materials. As cross-section of unidirectional fiber composite materials, fiber arrangement in the matrix can be simplified into the following ones (Fig. 8.2): ① random-packed array; ② square-packed array; ③ hexagonal-packed array. The typical unit cells and mechanical models are shown in the Fig. 8.3.

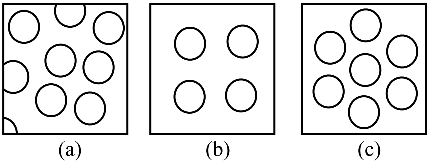


Fig. 8.2 Fiber arrangement of unidirectional fiber composites:
(a) random-packed array; (b) square-packed array; (c) hexagonal-packed array.

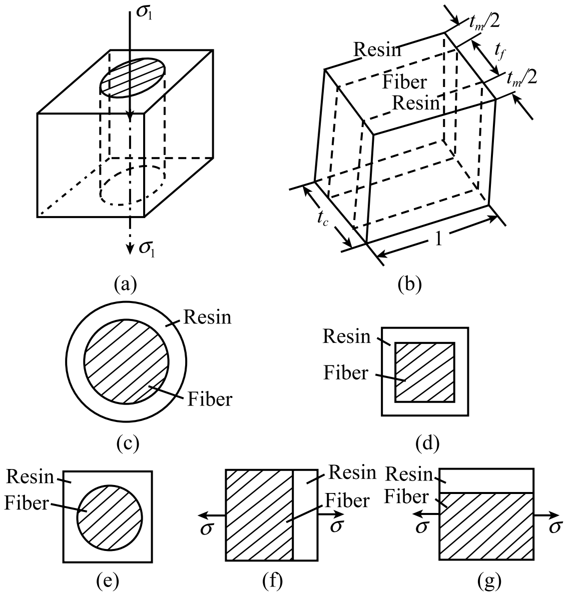


Fig. 8.3 Unit cell and simplified mechanical model of unidirectional fiber composites:
(a) volume unit; (b) representative volume unit; (c) concentric cylinders model; (d) concentric squares model; (e) model with square outer and circular inner; (f) serial model; (g) parallel model.

8.2 Tensile properties of unidirectional fiber composites

As said before, unidirectional fiber composite materials are composite materials in which continuous reinforcing fibers are arranged in the same direction, which is the basic element of composite laminates. By different loading direction its tensile properties can be divided into tension along the fiber direction (L direction, or longitudinal) and tension perpendicular to fiber surface (T direction, or transverse).

8.2.1 Longitudinal tensile properties

1) Longitudinal tensile stress σ_L, tensile modulus E_L

Longitudinal tension of unidirectional fiber composites is shown in Fig. 8.4, and the simplified mechanical model is shown in Fig. 8.5.

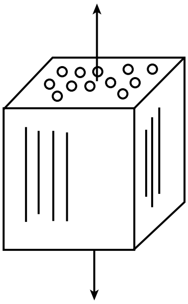


Fig. 8.4 Schematic of longitudinal tensile of unidirectional fiber composites.

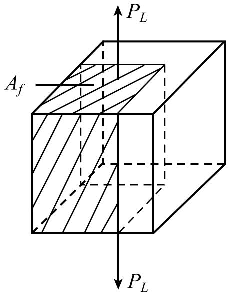


Fig. 8.5 Simplified mechanical model of longitudinal tension of unidirectional plate.

In simplified mechanical model, the power in the fiber direction is P_L, which bears by fiber and matrix respectively. Based on static equilibrium conditions and zero equal initial stress assumption:

$$P_L = P_f + P_m \tag{8.1}$$

P_f is load of fiber; P_m is load of matrix. By the stress there are:

$$\sigma_L A_L = \sigma_f A_f + \sigma_m A_m \tag{8.2}$$

In the formula (8.2) σ_L, σ_f and σ_m represent respectively the stress of composite material, fiber and matrix; A_L, A_f and A_m are respectively cross-section area of composites, fiber and matrix. For composite material with parallel fibers, the volume fraction of each component can be written by the cross-section area:

$$V_f = \frac{A_f}{A_L} \qquad V_m = \frac{A_m}{A_L} \tag{8.3}$$

So

$$\sigma_L = \sigma_f V_f + \sigma_m V_m \tag{8.4}$$

Due to the assumption of the ideal bonding between fiber and matrix, the interface does not slip. The strain of the fiber and matrix in composite materials are equivalent to each other, i.e., by the same deformation assumptions, we have:

$$\varepsilon_L = \varepsilon_f = \varepsilon_m \tag{8.5}$$

Where ε_L, ε_f and ε_m represent the strain of composites, fiber and matrix in L direction, respectively.

Take the derivative of the formula (8.4) to the strain, we get:

$$\frac{\mathrm{d}\sigma_L}{\mathrm{d}\varepsilon_L} = \frac{\mathrm{d}\sigma_f}{\mathrm{d}\varepsilon_f} V_f + \frac{\mathrm{d}\sigma_m}{\mathrm{d}\varepsilon_m} V_m \tag{8.6}$$

$\mathrm{d}\sigma/\mathrm{d}\varepsilon$ stands for the slope at a given point of the stress-strain curves, for example stress-strain curve is linear, its slope is a constant. That constant is the material's modulus.

If the fiber and matrix and composite materials show elastic deformation, by the linear elastic assumption, we have:

$$\sigma_L = E_L \varepsilon_L, \quad \sigma_f = E_f \varepsilon_f, \quad \sigma_m = E_m \varepsilon_m \tag{8.7}$$

Substitute (8.7) (8.5) into (8.4):

$$E_L = E_f V_f + E_m V_m \tag{8.8}$$

The formula (8.4) and (8.8) show that: the contribution of fiber and matrix to mechanical property of the composite material is proportional to its volume fraction, which is called the rule of mixtures. In the case of the void fraction V_V = 0, $V_f + V_m$ = 1, the formula (8.8) can be further rewritten as:

$$E_L = E_f V_f + E_m (1 - V_f) \tag{8.9}$$

Rule of mixtures (8.4) and (8.8) can be extended for:

$$\sigma_L = \sum_{i=1}^{n} \sigma_i V_i \tag{8.10}$$

$$E_L = \sum_{i=1}^{n} E_i V_i \tag{8.11}$$

Stress-strain curves of fiber and matrix can illustrate the formula (8.4) in an intuitive way. Let us study two types of composite materials. In both composite materials, the fiber has linear stress-strain curves up to destruction. One matrix material has a linear stress-strain curve, while the other has non-linear stress-strain curves [Fig. 8.6(a) and 8.6(b)]. Stress in a given strain may be calculated by the formula (8.4). First of all, from the corresponding stress-strain curves we find the stress of the matrix and fiber at a given strain, and then superimpose them based on the volume fraction. We repeat this process for many strains until the failure strain of the fibers. In this way, a complete stress-strain diagram of composite material is plotted. It should be pointed out that this method can be applied to the two above-mentioned composite materials, as in deducing the formula (8.4), no assumptions is made to the properties of component materials. Therefore, the stress-strain curve of composite material (a) is a straight line, while that of composite material (b) is not linear. The stress-strain curves of composite materials and the matrix become non-linear in the same point. However, because the fiber modulus is dominant, the composite material stress-strain curve may not obviously display its non-linearity, especially when the fiber volume fraction is high. At any time, the stress-strain curves of composite materials are between that of the matrix and the fiber. The actual location of the curve depends on the relative volume fraction of materials. If the fiber volume fraction is high, its stress-strain curve is near that of the fiber. In contrast, for a high volume fraction of matrix, its stress-strain curve is near that of the matrix. Accordingly, when predicting the stress of composite materials, the linear elastic assumption will not cause large errors.

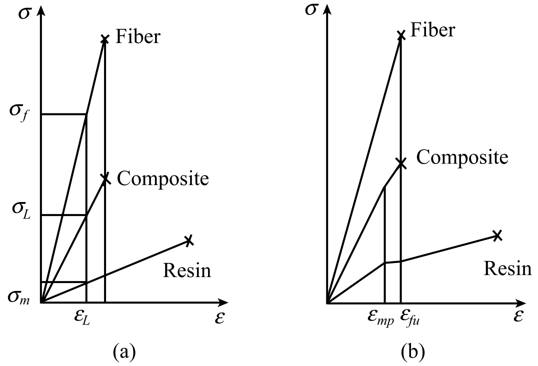


Fig. 8.6 Hypothetical longitudinal stress-strain curve of composites:
(a) stress-strain curve of resin is linear; (b) stress-strain curve of resin is nonlinear.

Under the tensile load, despite the simple rule of mixture, the tensile modulus calculated according to the formula (8.9) or (8.6) is very accurate and matches the experimental results very well. Under the compression load, however, there will be a larger deviation from the experimental results. For example, for carbon fiber/epoxy composite, when E_f = 180GPa, V_f = 0.548, E_m = 3GPa, then estimated $E_L = 1 \times 10^5$MPa, the measured tensile modulus is 103860MPa, which is close to the predictive value. The measured value of compression is 84500MPa, which is largely different from the predictive value. In general, the formula accords with the experiment with the extent of 90%∼100%, which is sufficiently accurate, but in order to further improve accuracy, we introduce correction factor

k_L into the formula (8.9) to reflect the differences between actual and ideal composite materials, such as the fiber straight degree and non-uniform distribution, then we have:

$$E_L = k_L(E_f V_f + E_m V_m) \tag{8.12}$$

Where, k_L = 0.90~1.00. If samples with good quality are chosen and all tests of fibers, matrix and composite materials are done accurately, or if the performance of fiber is reckoned from the experimental data of composite material samples by the formula (8.9), then $k_L = 0.95 \sim 1.00$.

Understanding how to distribute load in constituents of composite materials and the stress born by constituents has significant meaning. So by the formula (8.5) and (8.7), we get the ratio of stress and load.

$$\frac{\sigma_f}{\sigma_m} = \frac{E_f}{E_m} \qquad \frac{\sigma_f}{\sigma_L} = \frac{E_f}{E_L} \tag{8.13}$$

$$\frac{P_f}{P_m} = \frac{\sigma_f A_f}{\sigma_m A_m} = \frac{E_f \varepsilon_f \dfrac{A_f}{A_L}}{E_m \varepsilon_m \dfrac{A_m}{A_L}} = \frac{E_f}{E_m} \times \frac{V_f}{V_m} \tag{8.14}$$

The formula (8.13) shows that the stress distribution between fiber and matrix is based on their modulus. In order to achieve high stress in fibers to make full role of high-strength fiber, elastic modulus of the fiber should be much greater than that of the matrix. The load distribution is in accordance with elastic modulus and volume fraction. When $V_V = 0, V_f + V_m = 1$, the formula (8.14) can be rewritten as:

$$\frac{P_f}{P_m} = \frac{E_f}{E_m} \times \frac{V_f}{1 - V_f} \tag{8.15}$$

When V_f is a constant, P_f/P_m is directly proportional to E_f/E_m (Fig. 8.7). From the formula (8.15) and Fig. 8.7, we can see that with the increase of modulus and volume fraction of fiber, the load that the fiber bears increases. To further illustrate the relationship, the ratio between the load of fiber and the total load of composite materials can also be derived, that is, the function of the percentage that the load fiber bears accounts for the total load.

$$\begin{aligned} \frac{P_f}{P_L} &= \frac{\sigma_f A_f}{\sigma_L A_L} = \frac{E_f V_f}{E_L} = \frac{E_f V_f}{E_f V_f + E_m V_m} = \frac{E_f/E_m}{E_f/E_m + V_m/V_f} \\ &= \frac{E_f/E_m}{E_f/E_m + (1 - V_f)/V_f} \end{aligned} \tag{8.16}$$

The corresponding curve is shown in the Fig. 8.8.

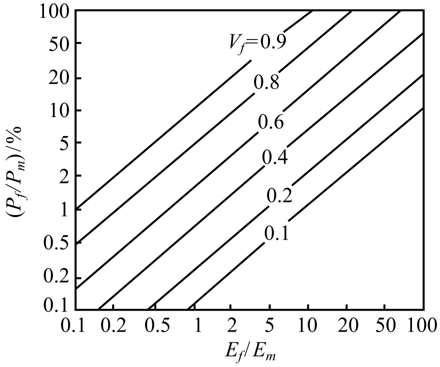


Fig. 8.7 Relationship of P_f/P_m and E_f/E_m under different V_f.

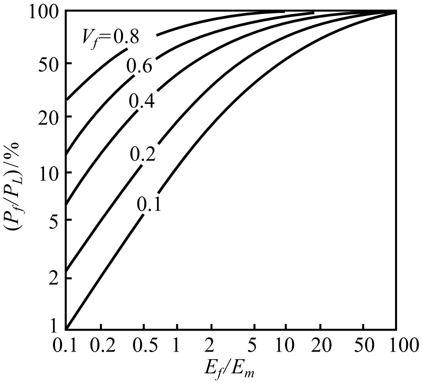


Fig. 8.8 Relationship of P_f/P_L and E_f/E_m under different V_f.

From the Fig. 8.7 and Fig. 8.8, we get:

(1) Increasing fiber modulus, that is raising the E_f/E_m, can increase the fiber loading proportion. As a result of the strength of fiber σ_{fu} greater than the strength of matrix σ_{mu}, the strength of composite materials σ_{Lu} can be improved. For glass fiber epoxy reinforced plastics, its E_f/E_m is about 20. Therefore, even if V_f= 10%, P_f/P_L can reach up to 70% approximately. In other words, 70% of load is borne by the fiber. However, if E_f/E_m is too large, the transmission of stress will be affected and stress concentration be formed in the interface, strength will reduce.

(2) For a given fiber, resin system E_f/E_m is constant, and if we wish to increase the fiber loading proportion, fiber volume fraction should be as high as possible. From the geometric arrangement, cylindrical fibers in the composite material is almost up to the maximum volume percentage of 91%, but usually if the value is more than 80%, the properties of composites will be undermined. That is because the matrix cannot wet and impregnte fiber bundles well, resulting in poor vesin content and formation of voidsin composite materials.

2) Stress-strain characteristics and longitudinal tensile strength σ_{Lu}

Rule of mixture can accurately predict the stress-strain characteristics of unidirectional composite material under longitudinal tensile load by using the formula (8.4) to calculate stress, the formula (8.6) to estimate the slope of stress-strain curves. However, using the elastic modulus instead of the slope to simplify the formula (8.6) to (8.8) is possible only when the two components of composite materials have shown elastic deformation. This is only suitable for a small parts of the stress-strain characteristics, and is mainly applied to glass fiber, carbon fiber, boron fiber or ceramic fiber reinforced thermosetting resin matrix composite materials. Usually, there are four phases of the deformation of a composite material: ① fiber and matrix deformation are both elastic; ② elastic deformation of the fiber, but non-elastic deformation of the matrix; ③ both non-elastic deformation of fiber and matrix; ④ fiber fracture, composites fracture followed.

The second phase may occur in the largest paragraphs of stress-strain curve of the composite material, especially in metal matrix composite materials. And at this stage the stress - strain curve of the matrix is only a very short straight line. In this case, the modulus of composite material should be calculate in each strain levels by the formula below:

$$E_L = E_f V_f + \left(\frac{\mathrm{d}\sigma_m}{\mathrm{d}\varepsilon_m}\right)_{\varepsilon_L} V_m \tag{8.17}$$

Where $(\mathrm{d}\sigma_m/\mathrm{d}\varepsilon_m)_{\varepsilon_L}$ is the slope of strain-stress curve of the matrix when the strain of composites is ε_L.

Although the third phase cannot be observed for brittle fibers, the elastic modulus of tough fiber composite material should be estimated by the formula (8.6). For necking damage of the toughness fiber, like fluid mechanics, the matrix imposed the lateral bound on fibers to prevent necking. These additional factors have led to the bias between estimate and test data.

The stress-strain curve of fluid statics composite material, made of ductile or brittle fiber and typical metal or ductile matrix, is shown in the Fig. 8.9. The stress - strain curve of composite materials is between that of the fiber and matrix. Brittle fiber composite materials usually fracture when the strain reaches fracture stain of fiber. However, if the fiber can produce plastic deformation in matrix, fracture strain of the fiber in the composite materials may be greater than that of the fiber alone (without matrix). Thus, the fracture strain of composite material can be more than that of fiber fracture. See Fig. 8.9. Differences between the two fracture strains increase similar to the reduction of V_f and the strength ratio's increase of the matrix and fiber.

The strength of composite materials σ_{Lu} is estimated based on rule of mixture (8.4), but related with fracture elongation of the chosen matrix ε_{mu}. So we must consider which component, fiber or matrix, will break at first. For the different relative size of ε_{fu} and ε_{mu}, the formula to estimate σ_{Lu} is different, several situations are discussed below.

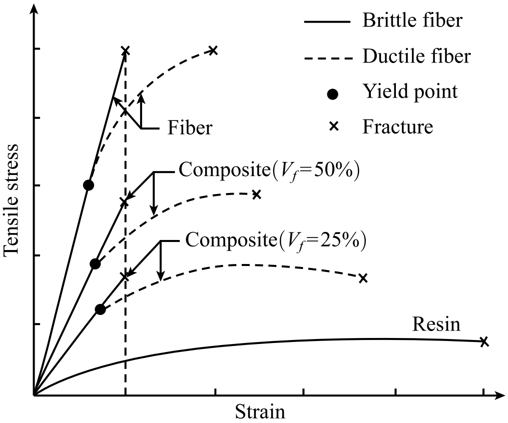


Fig. 8.9 Stress-strain curve of ductile, brittle fiber and fluid dynamic composite from ductile resin.

(1) $\varepsilon_{fu} = \varepsilon_{mu}$, that is the simplest ideal case, both the matrix and fiber materials are brittle. When $\varepsilon_L = \varepsilon_{fu}$, the fiber, matrix and composite materials fracture at the same time, so the stress in the formula (8.4) is replaced by strength directly:

$$\sigma_{Lu} = \sigma_{fu} V_f + \sigma_{mu}(1 - V_f) = \varepsilon_{fu}[E_f V_f + E_m(1 - V_f)] \tag{8.18}$$

(2) Both fiber and matrix are brittle, and $\varepsilon_{fu} > \varepsilon_{mu}$. Such several commonly used glass-fiber-reinforced thermosetting plastics, its stress - strain curve is shown in the Fig. 8.10.

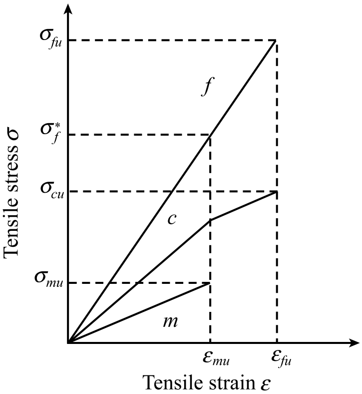


Fig. 8.10 Stress-strain curve of fiber, matrix and their composites: fiber and matrix are both brittle materials.

Under tensile load, the damage is from resin cracking, then fiber break. Resin cracking, the stress-strain curves of composite materials shows an inflexion point, which does not mean the final destruction of the material. Because the resin cannot appear fracture in the same cross-section, fiber can also continue to bear the tensile load until comprehensive fibers fracture when composite materials will fracture at the same time. Therefore, the longitudinal tensile fracture strain of composites is $\varepsilon_{Lu} = \varepsilon_{fu}$.

The stress of composite materials before the matrix cracking is:

$$\sigma_L = \sigma_f V_f + \sigma_m(1 - V_f)$$

Maximum stress is expressed:

$$\sigma_L = \sigma'_f V_f + \sigma_{mu}(1 - V_f) = \varepsilon_{mu}[E_f V_f + E_m(1 - V_f)] \tag{8.19}$$

Where, σ'_f is the stress of fiber when ε_f is equivalent to ε_{mu}.

The stress of composite materials after matrix cracking prior to fiber fracture:

$$\sigma_L = \sigma_f V_f$$

Maximum stress for:

$$\sigma_L = \sigma_{fu} V_f \tag{8.20}$$

The strength of composite materials σ_{Lu} is determined by (8.19) and (8.20):

$$\sigma_{Lu} = \varepsilon_{mu}\left[E_f V_f + E_m(1 - V_f)\right] \tag{8.21}$$

$$\sigma_{Lu} = \sigma_{fu} V_f \tag{8.22}$$

The relationship between σ_{Lu} and V_f is shown in Fig. 8.11. At the point of intersection of two straight lines, we can obtain the critical value of fiber volume content V'_{fcr}:

$$V'_{fcr} = \frac{\sigma_{mu}}{\sigma_{fu} - \varepsilon_{mu} E_f + \sigma_{mu}} \tag{8.23}$$

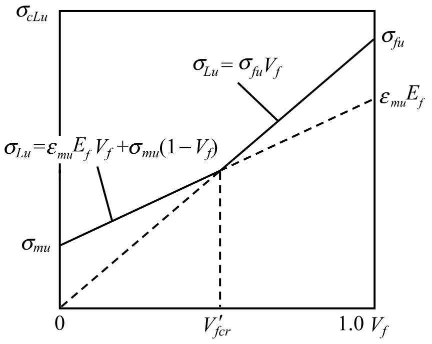


Fig. 8.11 Longitudinal tensile strength σ_{Lu} changes with V_f of brittle fiber and resin composites.

When $V_f > V'_{fcr}$, after matrix cracking, fiber will continue to carry load up to ε_{fu} when the composite material damage. Therefore, $\varepsilon_{Lu} = \varepsilon_{fu}$, the strength of composites is estimated by the formula (8.22). When $V_f < V'_{fcr}$, due to less fiber content, matrix cracks and the original load in matrix transfers to fiber. Fiber cannot bear the entire load, thus stress of fiber quickly reaches fracture stress σ_{fu}, and fiber fracture occurs and composite materials are destroyed. Therefore, we can think that $\varepsilon_{Lu} = \varepsilon_{mu}$, composite strength is estimated by the formula (8.21).

From the Fig. 8.11, we also can see that in such a situation, however many fibers are added, the longitudinal tensile strength of composite materials will be improved ($\sigma_{Lu} \geqslant \sigma_{mu}$). When $V_f > V'_{fcr}$, σ_{Lu} increases with increase of V_f and σ_{fu}, reinforcing effect is larger; when $V_f < V'_{fcr}$, σ_{Lu} depends not only on E_f and V_f, but also ε_{mu}, reinforcing effect is lower.

(3) When $\varepsilon_{fu} < \varepsilon_{mu}$, that is, the fiber compared with matrix is brittle. For example, for glass fiber, carbon fiber, boron fiber and tough epoxy resin or polyester resin composite materials, fibers displays brittle fracture, ductile matrix displays tough fracture, and the fracture strain of fiber ε_{fu} is less than that of matrix ε_{mu}, its stress-strain curve is shown in the Fig. 8.12.

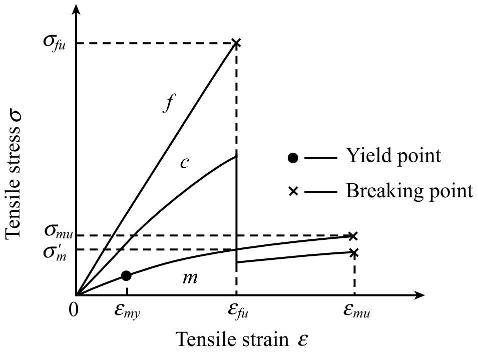


Fig. 8.12 Stress-strain curve of fiber, matrix and their composites: fiber is brittle and matrix is ductile.

The stress of composite materials before fiber fracture is given by:

$$\sigma_L = \sigma_f V_f + \sigma_m (1 - V_f)$$

At the yield point of matrix, the stress of composite materials is given by:

$$\sigma_L = \varepsilon_{my} [E_f V_f + E_m (1 - V_f)]$$

Where, ε_{my} is the strain the matrix depart from the linear elasticity. When ε_L reaches the fracture strain of fiber ε_{fu}, σ_L reaches the maximum. At this time, we get:

$$\sigma_L = \sigma_{fu} V_f + (\sigma_m)_{\varepsilon_{fu}} (1 - V_f) \tag{8.24}$$

Where, $(\sigma_m)_{\varepsilon_{fu}}$ is the stress of matrix when the strain of matrix is equal to the fracture strain of fiber.

After the fiber fracture and before matrix fracture, the stress of composite materials is given by:

$$\sigma_L = \sigma_m(1 - V_f)$$

When $\varepsilon_L = \varepsilon_{mu}$, σ_L also reaches up to a maximum, that is,

$$\sigma_L = \sigma_{mu}(1 - V_f) \tag{8.25}$$

In the Fig. 8.12, we can see from σ_L-ε_L curve when ε_L is equal to ε_{fu} and ε_{mu} respectively σ_L has two maximum, which can be obtained from the formula (8.24) and (8.25). The strength of composite materials is determined by the two formulas, that is,

$$\sigma_{Lu} = \sigma_{fu}V_f + (\sigma_m)_{\varepsilon_{fu}}(1 - V_f) \tag{8.26}$$

$$\sigma_{Lu} = \sigma_{mu}(1 - V_f) \tag{8.27}$$

And it is related to V_f. The relationship between V_f and σ_{Lu} is shown in the Fig. 8.13.

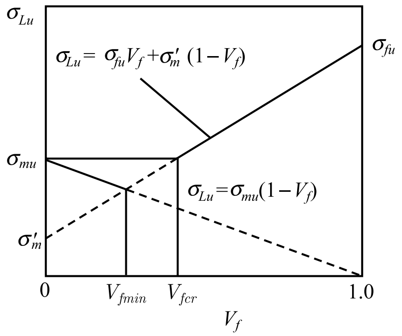


Fig. 8.13 Longitudinal tensile strength σ_{Lu}changes with V_f of unidirectional composites.

At the point of intersection of two straight lines, one fiber volume content V_{fmin} can be obtained from (8.26) and (8.27).

$$V_{fmin} = \frac{\sigma_{mu} - (\sigma_m)_{\varepsilon_{fu}}}{\sigma_{fu} + \sigma_{mu} - (\sigma_m)_{\varepsilon_{fu}}} \tag{8.28}$$

When $V_f < V_{fmin}$, even if all the fibers fracture the ultimate destruction of composite materials will not occur. As there are too few fibers, the remaining matrix can continue to bear the increased load, until ε_L goes up to ε_{mu}, and σ_L up to $\sigma_{mu}(1 - V_f)$. Then the composite material will eventually collapse. V_{fmin} is the volume content of fiber at the minimum value of the strength of composite materials. It is not the minimum of fiber volume content as people often misread. When V_f is lower than the V_{fmin}, the matrix determines damage mode of composite materials; when V_f is higher than V_{fmin} the fiber determines damage mode of composite materials, that is when $\varepsilon_L = \varepsilon_{fu}$, the fiber fractures, and the remaining matrix follows.

In the Fig. 8.13, we see that when V_f is very little, σ_{Lu} may be smaller than σ_{mu}. However, from the strength point of view, our objective to add fiber is for enhancing, that is, $\sigma_{Lu} > \sigma_{mu}$. Therefore, $\sigma_{Lu} = \sigma_{mu}$ is substituted into the formula (8.26) to obtain a critical fiber volume content V_{fcr}.

$$V_{fcr} = \frac{\sigma_{mu} - (\sigma_m)_{\varepsilon_{fu}}}{\sigma_{fu} - (\sigma_m)_{\varepsilon_{fu}}} \tag{8.29}$$

When $V_f < V_{fcr}$, fiber does not take effect. Actually, it reduces the strength of composite materials. Only when $V_f > V_{fcr}$, will the strength of composite materials be higher than the strength of the matrix. Therefore, for the selected V_f, it is important to make $V_f > V_{fcr}$.

From the two situations 2) and 3), we can see that in order to obtain a greater enhancement effect, fiber content should be greater than the critical value. At this time the longitudinal tensile strength of composites is determined by the formula (8.22) and (8.26) respectively. Due to very small $(\sigma_m)_{\varepsilon_{fu}}(1 - V_f)$, if negligible, then the formula (8.26) can be simplified as $\sigma_{Lu} = \sigma_{fu}V_f$, which is the same to the formula (8.22). Therefore, the longitudinal tensile strength of composites can be approximated as $\sigma_{Lu} = \sigma_{fu}V_f$, which means that the longitudinal tensile strength depends primarily on the strength and volume content of fiber.

Although the rule of mixture can well predict the longitudinal tensile properties of unidirectional fiber composites, there is also a difference between the measured value and calculated value. This is caused by the small inconsistency between our micromechanics assumption and the actual situation. For example, fiber is not straight, not parallel to each other; there is deviation of the direction, strength inhomogeneity, and broken ends; porosity and crack in the matrix; weak interface, internal stress and so on. Therefore, C.C.Chamis, etc., put forward a semi-empirical formula to amend the rule of mixture. We get the expression:

$$\sigma_{Lu} = \sigma_{fu}(\beta_f V_f + \beta_m V_m E_m / E_f) \tag{8.30}$$

Where, β_f and β_m are the theory - experiment correlation factor of fiber and matrix respectively, which depend on the production process of the fiber and composites.

3) Influencing factors of longitudinal strength and modulus

When deducing the formula to estimate longitudinal strength and stiffness of composite materials in the front the various physical parameters of the system were taken into account. A lot of simplifying assumptions was done. Some of assumptions have been clearly stated, while the others were implied. In actual materials, fully consistency with the assumptions is very rare, if not impossible. Consequently, the performance of actual material almost always deviates somewhat from the predicted results by formula. Among the many factors, a lot are trivial, that is, the bias caused by them is too small for any amendment to be necessary. However, in some special cases, the error can be significant, hence amendment needed. The main influencing factors on strength and stiffness include: ① fiber orientation error; ② uneven fiber strength; ③ discontinuous fiber; ④ interface situation; ⑤ residual stress.

The fiber direction relative to the load axis is an important parameter. The position of fiber has a direct impact on the load distribution between the fiber and matrix. When the fiber is parallel to the direction of the external load the fiber makes greatest contribution to the performance of composites; when not parallel composite materials have a reduction in the strength and stiffness. How much the strength and stiffness may reduce depends on the number of fibers not parallel to the load direction and the angle between fiber and the load axis. In fact, in the manufacture of composite materials, it is impossible to align all the fibers linearly. When the fiber orientation deviates in one or two degree, amendment is not needed. In laminated composite materials, the load in some ply may not be in fiber direction. In this case, laminated plate theory is required to analyze.

The strength of fiber has a direct impact on the strength of composite materials. Any reduction in fiber strength will lead to the strength decrease of composite materials. If all fibers have equal strength, composite materials will have a high strength. The strength of single metal fiber usually has a good reproducibility, while glass fiber or silica fibers have considerable strength dispersion. This may be caused by two factors: ① the fiber diameter and length changes caused in the manufacturing process; ② different fiber processing and different nature and concentration of surface treatment agent. Whenever there is heterogeneity in fiber strength, we can consider the introduction of an appropriate statistical model.

Based on the experimental observations on the failure of composite materials, the statistical model of composite material strength was developed. Some individual fiber fracture in composite materials begins under the load much less than that of composites failure. With the load increasing, more fiber damages, which occurs in different cross-sectional surface. Therefore, with the load increasing the number of damaged fibers gradually accumulates, which makes the cross-section of composite materials to be weakened. The model that fiber statistical cumulative damage causes weakening of the cross-section is often called the cumulative-weaken damage model. Through appropriate statistical parameters, this model takes into account the effect of an individual fiber breakage on the stress re-distribution to others nearby.

Second consideration of statistical model is that the fiber strength depends on the fiber length. This strength dependence on the length can be understood like this, where fiber is comparable to a long-chain consisting of many links, the chain will damage in the weakest link. The longer the chain, the higher probability it has the weakest link. Therefore longer fibers have a smaller strength. Another important point is that the actual composite material contains a large number of bundles of fibers with non-uniform strength, which is usually assumed that fiber strength obeys Weibull distribution. The average strength of a bundle of fiber is a little lower than the average of individual fiber experiment. Statistical tensile failure model takes into account the length- strength relationship, statistical changes of fiber strength as well as the difference between the strength of fiber bundles and the average strength of isolated fibers. Thus in the model fiber strength is used to predict the strength of composite materials.

In composite materials, the load is not directly imposed on the fiber. It is transferred by the resin to a small length of the fiber end and then to the fiber in a whole. When the fiber is much longer than the fiber length required for transferring stress, the end effect can be ignored, and the fiber is considered infinite, or in our terminology, continuous. Therefore, the stress of continuous fiber can be assumed a constant in its entire length. For short fiber composite materials, the end effect cannot be ignored. In general, their properties cannot be described by the formula (8.4) and (8.8). Considering that for the finite length of fiber end stress is less than the maximum fiber stress, it is necessary to make certain corrections to V_f and σ_f in the formula (8.4) and (8.24), which depends on the fiber length required transfer load from matrix to fiber. When the fiber length is much larger than the critical length, the correction is negligible. However, in discontinuous fiber-reinforced composite materials, it is difficult to control fiber into a straight line, so its performance is largely decreased.

In discontinuous fiber composite materials, another question to be considered is the stress concentration at the fiber end. This is particularly important in the damage process of composite materials containing brittle matrix. As the result of stress concentration, in a small external load the fiber end separates from the matrix and forms the micro-cracks. Continuous fiber-reinforced composite materials have a similar case when the fiber fractured in the weakest cross-section. The first micro-cracks in the end of fiber can lead to some alternate effects. Interfacial shear stress causes the expansion of cracks along the fiber length, so that the fiber is divorced from composite materials. When this happens, the fibers do not work and composite materials seem to play the role of a bundle of fibers. In such case, the strength of composites is not higher than the matrix strength. On the other hand, as a result of local stress concentration, cracks may expand in the direction perpendicular to the fiber, over the other fibers, causing the instantaneous destruction of composite materials. Even if the effect of such crack propagation does not take place, increasing load will result in further separation of fiber end with the matrix in discontinuous fiber composite materials and fiber fracture in more parts in continuous fiber composites. Each crack causes stress re-distribution nearby, and changes relative probability of the crack growth.

Bonding interface between the matrix and fiber has an important effect on the properties of composite material. Interface transfers load from the matrix to the fiber, thus the strength of composite materials is affected by the interface situation. In the discontinuous fiber composite materials and continuous fiber composite material, when some fibers fracture prior to the final destruction of composite materials, the load transfer mechanism through the interface is even more important. Interface determines the micro-crack propagation of fiber end. When bonding is strong between the fiber and matrix, the cracks are not extended along the fiber length. Fiber continues to play the role of reinforcement until the fiber fractures along its length at some points. Composite materials with strong adhesion have a higher transverse strength and good environmental performance. Usually improving the adhesion can also improve the water resistance of polymer matrix composite materials. When adhesion is particularly bad, the harmful effect of environmental condition will be worse under load. However, there is a property called fracture toughness that can be improved by reducing adhesion. Thus in order to optimize fiber properties, we might be able to find a good value for adhesion. Nonetheless, this is difficult because it affects the relationship between other properties of composite materials (such as fatigue and creep) and the interface properties.

In traditional fiber composites manufacturing processes the residual stress is generated in components and interfaces, residual stress is caused by two main reasons: ①different thermal expansion coefficient of components; ②different manufacture and use temperature.

In addition, different expansion of each layer can also result in residual stress in the laminates. Although component material of the layer is the same, as long as their relative direction is different, there still will be residual stress. Like other properties, thermal expansion coefficient of unidirectional composites also depends on the direction. Residual stress has a direct impact on the properties of the matrix and the actual stress state of composite laminates. Therefore, the effect of residual stress on strength of composite materials is similar to the response of materials to the mechanical load. When analyzing laminated composite materials accurately, the residual stress cannot be ignored.

4) Main Poisson's ratio μ_{LT}

According to Poisson's effect, when unidirectional fiber composite materials are stretched in the fiber direction, the contraction occurs in the transverse. The main Poisson's ratio is defined as:

$$\mu_{LT} = -\frac{\varepsilon_T}{\varepsilon_L} \tag{8.31}$$

We can use the simple model which is similar to the longitudinal tensile property to estimate μ_{LT}, see Fig. 8.14.

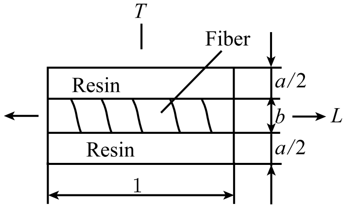


Fig. 8.14 Model of forecasting the main Poisson's ratio of unidirectional composite.

Firstly, considering the longitudinal deformation, from the assumption of the same deformation, we get:

$$\varepsilon_L = \varepsilon_{fL} = \varepsilon_{mL} \tag{8.32}$$

In the formula, ε_L is the longitudinal strain of composite material; $\varepsilon_{fL}, \varepsilon_{mL}$ is the longitudinal strain of fiber and matrix.

Transverse deformation of composite materials consists of the transverse deformation of the fiber and the matrix.

$$\varepsilon_T(a+b) = \varepsilon_{mT}a + \varepsilon_{fT}b \tag{8.33}$$

$$\varepsilon_T = \varepsilon_{mT}\frac{a}{a+b} + \varepsilon_{fT}\frac{b}{a+b}$$

$$\varepsilon_T = \varepsilon_{mT}V_m + \varepsilon_{fT}V_f \tag{8.34}$$

Substitute formula (8.32) and formula (8.34) into the formula (8.31), we can get:

$$\mu_{LT} = -\frac{\varepsilon_T}{\varepsilon_L} = -\frac{\varepsilon_{fT}V_f + \varepsilon_{mT}V_m}{\varepsilon_L} = -\frac{\varepsilon_{fT}}{\varepsilon_{fL}}V_f - \frac{\varepsilon_{mT}}{\varepsilon_{mL}}V_m \tag{8.35}$$

According to the definition of Poisson's ratio of the fiber and the matrix, we can get:

$$\mu_{LT} = \mu_f V_f + \mu_m V_m \tag{8.36}$$

It is to say, main Poisson's ratio can also be estimated by rule of mixture. Usually, $\mu_m > \mu_f$, so as V_f increases, μ_{LT} decreases.

5) Fiber volume fraction V_f

The longitudinal tensile properties of unidirectional fiber composite materials are discussed before, such as σ_L, E_L, σ_{Lu} and μ_{LT}. They are related to fiber volume fraction V_f. Now, we introduce the method to get V_f.

(1) Calculation by the resin content w_m.

The resin mass content w_m is the mass fraction of resin, that is to say, the resin accounts for the percentage of the total mass of composites.

$$w_m = \frac{G_m}{G_c} = \frac{G_m}{G_f + G_m} = \frac{V_m\rho_m}{V_m\rho_m + V_f\rho_f} \tag{8.37}$$

In the formula, G is mass; ρ is density; m, f, c stands matrix, fiber or composite material.

Fiber mass content w_f:

$$w_f = \frac{G_f}{G_f + G_m} = 1 - w_m \tag{8.38}$$

When $V_V = 0, V_m = 1 - V_f$, put them into formula (8.37), we have:

$$V_f = \frac{1}{1 + \dfrac{w_m}{1 - w_m} \cdot \dfrac{\rho_f}{\rho_m}} \tag{8.39}$$

Or

$$V_f = \frac{\rho_c}{\rho_f} w_f = \frac{\rho_c}{\rho_f}(1 - w_m) \tag{8.40}$$

For glass fiber composite materials, because of $\rho_f/\rho_m \approx 2$, formula (8.39) can be simplified to:

$$V_f = \frac{1 - w_m}{1 + w_m} \tag{8.41}$$

Composite material's w_m is connected to its molding method. w_m in winding molding is about 20%; for the composite material made by unidirectional tape, its w_m is about 30%; and w_m in wet hand lay-up is about 50%. w_m can be determined by experimental methods. For glass fiber composite materials, we can use burn ablation method, for carbon fiber composite materials, acid corrosion method can be used.

(2) Microscope method.

For unidirectional fiber composites, we will polish cross-section of the specimen along the direction vertical to fiber into a mirror, the fiber and the matrix on the cross-section can be seen using optical microscope. Take photos of two kinds of magnification. The photo which is enlarged 200 times is used to make statistics of the number of fiber per unit area, and the photo which is enlarged 1200 times is used to determinate the cross-section area of single fiber, we can get the area and volume fraction of fiber from these methods.

(3) Estimation method.

This is the method to calculate the V_f obtained by the areal density of single-layer prepreg or enhanced fabric and it doesn't need a lot of test time, which is particularly suitable for composite material panel made by unidirectional tape and fabric prepreg. Composite material panel's average volume fraction can be calculated by formula (8.42).

$$V_f = \frac{G_f \cdot n}{\rho_f \cdot t_c} \times 100\% \tag{8.42}$$

In the formula, G_f is the fiber mass of unidirectional or fabric prepreg per unit area, i.e., the areal density, g/cm^2; ρ_f is fiber density, g/cm^3; n is number of layers; t_c is thickness of composite material panel, cm; G_f/ρ_f is fiber's thickness of single-layer unidirectional prepreg or reinforced fabric, cm.

Formula (8.42) can also be used to estimate the number of stacking-ply of composite materials, that is to say that if we know G_f, V_f and expected thickness t_c, we can get n.

6) Density of composite material ρ_c and porosity V_V

(1) ρ_c.

Density of composite material can be estimated by density of component material, volume fraction of component material, using the rule of mixture.

$$\rho_c = \sum_{i=1}^{n} \rho_i V_i$$

$$\rho_c = \rho_f V_f + \rho_m V_m + \rho_V V_V$$

In the formula, ρ_c, ρ_f, ρ_m, ρ_V stands separately for the density of composite material, fiber, matrix and the void.

As ρ_V is approximate to 0, so we get:

$$\rho_c = \rho_f V_f + \rho_m V_m \tag{8.43}$$

If we estimate the density of composite material according to resin mass fraction w_m, we have:

$$\frac{1}{\rho_c} = \sum_{i}^{n} (w_i/\rho_i)$$

That is,

$$\frac{1}{\rho_c} = \frac{w_m}{\rho_m} + \frac{1 - w_m}{\rho_f} + V_V$$

If $V_V = 0$, we call the density of composite material the theoretical density, recorded as ρ_c.

$$\rho_c = \frac{\rho_f \rho_m}{\rho_f w_m + \rho_m (1 - w_m)} \tag{8.44}$$

If $V_V \neq 0$, we estimate the density of composite material according to the formula (8.45).

$$\rho = \frac{\rho_f \rho_m (1 - V_V)}{\rho_f w_m + \rho_m (1 - w_m)} \tag{8.45}$$

(2) Porosity ratio V_V.

The porosity of composite material can be determined by microscope, the method is the same as determining V_f using microscope. We can calculate V_V after determining the pore area per unit area of cross section.

We also use the density method to calculate the porosity of composite material.

$$V_V = \frac{\rho_c - \rho}{\rho_c} \tag{8.46}$$

In the formula, ρ_c is the theoretical density of composite material, calculated from formula (8.44); ρ is the measured density of composite material by Archimedes' principle of buoyancy.

8.2.2 Transverse tensile property

The longitudinal tensile property of unidirectional fiber composite material which is discussed before are mainly related to the fiber and its content. The transverse tensile property of unidirectional fiber composite material, however, is related to the performance of the matrix or the interface. It's the weakest section of unidirectional laminate. Transverse tensile property is low, but it is a basic state of stress of composite material, it is also the basic data for designing the composite material laminates. There are a lot of mechanical models which were used to predict the transverse tensile property, now we discuss it using Jones model and Zhu Yiling model.

1) Transverse tensile stress σ_T, modulus E_T

(1) Jones model.

Jones model is a series model, which is a simple model, constituted by sheets of even thickness of fiber and matrix (Fig. 8.15). When composite material is stressed in the transverse, its elongation in the load direction δ_T is the sum of the matrix's elongation and the fiber's elongation.

$$\delta_T = \delta_{fT} + \delta_{mT}$$

That is

$$\varepsilon_T t_c = \varepsilon_{fT} t_f + \varepsilon_{mT} t_m$$

$$\varepsilon_T = \varepsilon_{fT} \frac{t_f}{t_c} + \varepsilon_{mT} \frac{t_m}{t_c} = \varepsilon_{fT} V_f + \varepsilon_{mT} V_m \tag{8.47}$$

In elastic deformation scope, we use the Hooke's law, the formula above can be rewritten into:

$$\frac{\sigma_T}{E_T} = \frac{\sigma_{fT}}{E_{fT}} V_f + \frac{\sigma_{mT}}{E_{mT}} V_f \tag{8.48}$$

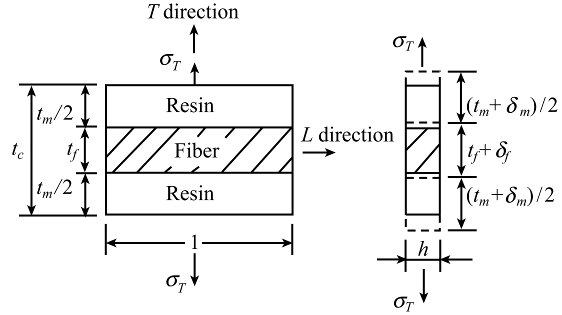


Fig. 8.15 Jones model.

Because the fiber and matrix is forced in series, the stress of the composite material, matrix and fiber is equal.

$$\sigma_T = \sigma_{fT} = \sigma_{mT}$$

The former formula can be simplified into:

$$\frac{1}{E_T} = \frac{V_f}{E_{fT}} + \frac{V_m}{E_m} \quad \text{or} \quad E_T = \frac{E_{fT}E_m}{E_{fT}V_m + E_mV_f} \tag{8.49}$$

Formula (8.49) can be promoted into transverse modulus of composite material with n components.

$$E_T = \frac{1}{\sum\limits_i^n (V_i/E_i)} \tag{8.50}$$

Formula (8.49) is the rule of mixtures in series relations of unidirectional fiber composite material's transverse tensile modulus. Likewise, longitudinal tensile modulus' formula (8.9) is thus called the rule of mixtures in parallel relations. The relationship of the two and V_f is shown by Fig. 8.16. From Fig. 8.16 we can see clearly that modulus of composite materials both E_L and E_T increase with the increase of the fiber volume fraction V_f and the modulus E_f.E_L increases linearly with the increase of V_f, but only in the scope of high V_f, E_f and V_f of fiber can give E_T a significant impact. For example, In order to improve the composite material's transverse modulus twice as the matrix's, the volume fraction of fiber needs to be more than 55%, but for the same goal of longitudinal modulus, we only need 11%. In theory, as long as there is 90% of the fiber, transverse modulus can be increased to 5 times of the matrix's modulus, but such fiber volume content cannot be realized. Rewrite formula (8.49):

$$\frac{E_T}{E_m} = \frac{1}{1 - \left(1 - \dfrac{E_m}{E_{Tf}}\right) V_f} \tag{8.51}$$

In the formula, E_T/E_m is called "coefficient of enhancing stiffness", or "coefficient of increasing modulus". It shows the increase in multiples of composite material's transverse tensile modulus E_T than that of matrix's. Fig. 8.17 and Table 8.3 clearly show the contribution to E_T for increasing E_{fT}/E_m and V_f.

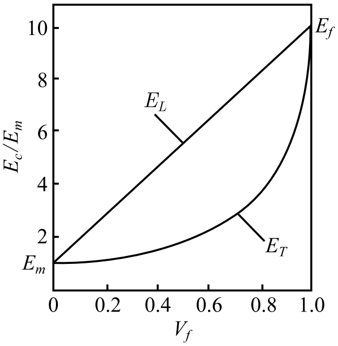


Fig. 8.16 Relationship of tensile modulus of composite materials and V_f.

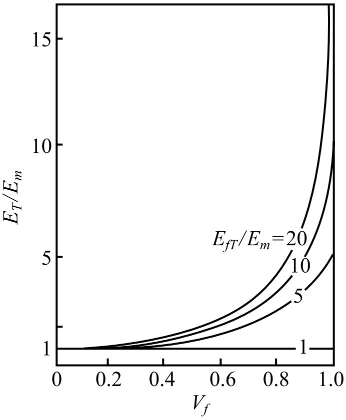


Fig. 8.17 Curve of E_T/E_m with V_f and E_{fT}/E_m.

Table 8.3 The relationship of E_T/E_m with V_f and E_{fT}/E_m

E_{fT}/E_m \ V_f	0	0.2	0.4	0.6	0.8	1.0
1	1	1	1	1	1	1
5	1	1.19	1.47	1.92	2.78	5
10	1	1.22	1.56	2.17	3.57	10
20	1	1.23	1.61	2.33	4.17	20
50	1	1.24	1.64	2.43	4.63	50
100	1	1.25	1.66	2.46	4.81	100

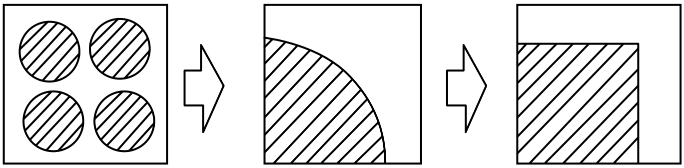
Jones model is elegant, but its result has large difference with the actual situation. Its estimates deviate much from the measured values.

(2) Zhu Yiling model.

Assume that fiber is arranged in square, and simplify the cylindrical fiber into the square fiber, we are eligible to use symmetry to choose the 1/4 to calculate, shown by Fig. 8.18. Without considering the Poisson's effect, the mechanical model is shown in Fig. 8.19. When we analyze it, we use (a) equal stress assumption and (b) equal strain assumption to derivate respectively.

① The equal stress assumption.

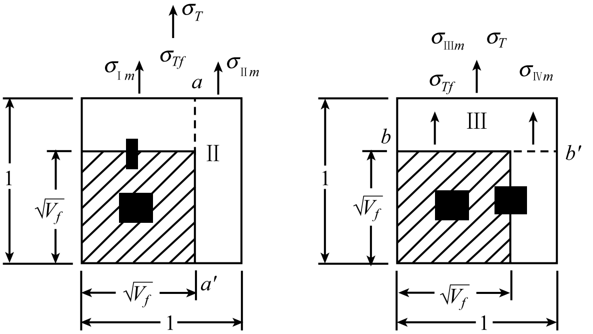
Divide the model into two areas by *aa*' plane, the left area I and the right area II. Area I consists of fiber and matrix of area, which are in series, then parallel with matrix of area II to constitute the overall model.



(a) (b) (c)

Fig. 8.18 Analytical unit and its simplification of Zhu Yiling model:

(a) square array; (b).analysis unit; (c) simplified analysis unit.



(a) (b)

Fig. 8.19 Zhu Yiling transverse tensile model:

(a) equal stress assumption; (b) equal strain assumption.

The content of the equal stress assumption is that the stress of the fiber and matrix in area I is equal, that is $\sigma_{\mathrm{I}m} = \sigma_{Tf}$. Note that the assumption keeps the strains of left and right side of *aa*’ plane unequal.

From the static equilibrium condition, we can get:

$$\sigma_T = \sigma_{Tf}\sqrt{V_f} + \sigma_{\mathrm{II}m}(1-\sqrt{V_f}) \tag{8.52}$$

Using the conditions of same deformation, areas I and II should have the same elongation as the composite material in the T direction.

$$\varepsilon_T = \varepsilon_{\mathrm{II}m} = \varepsilon_{\mathrm{I}m}(1-\sqrt{V_f}) + \varepsilon_{Tf}\sqrt{V_f}$$

Using Hooke’s law, and at the same time use $\sigma_{\mathrm{I}m}$ to substitute σ_{Tf}, we can get the relation formula of $\sigma_{\mathrm{I}m}$ and $\sigma_{\mathrm{II}m}.$

$$\varepsilon_T = \frac{\sigma_{\mathrm{II}m}}{E_m} = \frac{\sigma_{\mathrm{I}m}}{E_m}(1-\sqrt{V_f}) + \frac{\sigma_{\mathrm{I}m}}{E_{Tf}}\sqrt{V_f} \tag{8.53}$$

Using the above two formulae (8.52)~(8.53), we can get the relation formula of σ_T and $\sigma_{\mathrm{I}m}$, and σ_T and $\sigma_{\mathrm{II}m}$.

$$\sigma_T = \frac{1-\sqrt{V_f}(1-\sqrt{V_f})(1-E_m/E_{Tf})}{1-\sqrt{V_f}(1-E_m/E_{Tf})}\sigma_{\mathrm{II}m} \tag{8.54}$$

$$\sigma_T = [1 - \sqrt{V_f}(1 - \sqrt{V_f})(1 - E_m/E_{Tf})]\sigma_{\mathrm{I}m} \tag{8.55}$$

As $\varepsilon_T = \varepsilon_{\mathrm{II}m}$, we can get estimation formula of the transverse tensile modulus of composite material using the equal stress assumption.

$$E_T^{(a)} = \frac{1 - \sqrt{V_f}(1 - \sqrt{V_f})(1 - E_m/E_{Tf})}{1 - \sqrt{V_f}(1 - E_m/E_{Tf})} E_m \tag{8.56}$$

② The equal strain assumption.

Divide the model into two areas by *bb*' plane, the top area III and the bottom area IV. Area IV is composed by fiber and matrix in parallel, and then combines with matrix of area III in series. The content of the equal strain assumption is that in area IV fiber has the same strain with the matrix in the T direction, that is $\varepsilon_{Tf} = \varepsilon_{\mathrm{IV}m}$. Note that the assumption keeps stress of up and down sides of *bb*' plane unequal. By Hooke's law, we change $\varepsilon_{Tf} = \varepsilon_{\mathrm{IV}m}$ into the follow equation:

$$\frac{\sigma_{Tf}}{E_{Tf}} = \frac{\sigma_{\mathrm{IV}m}}{E_m} \tag{8.57}$$

From the static equilibrium conditions, σ_T is given by:

$$\sigma_T = \sigma_{\mathrm{III}m} = \sigma_{Tf}\sqrt{V_f} + \sigma_{\mathrm{IV}m}(1 - \sqrt{V_f}) \tag{8.58}$$

Combine formula (8.57) and formula (8.58), then we get:

$$\sigma_T = \left[1 - \sqrt{V_f}\left(1 - \frac{E_{Tf}}{E_m}\right)\right]\sigma_{\mathrm{IV}m} \tag{8.59}$$

From the deformation relations and the Hooke's law, we have:

$$\varepsilon_T = \frac{\sigma_T}{E_m}(1 - \sqrt{V_f}) + \frac{\sigma_{\mathrm{IV}m}}{E_m}\sqrt{V_f} \tag{8.60}$$

Using formula (8.59) to change the $\sigma_{\mathrm{IV}m}$ of formula (8.60) into σ_T, and $E_T = \sigma_T/\varepsilon_T$, so the formula of estimating transverse tensile modulus of composite material through the equal strain assumption is:

$$E_T^{(b)} = \frac{1 - \sqrt{V_f}(1 - E_{Tf}/E_m)}{1 - \sqrt{V_f}(1 - \sqrt{V_f})(1 - E_{Tf}/E_m)} E_m \tag{8.61}$$

Experiments have showed that it is more realistic to estimate the transverse tensile modulus of composite material through formula (8.62), after we have synthesized the equal stress assumption and the equal strain assumption.

$$E_T = (E_T^{(a)} + E_T^{(b)})/2 \tag{8.62}$$

The estimating formula above shows that E_T is related to V_f, E_m and E_f/E_m. If V_f increases, E_m increases and E_f/E_m increases, E_T of the composite will increase.

2) Transverse tensile strength σ_{Tu}

It is more difficult to analyze the transverse tensile strength than to analyze the transverse tensile modulus. The transverse tensile failure mode of unidirectional fiber composite materials might be: matrix's tensile failure, interface debonding and fiber tearing. Generally speaking, these failure modes worked together. That is to say, some components of the destruction surface were caused by the tensile failure of matrix, however, the others were caused by interface debonding or (and) fiber tearing. Because the strength of fiber is greater than that of matrix, the failure mechanism of transverse tensile strength σ_{Tu} depends mainly on the tensile strength of matrix or interface bond strength. The following analysis of σ_{Tu} is based on the "good interface" assumption or in other word, the strength of interface is always greater than matrix's strength such that the composite material's failure is based on the matrix's cohesive failure.

(1) Jones model.

Fiber's stress σ_{Tf}, matrix's stress σ_m, and composite material's stress σ_T are equal to each other.

$$\sigma_{Tf} = \sigma_m = \sigma_T$$

When $\sigma_m = \sigma_{mu}$, matrix is destroyed, and then the composite material is destroyed. So Jones model estimates that composite material's transverse tensile strength is equal to the matrix strength.

$$\sigma_{Tu} = \sigma_{mu} \tag{8.63}$$

(2) Zhu Yiling model.

In the equal strain assumption, we can know from formulas (8.58) and (8.59), $\sigma_T = \sigma_{\mathrm{III}m} > \sigma_{\mathrm{IV}m}$, i.e., the stress of matrix is less than that of composite material, there is no stress concentration phenomenon. The matrix's stress in area III $\sigma_{\mathrm{III}m}$ is greater than that of area IV $\sigma_{\mathrm{IV}m}$. Failure stress arises from the matrix of area III, $\sigma_{Tu} = \sigma_{mu}$.

In the equal stress assumption, we can know from formula (8.55), the matrix's stress in area I $\sigma_{\mathrm{I}m} > \sigma_T$, knowing from formula (8.54), the matrix's stress in area II $\sigma_{\mathrm{II}m} < \sigma_T$. Synthetically, it is $\sigma_{\mathrm{I}m} > \sigma_T > \sigma_{\mathrm{II}m}$. So there is a stress concentration in the matrix of area I, when $\sigma_{\mathrm{I}m} = \sigma_{mu}$, the composite material is destroyed.

$$\sigma_{Tu} = [1 - \sqrt{V_f}(1 - \sqrt{V_f})(1 - E_m/E_{Tf})]\sigma_{mu} \tag{8.64}$$

From analysis above, Zhu Yi-ling model's prediction of the transverse tensile strength should be based on the equal stress assumption. The estimate formula is (8.64), the strength of composite material σ_{Tu} is less than adhesive strength of matrix σ_{mu}.

As we can see, when composite material is under transverse tensile, there exists the phenomenon that the stress of matrix is greater than average stress, i.e., stress concentration. And we define the stress concentration factor S_{stress}.

$$S_{\text{stress}} = \frac{\sigma_{mmax}}{\sigma_T} \tag{8.65}$$

By formula (8.55), the stress concentration factor (*SCF*) of Zhu Yi-ling Model is:

$$S_{\text{stress}} = \frac{\sigma_{\text{I}m}}{\sigma_T} = \frac{1}{1-\sqrt{V_f}(1-\sqrt{V_f})(1-E_m/E_{Tf})} \tag{8.66}$$

The same as above, there is strain magnification factor (SMF), which show that strain of matrix is greater than average strain. If we use formula (8.55) to be divided by formula (8.56), we can get:

$$\frac{\varepsilon_{\text{I}m}}{\varepsilon_T} = \frac{\varepsilon_{mmax}}{\varepsilon_T} = S_{\text{strain}} = \frac{1}{1-(1-E_m/E_{Tf})\sqrt{V_f}} \tag{8.67}$$

Due to the existence of SCF and SMF, lots of composite materials have $\sigma_{Tu} < \sigma_{mu}$, $\varepsilon_{Tu} < \varepsilon_{mu}$.

For Zhu Yiling model, if we don't make the square column simplification and use the integral method to deduce, we also will get SCF and SMF of the following types.

$$S_{\text{stress}} = \frac{\sigma_{mmax}}{\sigma_T} = \frac{1-V_f(1-E_m/E_{Tf})}{1-\sqrt{\frac{4V_f}{\pi}}(1-E_m/E_{Tf})} \tag{8.68}$$

$$S_{\text{strain}} = \frac{\varepsilon_{mmax}}{\varepsilon_T} = \frac{1}{1-(1-E_m/E_{Tf})\sqrt{\frac{4V_f}{\pi}}} \tag{8.69}$$

Therefore, the transverse tensile strength and transverse tensile fracture strain should be decided by formula (8.70) and (8.71).

$$\sigma_{Tu} = \frac{\sigma_{mu}}{S_{\text{stress}}} \tag{8.70}$$

$$\varepsilon_{Tu} = \frac{\varepsilon_{mu}}{S_{\text{strain}}} \tag{8.71}$$

To improve the transverse tensile strength of the composite material, we can use the way of improving the matrix's strength or reducing the stress concentration factor S_{stress}. The increase of matrix's modulus not only is conductive to the improvement of composite material's transverse tensile modulus, but also can reduce S_{stress} (Fig. 8.20), leading to the improvement of transverse tensile strength. We can know from the Fig. 8.21, when V_f is higher than 0.60, the increase of

S_{stress} speeds up with the change of V_f. So, considering the longitudinal tensile properties and transverse tensile properties of composites, we should control fiber volume fraction V_f to between 0.60 and 0.65. In addition, there are other ways to the increase of the transverse tensile strength, such as reducing porosity and increasing interface strength between fiber and matrix. Experiment has revealed that for the same matrix, transverse tensile strength of carbon fiber composites is often superior to glass fiber composites. The reason may be related not only with the interface strength, but with the difference of transverse modulus of two kinds of fibers as well.

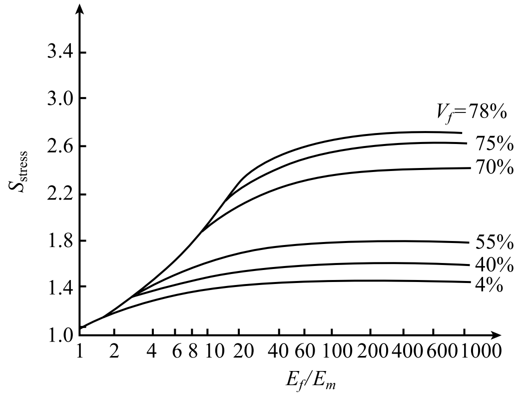


Fig. 8.20 Stress concentration factor of matrix under transverse tension.

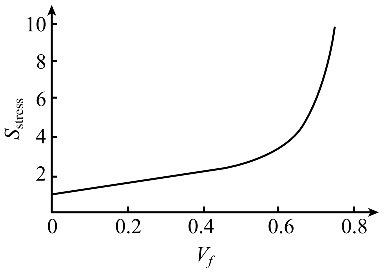


Fig. 8.21 Relation curve of stress concentration factor with V_f under transverse tension.

3) Transverse Poisson's ratio μ_{TL}

When unidirectional fiber composite material is tensile transversely, for the Poisson's effect, in the direction vertical to load, i.e., the fiber axial direction, there exists contraction too. The elastic coefficient that reflects the contraction is Poisson's ratio μ_{TL}, is defined as:

$$\mu_{TL} = -\frac{\varepsilon_L}{\varepsilon_T} \tag{8.72}$$

According to the Maxwell reciprocity law $\Bigg($transverse strain caused by unit longitudinal stress is equal to the longitudinal strain caused by unit transverse stress, i.e.,$\frac{\varepsilon_T}{\sigma_L} = \frac{\varepsilon_L}{\sigma_T}\Big)$, we neglect the effect of deformation caused by the difference of fiber and matrix's Poisson's ratio, and then we can get the formula of transverse tensile Poisson's ratio.

$$\mu_{TL} = \frac{E_T}{E_L}\mu_{LT} \tag{8.73}$$

In the formula, E_L, E_T and μ_{LT} are unidirectional fiber composite material's longitudinal tensile modulus, transverse tensile modulus and longitudinal tensile Poisson's ratio. Because $E_L > E_T$, μ_{TL} is far less than μ_{LT}, just as E_L is much greater than E_T.

8.3 Tensile properties of orthogonal fiber composite materials

In the last section, we discuss the tensile properties of unidirectional fiber composite material, and they are high in the fiber's direction, but low in the transverse direction. In practice applications, very few composite material structures are intended to be stressed only in single direction. In order to take full advantage of fiber and the features of composite material's design, we usually decide the fiber's direction, the number of layer and the sequence of layer (ply-stacking design) by actual load situation of the components, and then we get the multi-directional fiber composite materials. Two directional (orthogonal) composite materials are made of orthogonal fabrics (cloth) or 90° alternating unidirectional fiber prepregs. It is the simplest, but also the most basic multi-directional fiber composite materials. It can be expected that this kind of composite material has high tensile strength and stiffness in the two directions of orthogonal fibers, and therefore it can be used to undertake orthogonal stress in two directions.

8.3.1 Axial tensile properties of orthogonal composite materials

In the analysis of tensile orthogonal composite material in one fiber's direction (such as longitudinal direction), the orthogonal composite material can be seen as composed by two vertical layer of unidirectional composite material which have the same resin content. Its mechanical model is Fig. 8.22. Each unidirectional composite material's thickness is distributed by orthogonal composite's fiber volume in the latitude and longitude. Usually, the longitudinal direction is noted as L, the transverse is noted as T. Unidirectional composite material's transverse tensile strength mainly depends on the interface bonding strength and matrix cohesive strength, therefore, so when orthogonal composite material is tensile in one direction, we can ignore the role of transverse fiber, and treat the transverse fiber as a matrix. That is to say, when the fiber in $L(T)$ direction is stressed, the fiber content in T (L) direction is as if it is not there.

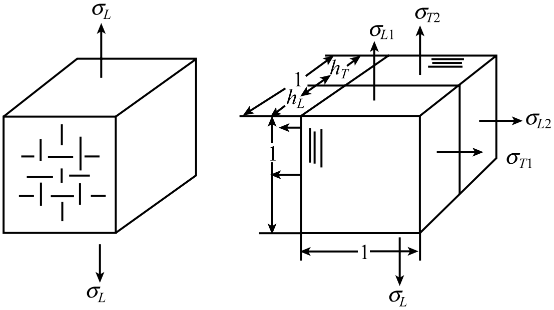


Fig. 8.22 Mechanical model of orthogonal composite material under uniaxial tension.

Suppose n_L and n_T are on behalf of the fiber's volume of L direction and T direction in the orthogonal composite material unit, the relative proportion of fiber in L direction and T direction are $\dfrac{n_L}{n_L+n_T}$ and $\dfrac{n_T}{n_L+n_T}$, that is also:

$$h_L = \frac{n_L}{n_L+n_T} \qquad h_T = \frac{n_T}{n_L+n_T}$$

So, the volume fraction of L direction fiber and T direction fiber is respectively:

$$V_{fL} = \frac{n_L}{n_L+n_T}V_f \qquad V_{fT} = \frac{n_T}{n_L+n_T}V_f$$

And

$$V_{fL} + V_{fT} = V_f \qquad V_f + V_m = 1$$

The ratio of n_L and n_T can be calculated by the fabric specifications, that is because:

$$n \propto \frac{N \times b}{\beta_0}$$

For example, specification of a plain weave cloth is shown:

	The count of strand β_0/plied number N	Weave density *b*/(end/cm)
Longitude	80/9	16
Latitude	80/8	10

So

$$n_L{:}n_T = \frac{9\times 16}{80}{:}\frac{8\times 10}{80} = 9:5$$

According to the rule of mixture, we estimate the tensile stress, modulus and strength in the L direction and T direction.

$$\sigma_L = \sigma_f V_{fL} + \sigma_m(1 - V_{fL}) = \sigma_m + (\sigma_f - \sigma_m)V_f \cdot \frac{n_L}{n_L+n_T} \tag{8.74}$$

$$\sigma_T = \sigma_f V_{fT} + \sigma_m(1 - V_{fT}) = \sigma_m + (\sigma_f - \sigma_m)V_f \cdot \frac{n_T}{n_L + n_T} \tag{8.75}$$

$$E_L = E_f V_{fL} + E_m(1 - V_{fL}) = E_m + (E_f - E_m)V_f \cdot \frac{n_L}{n_L + n_T} \tag{8.76}$$

$$E_T = E_f V_{fT} + E_m(1 - V_{fT}) = E_m + (E_f - E_m)V_f \cdot \frac{n_T}{n_L + n_T} \tag{8.77}$$

If we don't consider the question that which one of fiber and matrix is damaged first, and directly enter the strength of fiber and matrix (σ_{fu} and σ_{mu}) into stress formula, we will find the approximate longitudinal tensile strength and transverse tensile strength of orthogonal composite material (σ_{Lu} and σ_{Tu}).

$$\sigma_{Lu} = \sigma_{mu} + (\sigma_{fu} - \sigma_{mu})V_f \frac{n_L}{n_L + n_T} \tag{8.78}$$

$$\sigma_{Tu} = \sigma_{mu} + (\sigma_{fu} - \sigma_{mu})V_f \frac{n_T}{n_L + n_T} \tag{8.79}$$

The tensile Poison's ratio in L direction μ^*_{LT} of orthogonal composite material can be calculated by the coefficient of elasticity ($E_{L,}$, E_T, μ_{LT}) of unidirectional fiber composite material with the same resin content and n_L, n_T.

$$\mu^*_{LT} = \mu_{LT} \frac{E_T}{E_L \frac{n_T}{n_L + n_T} + E_T \frac{n_L}{n_L + n_T}} \tag{8.80}$$

For orthogonal composite material which is prepared by the $1{:}1$ cloth that has the same fiber volume in L and T direction, the μ^*_{LT} can be simplified as follows.

$$\mu^*_{LT} = \mu_{LT} \frac{2E_T}{E_L + E_T} \tag{8.81}$$

8.3.2 Tensile stress-strain curve of orthogonal composite materials

The longitudinal tensile stress - strain curve of unidirectional composite material is a straight line. However, the uniaxial tensile stress-strain curve of two-directional orthogonal composite material which uses unidirectional glass fiber prepreg layer is a broken line. The modulus are high before the inflexion point, we call it the first or initial modulus. After the inflexion point, the modulus start to decline, but the decline in volume is not large, and we call it the second modulus, as in the Fig. 8.23. In the experiment, we can hear cracking sound when it reaches the inflexion point, while some whitening appears on the sample.

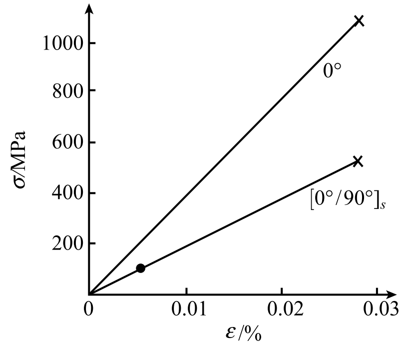


Fig. 8.23 Uniaxial tensile σ-ε curve of glass fiber / epoxy composite materials.

The reason to cause the above difference is that unidirectional longitudinal tensile strength and modulus depend on the fiber, but the impact of matrix is small. Therefore, for unidirectional fiber composite material, stress-strain curve reflects the mechanical characteristics of glass fiber, with a linear stress-strain relationship. When two-directional orthogonal composite material is tensile in the L direction, the initial modulus is the total sum of all layers. As a result of the low strength of 90° layer, when the 90° layer reaches the failure stress, matrix cracks come forth, and splitting sound can be heard at the same time, seeing the whitening of material. The failure of 90° layer makes the modulus of composite materials decrease showing the inflexion point in the stress - strain curves. The composite material will be suddenly destroyed if we continue loading up until the 0° layer reaches its failure stress.

The appearing time of stress-strain curves' inflection point is related to the matrix properties, fiber properties and stacking-ply, and so on. The greater the matrix toughness is, the larger threshold strain that produce cracks is and also the greater the inflexion point of the strain is. For carbon fiber composite material, σ-ε curve is generally linear, and there is no inflexion point, but a higher modulus. This is because the carbon fiber modulus is large and elongation at break is small, only about 1%, lower than the break strain of usual resin. This will ensure that before the broken of fiber, the matrix won't break, and play full role of the fiber strength, avoiding inflexion point.

For the glass cloth, the fibers are woven together vertically. Fiber is in bending and rotational state. Therefore when glass cloth composite material is under uniaxial tension, the strain of glass fiber and matrix is complex. From the tensile stress-strain curves (Fig. 8.24) of balance (1:1) and unidirectional fabric (4:1) epoxy GFRP, we can see that it is the same with above orthogonal glass fiber composite material; there is also an inflexion point in its stress-strain curves. This is due to the glass cloth in longitudinal stretching, the warp was gradually straightened. At this point, the weft become more curved (the deformation of weft is much larger than that of warp), simultaneously the thickness of cloth increased, resulting parallel matrix cracks in the surrounding of weft and inflexion point in the stress-strain curve. Due to the fact that bending degree of fiber in glass cloth is much bigger than that of unidirectional glass fiber laminate, and weaving process will greatly reduce the fiber strength, the strength of composite material made by glass cloth is lower than that of made by unidirectional glass fiber laminate.

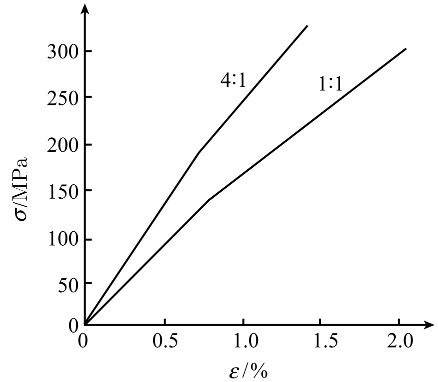


Fig. 8.24 Uniaxial tensile σ-ε curve of glass cloth/epoxy composite materials.

8.4 Compression performance of unidirectional fiber composite materials

Compared with the tensile properties, it seems to opposite stress direction of the analysis of tensile properties, will become compression performance. The actual problem is not that simple, such as a long rope can withstand a greater pulling force, but cannot afford to sustain a very small pressure, only when the rope is relatively short, there is sufficient stability in order to bear a certain degree of pressure. Therefore, here involves the problem of stability. Composite materials have a similar situation, only when the reinforcing fibers in composite material are supported by matrix, can they bear a certain degree of pressure action.

8.4.1 The estimation of compression elasticity coefficient

When we determine the compression modulus and Poisson's ratio, it is all under small load, thus not related to the stability of fiber. That is why we can estimate the compression elasticity coefficient using the mechanical model of analyzing tensile properties. The only thing we need to do is to exchange the tensile properties data such as fiber, the matrix into the corresponding performance data of compression properties. In structural design, we can think that the tensile and compression elastic constants are consistent, such as $E_{-L} = E_L, E_{-T} = E_T$, $\mu_{-LT} = \mu_{LT}$, $\mu_{-TL} = \mu_{TL}$.

8.4.2 Longitudinal compressive strength

There is not an easy way for estimating compressive strength, this is because the failure mechanism of compression is not clear and also we are lack of fiber compression strength data. Experiments show that for the glass fiber composite materials, compression strength of two-directional balanced 1:1 is close to the tensile strength, and compressive strength of unidirectional enhanced is about two-thirds of its tensile strength. The experimental results show that in the compression process, when the matrix cannot support the fiber, the fiber will buckle and composite materials will have unstable damage.

1) Longitudinal compression failure mode

Single fiber can withstand a lot of tension, but not under pressure. After the fiber and matrix are bonded into a whole composite material, it can bear the compressive force. That is to say, fiber can withstand the pressure under the support of matrix. Therefore, the compression strength of composite materials is related to the nature of matrix and interface.

When the composite material is under compressive force, the role of continuous fiber is like a thin cylinder, micro-buckling occurs. If the fiber content of composite materials V_f is very low ($< 40\%$), even if the matrix is still in the scope of the elastic strain, fiber will suffer micro-buckling. However, for common composite materials whose fiber content is greater than 40%, the micro-buckling of fibers only occur after the yield of matrix, interface degumming and matrix cracking. When the load length l is short, the axial compression damage of unidirectional composite materials may also began in transverse cracks, as the transverse tensile strain caused by Poisson's effect is likely to exceed the limits of composite lateral deformation capacity. Shear failure is another mode of axial compression damage. In that case, fiber remains stable until it is cut, and that is when the longitudinal compression strength is high.

From above it can be seen that the longitudinal compression damage of unidirectional composite material has at least three macro-failure modes, which are: buckling failure from fiber bending, the destruction of the longitudinal split, and the shear failure along the direction about 45° with the load direction, as shown in Fig. 8.25.

2) The factors affecting longitudinal compressive strength

From the damage modes of longitudinal compression, we know that the factors that affect longitudinal compressive strength of composite material are as follows: ① compression proportion limit of matrix σ_{-mp}, when the compression stress of matrix is higher than compression proportion limit of matrix, the matrix will yield, leading to fiber buckling; ② fiber compressive strength σ_{-fu}; ③ interface strength or interlaminar shear strength of composites τ_u; ④ transverse tensile strength of unidirectional composite materials σ_{Tu}; ⑤ the elastic modulus of matrix E_m, G_m; ⑥ fiber volume fraction V_f; ⑦ manufacturing process of composite material, since manufacturing process will affect the porosity and the interface strength; ⑧ factors to cause fiber instability, such as fiber diameter d_f, modulus E_f, test length l; ⑨ sample size, form of clamp at both ends and test conditions.

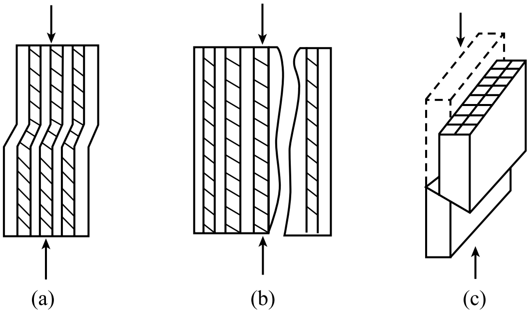


Fig. 8.25 Unidirectional fiber composite failure mode under longitudinal compression: (a) fiber buckling; (b) longitudinal split; (c) shear failure.

In fact, there are a lot of factors that affect the longitudinal compressive properties of composite materials, and longitudinal compression is also a wide range of failure modes, so it is difficult to propose a mechanical model of longitudinal compression failure. There have been many researches on longitudinal compression. According to the different failure modes, many scholars put forward their own estimation formula, but they all incur large difference from the measurement and most of them introduce empirical correction coefficient. When longitudinal compression failure happens, the compression stress of fiber is usually much lower than its compression strength.

3) Estimation of longitudinal compressive strength

(1) Calculate by the rule of mixture according to the strength of component materials.

Fiber is linear elastic material; matrix is elastic-plastic material, in accordance with the relative size of the fiber's ultimate compression strain ε_{-fu} and the matrix's ultimate proportion strain ε_{-mp}, we discuss in two cases.

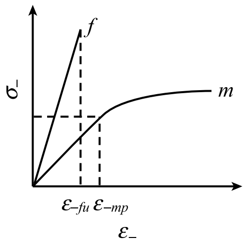


Fig. 8.26 Compression σ_--ε_- curve: $\varepsilon_{-fu} < \varepsilon_{-mp}$.

① $\varepsilon_{-fu} < \varepsilon_{-mp}$.

As the Fig. 8.26 for CFCM, when $\varepsilon = \varepsilon_{-fu}$, the matrix is still in the linear elastic range, strain has not reached ε_{-mp}. Therefore, fiber breakage is used as the reference (fiber compression failure mode). Now we apply the rule of mixture:

$$\sigma_{-Lu} = \sigma_{-fu} V_f + (\sigma_{-m})_{\varepsilon=\varepsilon_{-f\mu}} V_m$$

$$\frac{(\sigma_{-m})_{\varepsilon=\varepsilon_{-fu}}}{E_m} = \frac{\sigma_{-fu}}{E_f}$$

$$\sigma_{-Lu} = \sigma_{-fu}\left[V_f + V_m\left(\frac{E_m}{E_f}\right)\right]$$

$$\sigma_{-Lu} = \varepsilon_{-fu}[E_f V_f + E_m(1 - V_f)] \tag{8.82}$$

② $\varepsilon_{-fu} > \varepsilon_{-mp}$.

As the Fig. 8.27, matrix yields before the fiber breakage, and matrix's yielding will lead to fiber instability and compression destruction of composite material. Therefore, at this time we should base on $\varepsilon = \varepsilon_{-mp}$ as the reference (matrix compression yielding mode). We know the following using the rule of mixture:

$$\sigma_{-Lu} = (\sigma_{-f})_{\varepsilon=\varepsilon_{-mp}} V_f + \sigma_{-mp} V_m$$

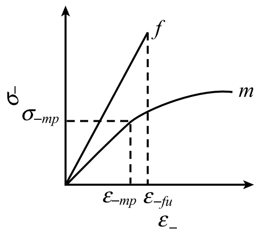


Fig. 8.27 Compression σ_{-}-ε_{-} curve: $\varepsilon_{-fu} > \varepsilon_{-mp}$.

$$\frac{(\sigma_{-f})_{\varepsilon=\varepsilon_{-mp}}}{E_f} = \frac{\sigma_{-mp}}{E_m}$$

$$\sigma_{-Lu} = \sigma_{-mp}\left[V_m + V_f\left(\frac{E_f}{E_m}\right)\right]$$

$$\sigma_{-Lu} = \varepsilon_{-mp}[E_f V_f + E_m(1 - V_f)] \tag{8.83}$$

Taking into account the effect of production processes, we introduce the correction factor, transforming the above (8.78), (8.79) into a semi-empirical formula.

When $\varepsilon_{-mp} < \varepsilon_{-fu}$,

$$\sigma_{-Lu} = \sigma_{-mp}\left[\beta_{-mp}\overline{V_m} + \beta_{-fu}\overline{V_f}\left(\frac{E_f}{E_m}\right)\right] \tag{8.84}$$

When $\varepsilon_{-mp} > \varepsilon_{-fu}$,

$$\sigma_{-Lu} = \sigma_{-fu}\left[\beta_{-fu}\overline{V_f} + \beta_{-mp}\overline{V_m}\left(\frac{E_f}{E_m}\right)\right] \tag{8.85}$$

In the formula, $\overline{V_f} = (1 - V_V)V_f$, $\overline{V_m} = (1 - V_V)(1 - V_f)$, β_{-mp} and β_{-fu} are the correction factors that are related to a specific manufacturing process.

(2) The method of fiber micro-buckling (fiber compression instability mode).

Rosen and others think that longitudinal compression failure is caused by the buckling instability of fiber which is supported by resin. In the compression tests, acoustic emission is almost concentrated near damage value, and its destruction is with some abruptness, and is close to the instability situation. Therefore, the longitudinal compressive strength is controlled by buckling critical load of fiber which is supported by resin. In order to facilitate the analysis, unidirectional fiber composite materials will be simplified into two parts of fiber sheet and resin sheet [Fig. 8.28(a)]. When compressed, the fiber and resin sheet will be under pressure, and fiber sheet instability phenomena may occur, being supported by transverse resin, which is equivalent to the instability problem of the bar in the elastic basis. There are two basic forms of instability, as shown in Fig. 8.28. One is the opposite directional buckling of two adjacent fiber sheets, at this time the resin is under transverse tension-compression stress, so called as tension-compression instability [Fig. 8.28(b)]; the other is the same directional buckling of two adjacent fiber sheets, with the resin under shear stress at that time, so called as shear-type instability [Fig. 8.28(c)].

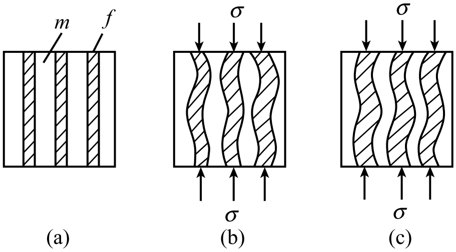


Fig. 8.28 Schematic of fiber's compression instabilty mode:
(a) simplified model; (b) tension-compression instability; (c) shear-type instability.

We use the energy method to calculate the extremum of critical stress of fiber sheet. When not considering load of resin bearing, the composite longitudinal compressive strength is:

① Tension-compression type.

$$\sigma_{-Lu} = 2V_f \left[\frac{E_f E_m V_f}{3(1-V_f)}\right]^{\frac{1}{2}} \tag{8.86}$$

② Shear-type.

$$\sigma_{-Lu} = \frac{G_f G_m}{(1-V_f)G_f + V_f G_m} \approx \frac{G_m}{1-V_f} \tag{8.87}$$

Illustrate the longitudinal compressive strength with fiber volume content, curves of the above two formulae are shown in Fig. 8.29. In the figure, the fiber volume content corresponding to the intersection of above two curves is called the critical fiber volume content V_{fcr}. When $V_f < V_{fcr}$, tension-compression type instability damage occurs. When $V_f > V_{fcr}$, shear-type instability damage occurs; When the distance between fibers is considerable large (V_f is small), tension-compression type instability occurs; when the distance between fibers is small (V_f is large), shear-type instability occurs.

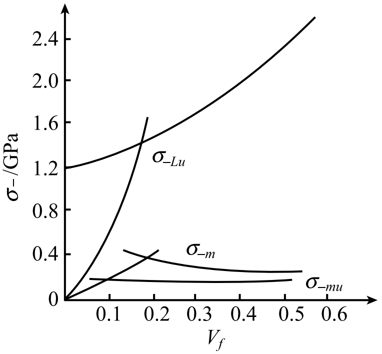


Fig. 8.29 Relationship between longitudinal compressive strength of unidirectional composite materials and V_f and the corresponding stress of resin.

Take E-GF/epoxy composite materials as an example. Assume E_f=70GPa, E_m=3.5 GPa, G_f=28 GPa, G_m=1.2 GPa, σ_{-mp}=100 MPa, σ_{-mu}=130 MPa, then we get V_{fcr} =17%. Therefore, in the usual composite materials (V_f is 60% or so) there is no tension-compression type of instability.

Calculated by the above two formulas, theoretical value of the compressive strength is larger than the measured values, and this is because some of these assumptions are not consistent with the actual situation. For example, the actual fiber composite materials are not sheet-shaped; fiber in the resin is not very straight; in resin matrix there exists internal stress, porosity, etc., all of above will cause the decline of strength. However, from the above two formulas and Fig. 8.29 we can get inspiration as follows: by increasing the fiber volume content (V_f), as well as fiber and resin matrix modulus [E_f ↑, E_m (G_m) ↑], we can improve the longitudinal compressive strength of unidirectional fiber composite materials.

As an amendment to the Rosen formula, we introduce the correction factor K. For different fiber composites, K value is different. For GFCM, K = 0.2; for CFCM, K = 0.5; for BFCM, K = 0.63.

① Tension-compression type.

$$\sigma_{-Lu} = 2V_f \left[\frac{KE_mE_fV_f}{3(1-V_f)}\right]^{\frac{1}{2}} \tag{8.88}$$

② Shear-type.

$$\sigma_{-Lu} = \frac{KG_m}{1-V_f} \tag{8.89}$$

In fact, according to Rosen's model, before compression instability of sample fiber remains a straight line state. At the instability moment, we can calculate the stress of resin matrix according to the equal strain assumption.

$$\sigma_{-m} = \sigma_{-Lu}\frac{E_m}{E_L} = \frac{\sigma_{-Lu}E_m}{E_f V_f + E_m(1-V_f)} = \frac{\sigma_{-Lu}}{1 - V_f\left(1 - \dfrac{E_f}{E_m}\right)}$$

Corresponding to the tension-compression type and shear-type instability, the resin matrix's stress is shown in follows respectively.

① Tension-compression type.

$$\sigma_{-m} = \frac{2V_f\left[\dfrac{E_f E_m V_f}{3(1-V_f)}\right]^{\frac{1}{2}}}{1 - V_f\left(1 - \dfrac{E_f}{E_m}\right)} \tag{8.90}$$

② Shear-type.

$$\sigma_{-m} = \frac{\dfrac{G_m}{1 - V_f\left(1 - \dfrac{G_m}{G_f}\right)}}{1 - V_f\left(1 - \dfrac{E_f}{E_m}\right)} \approx \frac{\dfrac{G_m}{1 - V_f}}{1 - V_f\left(1 - \dfrac{E_f}{E_m}\right)} \tag{8.91}$$

Fig. 8.29 also gives the curve of the corresponding resin matrix stress σ_{-m} with the fiber volume content V_f. It can be seen from it, only in the very low fiber volume content (V_f <0.075). The stress of resin matrix is lower than the compressive strength. Therefore, in the common fiber volume, the matrix resin always crushes first, and the two kinds of instability situations suggested by Rosen will not occur. So, the longitudinal compressive strength of the composite material should be controlled by the compression strength of the resin matrix (compression yielding stress σ_{-my}). That is to say, micro-fiber buckling is the result of the matrix's stress reaching the compression yielding stress. Therefore, the longitudinal compressive strength formula of composite material is:

$$\sigma_{-Lu} = \sigma_{-my}\left[1 + \left(\frac{E_f}{E_m} - 1\right)V_f\right] \tag{8.92}$$

(3) Delamination /in-plane shear failure mode.

In the longitudinal compression load, unidirectional composite materials may also be destroyed by the combined role of debonding and in-plane shear. It has been found that compressive strength depends on the in-plane shear strength. C. C. Chamis proposed the empirical formula of longitudinal compressive strength as follows:

$$\sigma_{-Lu} = 10\tau_{LTu} + 2.5\sigma_{mu} \tag{8.93}$$

In the formula, τ_{LTu} is in-plane shear strength of composite material; σ_{mu} is matrix's tensile strength.

N. Fried also proposed a similar empirical formula:

$$\sigma_{-Lu} = a + b\tau_{LTu} \tag{8.94}$$

In the formula, $a \approx \sigma_{-mu}$(compressive strength of the matrix), b=10~15.

From the above, we can see that the situation of a unidirectional fiber composite materials' longitudinal compression is very complicated. There are many influencing factors and many forms of damage. The current understanding on the failure mechanism is not enough, so there is not a mature theory which can accurately estimate their mechanical properties. Further study is demanded.

The major factors which impact the unidirectional fiber composite materials' longitudinal compressive strength is in the following ways.

① The effects of porosity V_V.

The existence of porosity reduces the strength of the matrix resin. C.C.Chamis proposed the relationship formula between the matrix's strength with porosity in and without porosity.

$$\sigma_{muv} = \left\{1 - \left[\frac{4}{T_V} \times \frac{V_V}{1 - V_V}\right]^{\frac{1}{2}}\right\} \sigma_{mu} \tag{8.95}$$

② The effect of matrix modulus.

L. B. Greszczuk studied the effect of matrix modulus on the longitudinal compressive strength through experiment. The results showed that micro-fiber buckling is likely to occur in the soft matrix ($G_m \leqslant$ 690MPa) composite materials, and the composite material which has a rigid matrix ($G_m \geqslant$ 690MPa) is damaged due to fiber breakage. Hahn's study also showed that the bulkling damage often appears in the form of composite materials that have large E_f/E_m.

③ The effect of fiber bending and angle deviation.

In the process of preparation of composite materials, it is very difficult to ensure absolute uniform direction of fibers. They all more or less suffer some bending. Under longitudinal compression, the initial bending of fibers will generate the transverse tension or compression in the matrix, so it is easy to cause matrix the longitudinal splitting or interface debonding, thus reducing the longitudinal compressive strength. The deviation angle (1° ~5°) of fiber arrangement will lead to the great decrease of longitudinal compression strength.

8.4.3 Transverse compressive strength

When the unidirectional composite material is under transverse compression, the shear failure like Fig. 8.30 often occurs, resulting in the matrix shear failure, and it may be accompanied by interfacial debonding and fiber damage. Therefore, the unidirectional composite material's transverse compression failure modes are as follows: ① matrix shear failure; ② the matrix shear failure with interfacial debonding and (or) broken fiber (pressure fold).

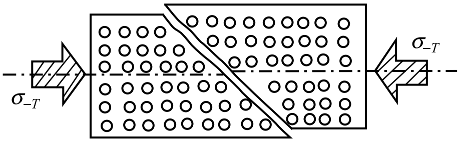


Fig. 8.30 Transverse compressive failure model of unidirectional fiber composite materials.

There are still no mature calculating formulae for transverse compressive strength, so many scholars give similar formula of the transverse compressive strength in accordance with the estimation method of the transverse tensile strength. However, transverse compression damage is mostly matrix shear failure and at the same time the stress concentration sensitivity on defects is much less than the tension, so the measured transverse compressive strength is usually 3~7 times of the measured transverse tensile strength. Clearly, the calculated value using the transverse compressive strength expression which is in accordance with the estimation method of the transverse tensile strength is significantly biased. According to the method of stress concentration factor, the transverse compressive strength should be lower than the compressive strength of the matrix, but in reality composite material's compressive strength is larger than the compression strength of matrix.

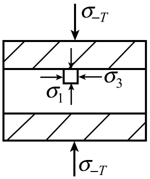


Fig. 8.31 Mechanical model of transverse compression.

When unidirectional composite material is compressed in transverse direction, due to the different Poisson's ratio of fiber and matrix, the unit of its internal matrix is compressive in the three directions (Fig. 8.31).

From the third strength theory (maximum shear stress theory), we can see that the destruction conditions of material are:

$$\sigma_1 - \sigma_3 \geqslant \sigma_{-mu}$$

In the formula, σ_1 is the maximum principal stress; σ_3 is the minimum principal stress.

As $\sigma_3 = \sigma_1 \dfrac{\varepsilon_3}{\varepsilon_1} = \mu_m \sigma_1$, so

$$\sigma_{-Tu} = \sigma_1 = \frac{1}{1-\mu_m}\sigma_{-mu} \tag{8.96}$$

By the style, we can see that the composite material's transverse compressive strength is greater than the compressive strength of the matrix, and it is more in line with the actual situation.

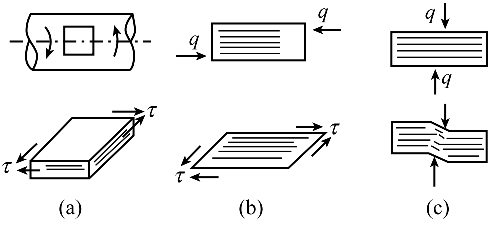
Collings' experimental studies of carbon fiber composite materials have shown that transverse compression damage is caused by the shear force vertical to the fiber in the plane parallel to the fiber and the destruction plane has a angle with the load's direction $\Phi(30^\circ \sim 45^\circ)$. Collings think that the fiber and resin's debonding leads to the material damage (cracks and defects in the matrix, interface and fiber take part in the failure process as weak points). Therefore, the transverse compressive strength must be less than the longitudinal compressive strength. However, if the constraint is imposed on the specimen, to prevent composites from deforming in the direction perpendicular to the load-fiber plane, we can get the transverse compressive strength which is comparable with the longitudinal compressive strength. This is because at this time fiber also suffers shear failure, and fiber's shear strength is higher than matrix's shear strength and interface's bond strength.

From above discussion, the impact factors of transverse compressive strength include the matrix compressive strength σ_{-mu}, the interface bond strength and porosity content. In addition, when the matrix toughness, deformation capacity and fiber volume fraction V_f increase, the transverse compressive strength will also increase.

8.5 The shear behaviors of unidirectional and orthogonal composites

8.5.1 Introduction

Composites belong to anisotropic materials, so shear properties of them are also anisotropic which are related to the direction of shear stress. According to the direction of shear stress, three conditions of shear behaviors are shown in Fig. 8.32.



(a) (b) (c)

Fig. 8.32 Shear types of composites:
(a) edge shear; (b) interlaminar shear; (c) vertical plate shear.

1) Edge shear

Shear stress acts along the edge of composites each layer, and the relevant shear deformations is in parallel layer plane (*LT* plane), no angle strain in *LN*, *TN* plane.

For torsion of thin-walled cylinder, the cylinder wall is such shear, so the edge shear is also called torsional shear, in-plane shear, or LT shear. When composites rotor blade is torted, such shear will occur.

2) Interlaminar shear

Shear stress vertically acts on the edge of composites each layer (action on the parallel layers section) and the shear deformations is in plane vertical to each layer (*LN* or *TN* plane). There is no angle strain in *LT* plane. Although the shear stress appears in pairs, the failure is always interlaminar shear damage and not cutting fiber like below 3). τ_{LN} is longitudinal interlaminar shear, τ_{TN} is transverse interlaminar shear. This shear occurs in conditions of such as composites plate or beam bearing flexure.

3) Vertical (plate) shear

When shear stress acts vertically to composites plate and shear deformation in plane of vertical each layers, that is vertical (plate) shear. Such shear generates in composite joint. Its damage is cutting fiber which has high properties.

The weakest location of composites are edge shear and interlaminar shear, we only discuss these two shears here.

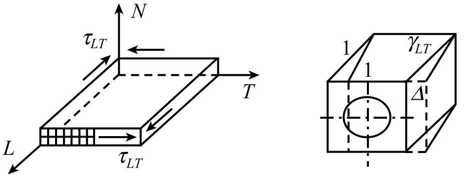
For unidirectional fiber composites, because of its transverse isotropy there is no difference between *LN* plane and *LT* plane, so $\tau_{LT} = \tau_{LN} \neq \tau_{TN}$, that is to say the longitudinal interlaminar shear of unidirectional fiber composites is the same as LT (edge) shear, but different from transverse interlaminar shear. For 1:1 orthogonal fiber composites, there is no difference in L and Tdirections, so $\tau_{LN} = \tau_{TN} \neq \tau_{LT}$, that is to say the longitudinal interlaminar shear is the same as transverse interlaminar shear, but different from LT shear. For non 1:1 orthogonal fiber composites, they are all different, i.e., $\tau_{LT} \neq \tau_{LN} \neq \tau_{TN}$.

8.5.2 The estimation of unidirectional composites' shear behaviors

1) Estimation of edge shear behavior G_{LT}, τ_{LT}

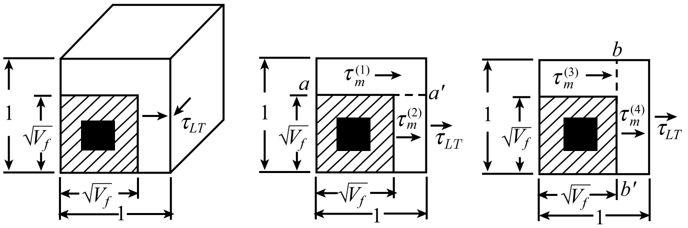
When using composites, they are usually in-plane stress condition where stress acts along the direction of composites layer (*LT* plane). Thus the in-plane stress is common case in use of composites. Shear properties in *LT* plane (G_{LT}, τ_{LTu}) are also the basic data of mechanical behavior for designing composites.

The load condition of edge shear of unidirectional fiber composites and its typical unit cell are shown in Fig. 8.33. Like estimation in transverse tensile properties using Zhu Yiling method, we can obtain the simplified unit cell and the mechanical model with the equal stress, equal strain assumption (Fig. 8.34). The model can be artificially divided into areas of I, II, III and IV. At the precondition of four points of hypotheses (equal initial stress, consistent deformation, linear elasticity and unconcerned Poisson's effect), we develop derivation according to assumption of equal stress and of equal strain respectively.



(a) (b)

Fig. 8.33 Unidirectional composites edge shear and typical unit cell:
(a) LT shear; (b) typical unit cell.



(a) (b) (c)

Fig. 8.34 Mechanical model of in-plane shear of unidirectional composites:
(a) simplified unit cell; (b) equal stress assumption; (c) equal strain assumption.

(1) Estimation of G_{LT}.

① The equal stress assumption.

The equal stress assumption is that matrix stress in II is equal to fiber stress, i.e., $\tau_f = \tau_m^{(2)}$. According to the load in balance, we have:

$$\tau_{LT} \cdot 1 \cdot 1 = \tau_m^{(1)}(1 - \sqrt{V_f}) \cdot 1 + \tau_f \sqrt{V_f} \cdot 1$$

According to the total consistent deformation, thus we get:

$$1 \cdot 1 \cdot \gamma_{LT} = \frac{\tau_{LT}}{G_{LT}} = \frac{\tau_m^{(1)}}{G_m} \cdot 1 \cdot 1 = \frac{\tau_m^{(2)}}{G_f} \cdot \sqrt{V_f} \cdot 1 + \frac{\tau_m^{(2)}}{G_m}(1 - \sqrt{V_f}) \cdot 1$$

Combine the above two formulae, thus we get:

$$G_{LT}^{(\mathrm{a})} = \frac{1 - \sqrt{V_f}(1 - \sqrt{V_f})\left(1 - \dfrac{G_m}{G_f}\right)}{1 - \sqrt{V_f}\left(1 - \dfrac{G_m}{G_f}\right)} G_m \tag{8.97}$$

$$\tau_{LT} = \left[1 - \sqrt{V_f}(1 - \sqrt{V_f})\left(1 - \frac{G_m}{G_f}\right)\right]\tau_m^{(2)} \tag{8.98}$$

The result of formula (8.97) and (8.98) are completely identical to the derivation result of transverse tension, which only change σ, E to τ, G.

② The equal strain assumption.

The equal strain assumption, i.e., $\gamma_m^{(3)} = \gamma_f$, from the Hooke's law, we have:

$$\frac{\tau_m^{(3)}}{G_m} = \frac{\tau_f}{G_f}$$

According to the load balance, we obtain:

$$\tau_{LT} = \tau_m^{(4)} = \tau_f\sqrt{V_f} + \tau_m^{(3)}(1 - \sqrt{V_f})$$

According to the deformation, we obtain:

$$1 \cdot 1 \cdot \gamma_{LT} = \frac{\tau_m^{(4)}}{G_m}(1 - V_f) + \frac{\tau_m^{(3)}}{G_m}\sqrt{V_f}$$

Combine the above three formulae, thus we get:

$$G_{LT}^{(\mathrm{b})} = \frac{\tau_{LT}}{\gamma_{LT}} = \frac{1 - \sqrt{V_f}\left(1 - \dfrac{G_f}{G_m}\right)}{1 - \sqrt{V_f}(1 - \sqrt{V_f})\left(1 - \dfrac{G_f}{G_m}\right)} G_m \tag{8.99}$$

The estimation value of G_{LT} is the average of (8.97) and (8.99), i.e.,

$$G_{LT} = \frac{1}{2}(G_{LT}^{(\mathrm{a})} + G_{LT}^{(\mathrm{b})}) \tag{8.100}$$

Therefore, factors affecting G_{LT} are G_m, V_f and G_f/G_m.

(2) Estimation of τ_{LTu}.

The same as transverse tension, in the case of the equal strain assumption $\tau_m^{(4)} = \tau_{LT} > \tau_m^{(3)}$, so $\tau_{LTu} = \tau_{mu}$; in the case of the equal stress $\tau_m^{(2)} = \tau_{LT} > \tau_m^{(1)}$, so the edge shear strength can be obtained from the formula (8.98).

$$\tau_{LTu} = \left[1 - \sqrt{V_f}(1 - \sqrt{V_f})\left(1 - \frac{G_m}{G_f}\right)\right]\tau_{mu} \tag{8.101}$$

The matrix also has the phenomenon of stress concentration and strain magnification, and stress concentration coefficient SCF is given by the formula (8.102).

$$\mathrm{SCF} = \frac{\tau_{mu}}{\tau_{LTu}} = \frac{1}{1 - \sqrt{V_f}\,(1 - \sqrt{V_f})\left(1 - \dfrac{G_m}{G_f}\right)} \tag{8.102}$$

Factors effecting τ_{Ltu} are $\tau_{mu}, V_f, V_V, G_m/G_f$ and interface.

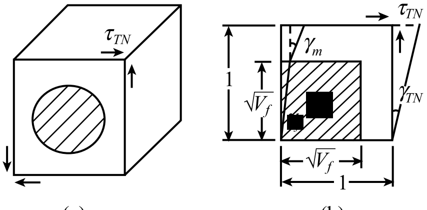
2) Estimation of interlaminar shear properties

(1) Longitudinal interlaminar shear properties G_{LN}, τ_{LN}.

For ideal unidirectional fiber composites, the longitudinal interlaminar shear properties are the same as the edge shear properties, $G_{LN} = G_{LT}$, $\tau_{LN} = \tau_{LT}$.

(2) Transverse interlaminar shear behavior G_{TN}, τ_{TN}.

Fig. 8.35 shows the mechanical model of transverse interlaminar shear.



(a) (b)

Fig. 8.35 Mechanical model of transverse interlaminar shear of unidirectional composites: (a) unit cell; (b) mechanical model.

Because

$$\tau_{TN} = \tau_f = \tau_m$$

So the average shear strain is given by:

$$\gamma_{TN} = \frac{\tau_{TN}}{G_f}\sqrt{V_f} + \frac{\tau_{TN}}{G_m}(1 - \sqrt{V_f})$$

$$G_{TN} = \frac{\tau_{TN}}{\gamma_{TN}} = \frac{G_m}{1 - \sqrt{V_f}\left(1 - \dfrac{G_m}{G_f}\right)} \tag{8.103}$$

Transverse interlaminar shear strength is the shear strength of resin matrix $\tau_{TNu} = \tau_{mu}$, and τ_{TNu} is also affected by interfacial strength, porosity, and so on.

8.5.3 The orthoaxis shear behavior of orthogonal composites

1) G_{LT}, τ_{LT} of 0°/90° ply orthogonal composites

For the 0°/90° ply orthogonal composites made by cross ply stacking of unidirectional tape, its orthoaxis edge shear behavior (G_{LT}, τ_{LT}) is identical to the behavior of unidirectional composites which contain the same resin content.

2) The measured results of G_{LT}, τ_{LT}

The measured results of edge shear behavior of orthogonal composites showed that:

1:1 fabric orthogonal composites>unidirectional fabric orthogonal composites> $0°/90°$ ply orthogonal composites

8.5.4 Estimation of 45° edge shear properties of orthogonal composites

1) Estimation of $\tau_{45°}$

The in-plane shear behavior of unidirectional fiber composites is bad. Thus, when the in-plane shear stress is the crux of designing structure parts, in order to make full use of fiber, we should arrange the fiber in the main stress direction, i.e., in the direction of ±45° with shear stress, as seen in Fig. 8.36. From the mechanics of materials, a unit body under in-plane shear is like a component bearing tension-compression. That is, shear stress can be transformed into tension-compression stress in the diagonal line, and

$$|\tau| = |\sigma^+| = |\sigma^-|$$

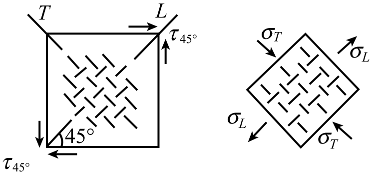


Fig. 8.36 In-plane shear that fiber are arranged in the main stress direction.

So in-plane shear stress $\tau_{45°}$ of ±45° composite is given by:

$$|\tau_{45°}| = |\sigma_L| = |\sigma_T|$$

Therefore, we change the discussion from shear problem to tension-compression problem. When material is under two-directional normal stress, according to the Mohr strength criterion, if $\dfrac{\sigma^+}{[\sigma^+]} + \dfrac{\sigma^-}{[\sigma^-]} \geqslant 1$, material will failure.

In the formula, σ^+ and σ^- are the tensile stress and compressive stress in unit body respectively; $[\sigma^+]$ and $[\sigma^-]$ are the tensile strength and compressive strength of materials respectively.

When put $|\tau| = |\sigma^+| = |\sigma^-|$ in the above formula, it becomes:

$$\tau_u = \frac{[\sigma^+][\sigma^-]}{[\sigma^+] + [\sigma^-]}$$

That is to say when the stress $\tau = \tau_u$, materials are damaged by shear.

So for the composites (unidirectional and orthogonal composites), 45° direction in-plane shear strength is

$$\tau_{45°u} = \frac{\sigma_{Lu} \cdot \sigma_{-Tu}}{\sigma_{Lu} + \sigma_{-Tu}} \tag{8.104}$$

Especially, for the 45° direction in-plane shear strength of 1:1 orthogonal composites, in case of

$$\sigma_{Lu} = \sigma_{-Tu}$$

So

$$\tau_{45°u} \approx \frac{\sigma_{Lu}}{2}$$

This formula shows that ±45° in-plane shear strength of composites is half of its tensile strength σ_{Lu}, so it is much higher than orthoaxis in-plane shear strength τ_{LTu}. Therefore, in engineering, the parts under big shear stress, such as aircraft skin, always uses the ± 45° layers.

2) Estimation of G_{45°

According to Fig. 8.37, unit body $ABCD$ bears edge shear that produces angle strain γ.

When γ is very small, $ABC'D'$ can be considered as rhombus, so $\angle D'AO' = \dfrac{90^\circ + \gamma}{2}$.

Let diagonal line $AC = BD = 1$, then after deformation, we have:

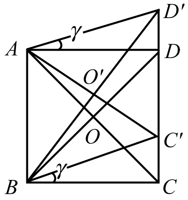


Fig. 8.37 In-plane shear deformation relation.

$$BD' = 1 + \varepsilon_1, AC' = 1 - \varepsilon_2$$

$$\tan\angle D'AO' = \tan\left(45^\circ + \frac{\gamma}{2}\right) = \frac{BD'}{AC'} = \frac{1+\varepsilon_1}{1-\varepsilon_2}$$

According to tangent trigonometric function, we have:

$$\tan\left(45^\circ + \frac{r}{2}\right) = \frac{1+\tan\frac{r}{2}}{1-\tan\frac{r}{2}} \approx \frac{1+\frac{r}{2}}{1-\frac{r}{2}}$$

That is

$$\frac{1+\frac{r}{2}}{1-\frac{r}{2}} = \frac{1+\varepsilon_1}{1-\varepsilon_2}$$

Expand the formula above, neglect the second-order micro-variable, thus we get:

$$\gamma = \varepsilon_1 + \varepsilon_2$$

The formula shows that the shear strain of composites is identical to the sum of normal strain along the diagonal direction, and if it is applied to the 45° shear composites, then

$$\gamma_{45^0} = \varepsilon_L + \varepsilon_T \tag{8.105}$$

By using the generalized Hooke's law under two-directional normal stress, linear strain of composites is given by:

$$\varepsilon_L = \frac{\sigma_L}{E_L} + \mu_{TL}\frac{\sigma_T}{E_T}$$

$$\varepsilon_T = \frac{\sigma_T}{E_T} + \mu_{LT}\frac{\sigma_L}{E_L}$$

According to the Maxwell reciprocity law:

$$\mu_{TL} = \mu_{LT}\frac{E_T}{E_L}$$

While

$$|\tau_{45^\circ}| = |\sigma_L| = |\sigma_T|$$

So

$$\gamma_{45^\circ} = \varepsilon_L + \varepsilon_T = \frac{\tau_{45^\circ}}{E_L}\left(1 + \frac{E_L}{E_T} + 2\mu_{LT}\right)$$

Therefore

$$G_{45^\circ} = \frac{\tau_{45^\circ}}{\gamma_{45^\circ}} = \frac{E_L}{1 + \dfrac{E_L}{E_T} + 2\mu_{LT}} \tag{8.106}$$

For 1:1 orthogonal composites, as $E_L = E_T$, so

$$G_{45^\circ(1:1)} = \frac{E_L}{2(1 + \mu_{LT})}$$

8.5.5 Testing principle of shear behaviors

1) Testing methods of τ_{LT} and G_{LT}

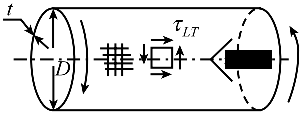


Fig. 8.38 Thin-wall cylinder torsion test.

(1) Torsional test of thin-wall cylinder.

See Fig. 8.38, the thin-wall cylinder ($t \ll D$) of hoop and axial fiber (1:1) composites, is carried out torsion experiment. It is known from the mechanics of materials that composites are acted by pure shear stress τ_{LT}, and we have:

$$\tau_{LT} = \frac{M_K R}{J_P} \tag{8.107}$$

In the formula, M_K is torque; R is cylinder radius; J_P is polar moment of inertia.

$$J_P = 2\pi R^3 t$$

Where t is wall thickness.

In order to measure the linear strain in ±45° direction, we attach the strain tablets in ±45° angle with the fiber. In-plane shear strain can be calculated with the below formula:

$$\gamma_{LT} = \varepsilon_{+45^\circ} + \varepsilon_{-45^\circ}$$

$$G_{LT} = \tau_{LT}/\gamma_{LT}$$

(2) Method of 45° directional diagonal tension of 1:1 orthogonal composites (±45° laminate tensile method).

See Fig. 8.39, ±45° laminate samples are in tensile test, measure its external stress σ_{45° and linear strain in loading direction and in vertical direction, ε_{+45° and ε_{-45°.

Because

$$\tau_u = \frac{[\sigma^+]\cdot[\sigma^-]}{[\sigma^+]+[\sigma^-]}$$

So

$$\tau_{LTu} = \frac{[\sigma^+_{45^\circ}]\cdot[\sigma^-_{45^\circ}]}{[\sigma^+_{45^\circ}]+[\sigma^-_{-45^\circ}]}$$

Hypothesis $[\sigma^+_{45^\circ}] = [\sigma^-_{-45^\circ}]$

$$\tau_{LTu} = \frac{\sigma_{45^\circ u}}{2} = \frac{P_{45^\circ u}}{2A} \qquad (8.108)$$

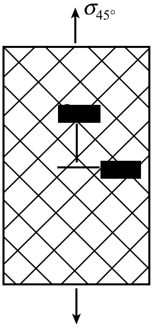


Fig. 8.39 ±45° laminate tensile method for in-plane shear properties.

Because

$$\gamma_{LT} = \varepsilon_{+45^\circ} + \varepsilon_{-45^\circ}$$

$$\tau_{LT} = \sigma_x \sin\alpha\cos\alpha = \sigma_{45^\circ}\sin 45^\circ\cos 45^\circ = \frac{\sigma_{45^\circ}}{2}$$

So

$$G_{LT} = \frac{\tau_{LT}}{\gamma_{LT}} = \frac{P_{45^\circ}}{2A(\varepsilon_{45^\circ}+\varepsilon_{-45^\circ})} \qquad (8.109)$$

As the tensile test is simpler than torsion test in the sample preparation and measurement, the national standard GB3355—82 has prescribed tensile test method as the measurement of the in-plane shear parameter. It also has measured 45° directional tensile behaviors $\sigma_{45^\circ u}$, E_{45° and μ_{45° of 1:1 orthogonal composites meanwhile.

2) Interlaminar shear test

The interlaminar shear strength of composites is mainly due to the shear strength of matrix and interface, it is the weakest link in the strength behavior of composites. This is because the resin matrix has low shear strength itself, and defects such as pores formed in composite processing which will make the strength of matrix and interface decline. Therefore, we should avoid suffering interlaminar shear in using composites. There are three main experimental methods measuring the interlaminar shear strength of composites which are double notch shear, short beam bending shear (see Fig. 8.40) and Iosipescu shear.

(1) Double notch shear test.

The shear strength which is tested by double notch shear is not only related

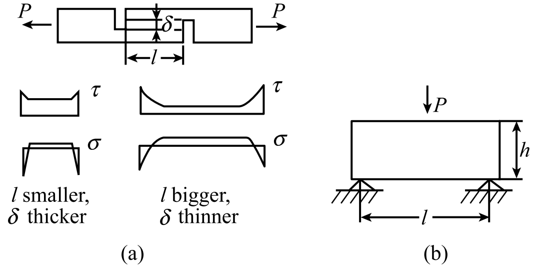


Fig. 8.40 Interlaminar shear test of composites:

(a) double notch shear; (b) short beam bending shear.

to the performance of the sample materials, but also has a large relationship with geometry size and shape of the shear segment of sample. It behaves as: (a) effect of length (l) of shear segment. The greater length of shear segment will lead to the more non-uniform distribution of shear stress, with big stress at both ends and small stress at the middle part; conversely, the shorter length of shear segment, the more uniform distribution of stress is. (b) Effect of thickness (δ) of shear segment. The bigger thickness of shear segment will lead to the more uniform stress distribution of shear segment.

In the test, there has a bigger tensile stress at the end of shear segment, so the destruction of the sample is not a single interlaminar shear failure. In addition, the double-notched sample processing should be strict, otherwise we cannot guarantee that the shear segment forced by a single shear effect. Therefore this method is rarely used at present.

The shear strength in double-notched shear experiment is calculated as follow:

$$\tau = \frac{P}{bl} \tag{8.110}$$

In the formula, P is rupture load measured by test; b is width of sample; l is length of shear segment.

(2) Bending shear of short beam (bending shear test).

In short-beam bending shear test, the ratio of sample thickness (height) h and test span h/l is about 1/4$\sim$1/5. Three point bending test is adopted. Except for some partial bear-loading areas, this test has a relatively uniform shear stress in neutral layer. The interlaminar shear strength in bending shear test has the following calculation formula:

$$\tau = \frac{3}{2}\frac{Q}{bh} = \frac{3}{4}\frac{P}{bh} \tag{8.111}$$

In the formula, Q is shear load, (in the three-point bending test, $Q = P/2$); P is bending load; b is sample width; h is sample thickness.

The short-beam bending shear test has been standardized by GB3357—85, $l/h = 5$; thickness of the sample is 2$\sim$5mm; so the test sample is small and can be easily prepared. It is commonly used to evaluate the matrix properties and interface bonding strength of composites, and as τ is greatly influenced by V_V, it can also be used to select technology and determine the pressure point of composite materials.

(3) Iosipescu shear.

The latest research results put forward the Iosipescu shear test method. The fixture and force condition of sample are shown in Fig. 8.41. Sample is the beam that height is larger than thickness, which has two 90° incisions on its both sides up-down in the mid-point of length, with the depth about 20% to 30% of the height. Interlaminar shear stress tested by this method is in more uniform state in local areas between the incisions, and the shear stress is:

$$\tau = \frac{P}{wt} \tag{8.112}$$

In the formula, w is the distance between two incisions; t is thickness of the sample.

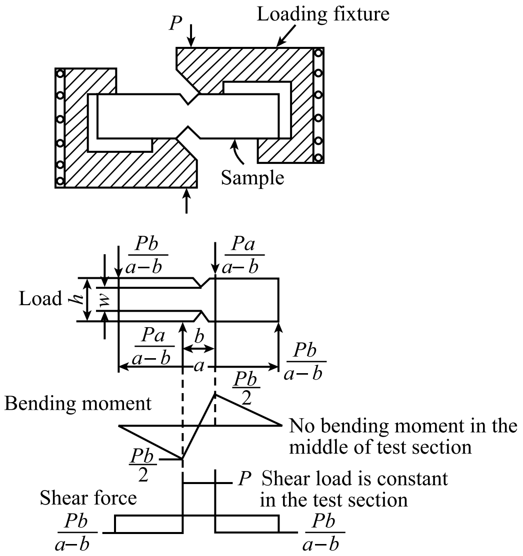


Fig. 8.41 Fixture of Iosipescu shear test and its force diagram.

8.6 The bending properties of composites

The stress state of composites under bending is so complex that they include tensile stress, compression stress, as well shear stress and partial extrusion stress, so it is difficult to make simple and precise mechanical analysis on the bending properties of composites. At present flexural properties of composites are determined by practical measure methods. Because of the complexity in the state of the bending stress, it proves to be a comprehensive measure of the properties of composites in general. Meanwhile its sample machining is easy, and test and calculation are easy too, so currently the bending experiment has been most commonly used in evaluating the properties of composites. It is especially popular in the screening and determination of materials, formulations and technological conditions. Usually, we use the simple supported beam three-point bending methods for test. The longitudinal bending strength σ_{Fu} is calculated as formula (8.113).

$$\sigma_{Fu} = \frac{3}{2} \cdot \frac{P_b l}{bh^2} \tag{8.113}$$

In the formula, P_b is failure load; l is span of test; b is sample width; h is sample thickness.

Bending modulus can be calculated as formula (8.114):

$$E_F = \frac{\Delta P}{\Delta f} \cdot \frac{l^3}{4bh^3} \tag{8.114}$$

In the formula, ΔP is increment of the load; Δf is deflection related to ΔP in the middle of span.

The flexural properties of composites depend on its destruction types (such as tensile failure, compressive failure and shear failure, etc.). The destruction types are not only related to fiber, matrix and interface properties as well as the relative content of fibers and porosity and the test conditions (such as loading speed, test temperature, etc.), but are also closely related to the span-height ratio of sample and deflection.

Based on material mechanics, the internal force and stress distribution of three-point bending specimen are shown in Fig. 8.42. The shear force Q has no relationship with the span l. The maximum shear force $Q_{max} = P/2$. Bending moment M is related to l. The maximum bending moment $M_{max} = Pl/4$, which occurs in the mid-point of span. According to the planar bending theory and the assumption that tensile modulus is equal to flexural modulus, we can obtain the stress distribution of specimen which is shown in Fig. 8.42(c) and 8.42(e). The largest longitudinal compression stress and tensile stress appear on upper and lower surfaces which has the maximum bending moment, it is:

$$\sigma_{\max} = \frac{3Pl}{2bh^2} = \frac{3}{2} \cdot \frac{P}{A} \cdot \frac{l}{h} \tag{8.115}$$

In formula, A is cross sectional area of specimen (=bh). l/h is span-height ratio (the max longitudinal stress will depend on the span-height ratio l/h when specimen bears loading).

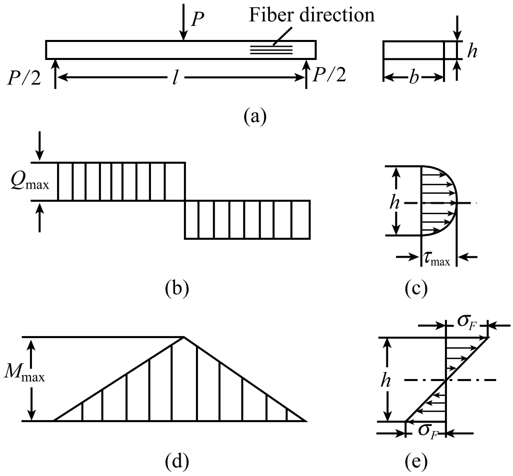


Fig. 8.42 Internal force and stress diagram of three-point bending under simple supported beam:

(a) three-point bending; (b) shear force; (c) shear stress; (d) bending moment; (e) normal stress.

The largest bending shear stress appears in the neutral axis area of specimen.

$$\tau_{\max} = \frac{3}{2}\tau_{\text{average}} = \frac{3}{2}\cdot\frac{Q}{A} = \frac{3P}{4A} \tag{8.116}$$

We see that the largest shear stress has no relation with the span-height l/h.

Three-point bending specimen is forced not only by normal stress, but also by shear stress. So there are three types of destruction. If the maximum normal stress $\sigma_{\max}$ reach the tensile (or compression) strength limit σ_b of the composites first, specimen will develop longitudinal tensile or compression failure. Load at this time is the load P_σ that longitudinal tensile-compression failure occurs.

$$P_\sigma = \frac{2A\sigma_b}{3}\cdot\frac{h}{l} \tag{8.117}$$

From formula (8.117), P_σ is function of span-height ratio l/h, which decline in inverse proportion with the increase of l/h (Fig. 8.43).

If the maximum shear stress reaches the interlaminar shear strength τ_b of composites first, specimen develops interlaminar shear damage. Load at this time is the load P_τ when interlaminar shear failure occurs.

$$P_\tau = \frac{4A\tau_b}{3} \tag{8.118}$$

P_τ has no relationship with the span-height ratio, so it is the line parallel to l/h axis in the figure P-l/h (Fig. 8.43).

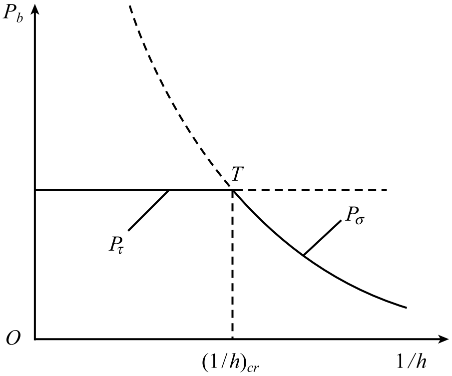


Fig. 8.43 Relation curve of bending failure load and the span-height ratio.

If $\sigma_{\max}$ and $\tau_{\max}$ both reach its strength limit respectively, it will develop mixed destruction. At this time load $P = P_\sigma = P_\tau$, that is the intersection of two curves in Fig. 8.43, and l/h at this point is called critical span-height ratio $(l/h)_{cr}$, the value is:

$$\left(\frac{l}{h}\right)_{cr} = \frac{\sigma_b}{2\tau_b} \tag{8.119}$$

While $(l/h) > (l/h)_{cr}, P_\tau > P_\sigma$, specimen develops tensile-compression failure. While $(l/h) < (l/h)_{cr}, P_\tau < P_\sigma$, specimen develops interlaminar shear failure. Composites are consisted with three structural elements which are fiber, matrix and interface. As the tensile-compression modulus of fiber E_f is much bigger than the tensile-compression modulus of matrix E_m, bending normal stress which distributes based on the stiffness ratio is mainly taken by the fiber. So composites that develop tensile-compression bending damage have high mechanical properties. The bending shear stress is caused by different axial forces (different longitudinal forces), and mainly taken by interface and matrix, so it represents poor mechanical properties. Generally, bending strength and modulus of composites is referred to what is generated by the longitudinal tensile compression bending stress. In order to avoid developing interlaminar shear damage, the span-height ratio l/h of specimen in test should be larger than $(l/h)_{cr}$. Generally, the span-height ratio of bending specimen of glass fabric and short glass fiber composites is $l/h \geqslant 20$; $l/h \geqslant 16$ for unidirectional glass fiber composites; $l/h \geqslant 32$ for unidirectional carbon fiber composites.

The deflection (f) is attributed to the additional bending moment M' which caused by support veaction force N on specimen cross section. See Fig. 8.44.

Based on the condition of equilibrium:

$$N_y = \frac{P}{2}$$

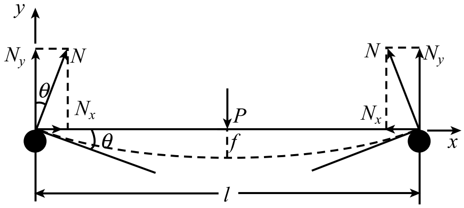


Fig. 8.44 Deflection effect on the bending strength.

Then

$$N_x = N_y \cdot \tan\theta$$

Let

$$\tan\theta \approx \frac{2f}{l}$$

Then

$$N_x = P \cdot \frac{f}{l}$$

The additional bending moment M' that caused by horizontal component N_x of the support reaction force N on the mid-point of beam is:

$$M' = N_x f = \frac{Pf^2}{l}$$

At this time, the maximum bending moment of sample is:

$$M_{\max} = \frac{Pl}{4} + N_x f = \frac{Pl}{4} + \frac{Pf^2}{l} \tag{8.120}$$

The maximum bending normal stress is:

$$\sigma_{\max} = \frac{1}{bh^2/6}\left(\frac{Pl}{4} + \frac{Pf^2}{l}\right) = \frac{3Pl}{2Ah}\left[1 + 4\left(\frac{f}{l}\right)^2\right] \tag{8.121}$$

When $\dfrac{f}{l} < \dfrac{1}{10}$, the impact of deflection f is less than 4% which can be neglected. The maximum deflection value of three-point bending rectangular beam is:

$$f = -\frac{Pl^3}{48EJ} = -\frac{Pl^3}{48E \cdot \dfrac{bh^3}{12}} = -\frac{P}{4bE}\left(\frac{l}{h}\right)^3 \tag{8.122}$$

Known from (8.122), the deflection f increased by cubic of span-height ratio l/h. Therefore, when measuring the bending strength of composites, we should take $l/h > (l/h)_{cr}$ but only moderately greater.

In condition of the three-point bending loading, deflection of sample is not only the deflection f_σ caused by bending normal stress, but also the deflection f_τ caused by bending shear stress.

$$f_\tau = \int_0^{l/2} \frac{\tau}{G}\mathrm{d}l = \int_0^{l/2} \frac{Q}{AG}\mathrm{d}l = \int_0^{l/2} \frac{P}{2AG}\mathrm{d}l = \frac{Pl}{4AG}$$

$$f = f_\sigma + f_\tau = \frac{Pl^3}{48EJ} + \frac{Pl}{4AG} = \frac{Pl^3}{48EJ}\left[1 + \frac{E}{G(l/h)^2}\right] \tag{8.123}$$

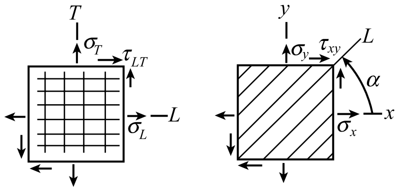
Calculations show that, when l/h = 100, shear deflection f_τ reduce to 1%-2% of bending deflection f_σ. At this time, the shear deflection can be neglected. Therefore in the measurement of bending modulus, in order to reduce the effect of shear stress on deflection, the span-height ratio of specimen should take a larger value. Normally l/h = 100.

8.7 The off-axis mechanical properties of composites

We have discussed the orthoaxis mechanical properties of unidirectional composites in the former, i.e., the mechanical properties when the referential coordinate axis x-y coincides with the main axis L-T, they are the most basic mechanical properties of composites. However, the coordinate system in engineering design does not often coincide with the orthoaxis coordinate system of the materials. Often there is an angle α. The mechanical properties at this time, called off-axis mechanical properties of composites, refer to those that have an arbitrary angle α with the fiber direction (L direction). We will see that the off-axis mechanical properties can be derived from the orthoaxis mechanical properties. In this section, we will discuss the relationship between mechanical properties of composites and load direction: the anisotropy of composites.

8.7.1 Stress direction and symbolic rules

See Fig. 8.45, the in-plane stress effect on composites may be divided into three stress components σ_L, σ_T and τ_{LT} in orthoaxis direction (L-T coordinates system), or three stress components σ_x, σ_y and τ_{xy} in off-axis direction



(a) (b)

Fig. 8.45 The coordinates system of composites subject to plane stress: (a) in-axis plane stress; (b) off-axis plane stress.

(x-y coordinate system). The joint angle α (the joint angle of x with L axis) is called ply directional angle.

1) Definition of positive and negative direction of ply directional angle α

Let α be the joint angle of the referenced axis (off-axis, x-y axis) to the main L-T axis of material. We define the anti-clockwise rotation from the x direction to the L direction to be positive ($+\alpha$) and clockwise rotation to be negative ($-\alpha$).

2) Stress symbolic rules

Let the coordinates axis as reference, it is defined that the stress components in positive side is positive when it points at the same direction as the coordinates direction, and the stress components in negative side is positive when it is opposite to the coordinates direction. That is, the positive side in positive direction means positive, the negative side in negative direction means positive; the positive side in negative direction means negative, the negative side in positive direction means negative. The positive side means the exterior normal direction that is consistent with the coordinates direction, the negative side means the exterior normal direction that is opposite to the coordinate direction. In fact, this seemingly complex definition is consistent with the habits that tensile stress is positive and compressive stress is negative. For shear stress, two pairs of shear stress marked in Fig. 8.45 is positive, shear stress in opposite direction is negative.

8.7.2 Estimation of α directional strength σ_{xu}, τ_{xyu} of unidirectional fiber composites

Suppose $\sigma_x \neq 0$, $\sigma_y = 0$, $\tau_{xy} = 0$ (i.e., single effect of σ_x), the unit body is shown in Fig. 8.46.

Based on the condition of static equilibrium:

$$\sum P_L = 0 \qquad \sigma_L \cdot \frac{1}{\cos\alpha} = \sigma_x \cdot 1 \cdot \cos\alpha$$

So

$$\sigma_L = \sigma_x \cos^2\alpha$$

$$\sum P_T = 0 \qquad \sigma_T \cdot \frac{1}{\sin\alpha} = \sigma_x \cdot 1 \cdot \sin\alpha$$

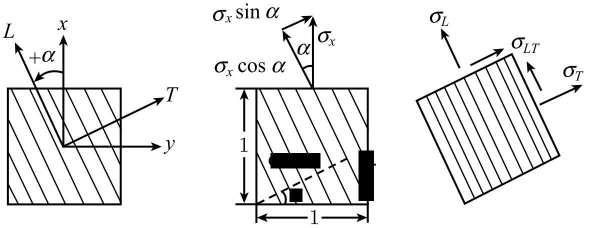


Fig. 8.46 The relation of off-axis tensile stress with stress in L-T direction.

So

$$\sigma_T = \sigma_x \cdot \sin^2\alpha$$

$$\sum Q_{LT} = 0 \qquad -\tau_{LT} \cdot \frac{1}{\cos\alpha} = \sigma_x \cdot 1 \cdot \sin\alpha$$

So that

$$\tau_{LT} = -\sigma_x \sin\alpha\cos\alpha$$

That is

$$\left.\begin{aligned} \sigma_L &= \sigma_x \cos^2\alpha \\ \sigma_T &= \sigma_x \sin^2\alpha \\ \tau_{LT} &= -\sigma_x \sin\alpha\cos\alpha \end{aligned}\right\} \tag{8.124}$$

This shows that the single off-axis stress σ_x that is applied to unidirectional composite can be decomposed into several orthoaxis stress. The effect of σ_x is equivalent to the effect of stress σ_L and σ_T in L and T directions, and also with shear stress τ_{LT}. On the effect of in-plane stress $(\sigma_L, \sigma_T, \tau_{LT})$, the failure criterion of composites is given by:

$$\left(\frac{\sigma_L}{\sigma_{Lu}}\right)^2 - \frac{\sigma_L \cdot \sigma_T}{\sigma_{Lu} \cdot \sigma_{Tu}} + \left(\frac{\sigma_T}{\sigma_{Tu}}\right)^2 + \left(\frac{\tau_{LT}}{\tau_{LTu}}\right)^2 \geqslant 1 \tag{8.125}$$

Insert formula (8.124) to (8.125), we obtain the estimation formula of tensile strength σ_{xu} of unidirectional composites.

$$\frac{1}{\sigma_{xu}^2} = \frac{\cos^4\alpha}{\sigma_{Lu}^2} + \frac{\sin^4\alpha}{\sigma_{Tu}^2} + \left(\frac{1}{\tau_{LTu}^2} - \frac{1}{\sigma_{Lu} \cdot \sigma_{Tu}}\right)\frac{\sin^2 2\alpha}{4} \tag{8.126}$$

In the same way, single effect of σ_y can be divided into three stresses (σ_L, σ_T, τ_{LT}) in L-T direction.

$$\left.\begin{aligned} \sigma_L &= \sigma_y \sin^2\alpha \\ \sigma_T &= \sigma_y \cos^2\alpha \\ \tau_{LT} &= \sigma_y \sin\alpha\cos\alpha \end{aligned}\right\} \tag{8.127}$$

Substitute into strength criterion (8.125) and obtain the estimation of σ_{yu}:

$$\frac{1}{\sigma_{yu}^2} = \frac{\sin^4\alpha}{\sigma_{Lu}^2} + \frac{\cos^4\alpha}{\sigma_{Tu}^2} + \left(\frac{1}{\tau_{LTu}} - \frac{1}{\sigma_{Lu} \cdot \sigma_{Tu}}\right)\frac{\sin^2 2\alpha}{4} \tag{8.128}$$

Single effect of τ_{xy} can be divided into three stresses (σ_L, σ_T, τ_{LT}) in L-T direction.

$$\left.\begin{aligned} \sigma_L &= \tau_{xy} \sin 2\alpha \\ \sigma_T &= -\tau_{xy} \sin 2\alpha \\ \tau_{LT} &= \tau_{xy} \cos 2\alpha \end{aligned}\right\} \tag{8.129}$$

Substitute into strength criterion (8.125) and obtain the estimation of τ_{xyu}.

$$\frac{1}{\tau_{xyu}^2}=\frac{\cos^2 2\alpha}{\tau_{LTu}^2}+\left(\frac{1}{\sigma_{Lu}^2}+\frac{1}{\sigma_{Lu}\cdot\sigma_{Tu}}+\frac{1}{\sigma_{Tu}^2}\right)\sin^2 2\alpha \tag{8.130}$$

The stress transformation equation is to convert the in-plane stress (σ_x, σ_y, τ_{xy}) in x-y direction into the in-plane stress (σ_L, σ_T, τ_{LT}) in L-T direction. Put formulae (8.124), (8.127) and (8.129) all together, and wrote in matrix form, that is:

$$\left\{\begin{array}{c}\sigma_L\\ \sigma_T\\ \tau_{LT}\end{array}\right\}=\left[\begin{array}{ccc}m^2 & n^2 & 2mn\\ n^2 & m^2 & -2mn\\ -mn & mn & m^2-n^2\end{array}\right]\left\{\begin{array}{c}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{array}\right\} \tag{8.131}$$

$$\left\{\begin{array}{c}\sigma_L\\ \sigma_T\\ \tau_{LT}\end{array}\right\}=[\tau_\sigma]\left\{\begin{array}{c}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{array}\right\}$$

Where

$$m=\cos\alpha \qquad n=\sin\alpha$$

In the formula, $[\tau_\sigma]$ is stress transformation matrix.

Based on formula (8.126), (8.128) and (8.130), we know that $\sigma_{xu}(\sigma_{yu})$ and τ_{xyu} are the functions of sin α and cos α, so it is the periodic function of angle; and it is also the symmetric function, α=0° as symmetric axis, i.e. strength value of $\alpha°$ is equal to strength value of $-\alpha°$. As long as axial strength values σ_{Lu}, σ_{Tu} and τ_{LTu} of unidirectional fiber composites are known, we can obtain strength values in any direction (α). These equations which express the relationship between tensile or shear properties in any α direction and the orthoaxial properties of fiber composites is called directional equation.

Following is the application of the directional equation.

[Example 8.1] Now the composites are made of glass cloth that the longitude and latitude directional fiber amount ratio is 1:1, known σ_{Lu}=2500 kg/cm^2, σ_{Tu}= 2500kg/cm^2, τ_{LTu}=500 kg/cm^2. Please use formulae to calculate tensile and shear strength in the direction of 15° interval, the calculation value should be expressed in polar coordinates.

Solution According to formula (8.126) and (8.130), the calculated σ_{xu} and τ_{xyu} are shown in Fig. 8.47. It shows that σ_x in direction of 0° and 90°, i.e., σ_L and σ_T are the maximum, $\sigma_{45°}$ is the minimum in 45°; τ_{xy} is on the contrary, $\tau_{45°}$ is the maximum in 45°, and the minimum in 0° and 90°, i.e., τ_{LT}, σ_x and τ_{xy} are symmetric to coordinates axis from 0° to 180° and from 90° to 270°. Therefore, the relationship between strength of composites and load direction can be indicated by the direction curve in the first quadrant, data of other quadrants can be reflected by corresponding symmetry axis.

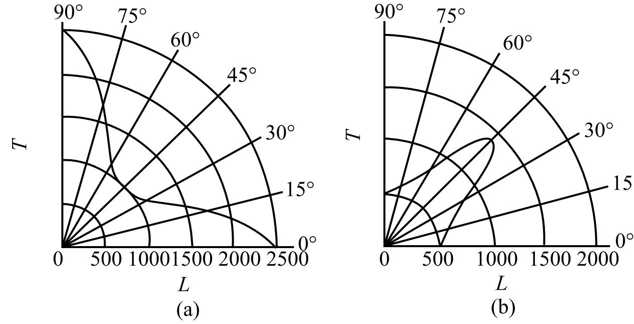


Fig. 8.47 The relation of off-axis strength σ_{xu}, τ_{xyu} of 1:1 two-directional balancing GFRP with directional angle:

(a) σ_{xu}; (b) τ_{xyu}.

8.7.3 Estimation of α directional elastic coefficient of undirectional composites

1) Unidirectional tensile elastic coefficient E_x, E_y and μ_{xy}

Suppose $\sigma_x \neq 0$, $\sigma_y = 0, \tau_{xy} = 0$ (single effect of σ_x).

(1) Analysis of stress.

This has been discussed previously. Single σ_x can be divided into three stress components (σ_L, σ_T, τ_{LT}) in L-T direction. See formula (8.124).

(2) Analysis of strain.

Select the unit body along L, T direction, seen in Fig. 8.48 (a), to make a strain analysis. Single ε_L make dL generate an increment d$L \cdot \varepsilon_L$ in L direction [see Fig. 8.48(b)]. When β angle is very small, the increment generated in x direction may be nearly equal to d$L \cdot \varepsilon_L \cdot$ cos α. Single ε_T make dT generate a increment d$T \cdot \varepsilon_T$ in T direction [see Fig. 8.48(c)]. When β angle is very small, the increment generated in x direction may nearly be equal to d$T \cdot \varepsilon_T \cdot$ sin α. Single γ_{LT} generated the deformation $-$d$L \cdot \gamma_{LT} \cdot$ sinα in x direction [see Fig. 8.48(c)].

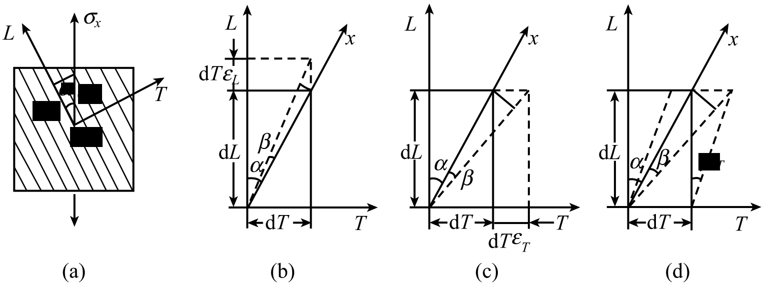


Fig. 8.48 The relation of off-axis tensile strain with L-T directional strain:

(a) unit cell; (b) effect of ε_L; (c) effect of ε_T; (d) effect of γ_{LT}.

Therefore, because the increment of $\mathrm{d}x \cdot \varepsilon_x$ which is generated by σ_x in x direction, it is identical to the sum of above three increments, that is:

$$\varepsilon_x \mathrm{d}x = \varepsilon_L \cos\alpha \mathrm{d}L + \varepsilon_T \sin\alpha \mathrm{d}T - \gamma_{LT} \sin\alpha \mathrm{d}L$$

While $\dfrac{\mathrm{d}L}{\mathrm{d}x} = \cos\alpha$, $\dfrac{\mathrm{d}T}{\mathrm{d}x} = \sin\alpha$, so

Analyze the relationship of deformation in the same way, we get:

$$\left.\begin{aligned} \varepsilon_x &= \varepsilon_L \cos^2\alpha + \varepsilon_T \sin^2\alpha - \gamma_{LT} \sin\alpha\cos\alpha \\ \varepsilon_y &= \varepsilon_L \sin^2\alpha + \varepsilon_T \cos^2\alpha + \gamma_{LT} \sin\alpha\cos\alpha \\ \gamma_{xy} &= (\varepsilon_L - \varepsilon_T)\sin 2\alpha + \gamma_{LT}\cos 2\alpha \end{aligned}\right\} \tag{8.132}$$

Written in matrix mode, that is:

$$\begin{Bmatrix} \varepsilon_x \\ \varepsilon_y \\ \gamma_{xy} \end{Bmatrix} = \begin{bmatrix} m^2 & n^2 & -mn \\ n^2 & m^2 & mn \\ 2mn & -2mn & m^2 - n^2 \end{bmatrix} \begin{Bmatrix} \varepsilon_L \\ \varepsilon_T \\ \gamma_{LT} \end{Bmatrix} \tag{8.133}$$

(3) E_x, μ_{xy}.

The effect of σ_L, σ_T, τ_{LT} in orthoaxis direction, the generated strain in orthoaxis direction obey the generalized Hooke's law.

$$\left.\begin{aligned} \varepsilon_L &= \frac{\sigma_L}{E_L} - \mu_{TL}\frac{\sigma_T}{E_T} \\ \varepsilon_T &= -\mu_{LT}\frac{\sigma_L}{E_L} + \frac{\sigma_T}{E_T} \\ \gamma_{LT} &= \frac{\tau_{LT}}{G_{LT}} \end{aligned}\right\} \tag{8.134}$$

By the Maxwell reciprocity law, there is:

$$\mu_{TL} = \mu_{LT}\frac{E_T}{E_L} \tag{8.135}$$

Insert (8.124) and (8.135) to (8.134), then be inserted to (8.132), we obtain:

$$\left.\begin{aligned}
\varepsilon_x &= \frac{\sigma_x}{E_L}\cos^4\alpha + \frac{\sigma_x}{E_T}\sin^4\alpha - 2\mu_{LT}\frac{\sigma_x\cos^2\alpha\sin^2\alpha}{E_L} + \frac{\sigma_x\cos^2\alpha\sin^2\alpha}{G_{LT}}\\
\varepsilon_y &= \frac{\sigma_x}{E_L}\left[\cos^2\alpha\sin^2\alpha + \frac{E_L}{E_T}\cos^2\alpha\sin^2\alpha\right.\\
&\quad\left. -\mu_{LT}(\cos^4\alpha+\sin^4\alpha) - \frac{E_L}{G_{LT}}\sin^2\alpha\cos^2\alpha\right]\\
&= \varepsilon_x E_x\left[\frac{1}{4}\left(\frac{1}{E_L}+\frac{1}{E_T}+\frac{2\mu_{LT}}{E_L}-\frac{1}{G_{LT}}\right)\sin^2 2\alpha - \frac{\mu_{LT}}{E_L}\right]\\
\gamma_{xy} &= -\frac{\sigma_x}{E_L}\left[\frac{E_L}{E_T}+\mu_{LT}-\frac{1}{2}\frac{E_L}{G_{LT}} - (1+2\mu_{LT}+\frac{E_L}{E_T}-\frac{E_L}{G_{LT}})\cos^2\alpha\right]\\
&\quad\times\sin 2\alpha = -m_x\frac{\sigma_x}{E_L}
\end{aligned}\right\} \tag{8.136}$$

Where, m_x is the additional strain coefficient or crossed elastic coefficient:

$$m_x = \left[\frac{E_L}{E_T}+\mu_{LT}-\frac{1}{2}\frac{E_L}{G_{LT}} - \left(1+2\mu_{LT}+\frac{E_L}{E_T}-\frac{E_L}{G_{LT}}\right)\cos^2\alpha\right]\sin 2\alpha \tag{8.137}$$

So

$$\frac{1}{E_x} = \frac{\varepsilon_x}{\sigma_x} = \frac{\cos^4\alpha}{E_L} + \frac{\sin^4\alpha}{E_T} + \frac{1}{4}\left[\frac{1}{G_{LT}} - \frac{2\mu_{LT}}{E_L}\right]\sin^2 2\alpha \tag{8.138}$$

$$\mu_{xy} = -\frac{\varepsilon_y}{\varepsilon_x} = -E_x\left[\frac{1}{4}\left(\frac{1}{E_L}+\frac{1}{E_T}+\frac{2\mu_{LT}}{E_L}-\frac{1}{G_{LT}}\right)\sin^2 2\alpha - \frac{\mu_{LT}}{E_L}\right] \tag{8.139}$$

Similarly, suppose $\sigma_y \neq 0, \sigma_x = 0, \tau_{xy} = 0$, that is, off-axis elastic coefficient under single σ_y effect can be deduced.

$$\frac{1}{E_y} = \frac{\sin^4\alpha}{E_L} + \frac{\cos^4\alpha}{E_T} + \frac{1}{4}\left(\frac{1}{G_{LT}} - \frac{2\mu_{LT}}{E_L}\right)\sin^2 2\alpha \tag{8.140}$$

$$\gamma_{xy} = -m_y\cdot\frac{\sigma_y}{E_L} \tag{8.141}$$

Where, m_y is the additional strain coefficient or crossed elastic coefficient:

$$m_y = \left[\ \frac{E_L}{E_T}+\mu_{LT}-\frac{E_L}{2G_{LT}} - \left(1+2\mu_{LT}+\frac{E_L}{E_T}-\frac{E_L}{G_{LT}}\right)\sin^2\alpha\ \right]\sin 2\alpha \tag{8.142}$$

This shows that when unidirectional composite is in off-axis single stress, it has not only normal strain in x and y directions, but also shear strain in x-y direction.

2) Shear behaviors G_{xy}

Suppose σ_x=0, σ_y=0, τ_{xy} $\neq$0 (single effect of τ_{xy}). Select the unit body which is shown in Fig. 8.49.

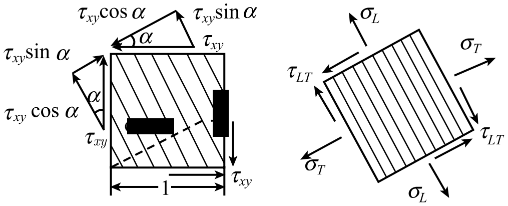


Fig. 8.49 The relation between off-axis shear stress with L-T directional stress.

Base on the condition of static equilibrium:

$$\left.\begin{aligned}\sigma_L &= \tau_{xy}\sin\alpha\cos\alpha+\tau_{xy}\cos\alpha\sin\alpha=\tau_{xy}\sin 2\alpha\\ \sigma_T &= -\tau_{xy}\cos\alpha\sin\alpha-\tau_{xy}\sin\alpha\cos\alpha=-\tau_{xy}\sin 2\alpha\\ \tau_{LT} &= \tau_{xy}\cos\alpha\cos\alpha-\tau_{xy}\sin\alpha\sin\alpha=\tau_{xy}\cos 2\alpha\end{aligned}\right\}\tag{8.143}$$

Insert formula (8.143) to (8.134), obtain:

$$\left.\begin{aligned}\varepsilon_L &= \frac{\tau_{xy}}{E_L}\sin 2\alpha+\frac{\tau_{xy}}{E_T}\mu_{TL}\sin 2\alpha\\ \varepsilon_T &= -\frac{\tau_{xy}}{E_T}\sin 2\alpha-\frac{\tau_{xy}}{E_L}\mu_{LT}\sin 2\alpha\\ \gamma_{LT} &= \frac{\tau_{xy}}{G_{LT}}\cos 2\alpha\end{aligned}\right\}\tag{8.144}$$

Insert (8.144) and (8.135) to (8.132), we get:

$$\left.\begin{aligned}\varepsilon_x &= -m_x\frac{\tau_{xy}}{E_L}\\ \varepsilon_y &= -m_y\frac{\tau_{xy}}{E_L}\\ \gamma_{xy} &= \frac{\tau_{xy}}{E_L}\left(\frac{E_L}{E_T}+2\mu_{LT}+1\right)\sin^2 2\alpha+\frac{\tau_{xy}}{G_{LT}}\cos^2 2\alpha\end{aligned}\right\}\tag{8.145}$$

So that

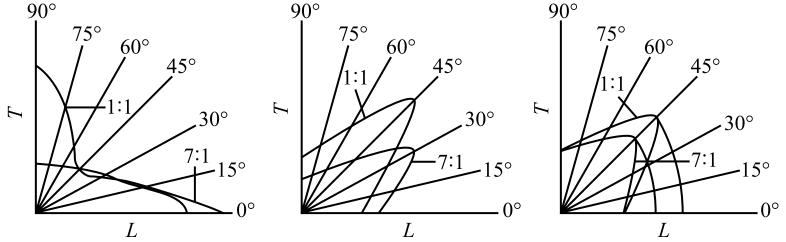
$$\frac{1}{G_{xy}}=\frac{\gamma_{xy}}{\tau_{xy}}=\frac{\cos^2 2\alpha}{G_{LT}}+\left(\frac{1}{E_L}+\frac{1}{E_T}+\frac{2\mu_{LT}}{E_L}\right)\sin^2 2\alpha \tag{8.146}$$

This shows that when off-axis of unidirectional composite is in shear, not only producing shear strain, but also the liner strain.

3) Examples of directional equation

From the formula deduced above about off-axis elastic coefficients, we know that the elastic coefficients E_x, G_{xy}, μ_{xy} of unidirectional fiber composites is the periodic function of the stacking-ply directional angle α; it is also a symmetric function, α= 0° is the symmetric axis, with the same elastic coefficient of the angle α and $-\alpha$. The elastic coefficient will not change in symmetric crossed plies ($\pm\alpha$). Similar to strength, elastic coefficients in any other directions can be calculated so long as the orthoaxis elastic coefficients E_L, E_T, G_{LT} and μ_{LT} of unidirectional composites are known.

Fig. 8.50 shows the relationship between loading direction and E_x, G_{xy}, μ_{xy} of orthogonal fiber composites which were made with glass cloth of 1:1 and 7:1. From the figure, E_x of 1:1 cloth in direction of 0° and 90° is the maximum, and G_{xy} is the minimum; E_x in 45° is the minimum, G_{xy} and μ_{xy} are the maximum. E_x of 7:1 cloth in 0° is the maximum, E_x in 90° is the minimum; G_{xy} in 90° is the minimum; G_{xy} in about 30° is the maximum; μ_{xy} in 90° is the minimum, μ_{xy} in 45° is the maximum.



(a) (b) (c)

Fig. 8.50 The relation of E_x, G_{xy}, μ_{xy} with loading direction: (a)E_x; (b) G_{xy} ; (c) μ_{xy}.

8.7.4 The physical meaning of additional strain coefficient m_x and m_y

When isotropic materials under stress, the normal stress does not form shear strain and shear stress does not form normal strain. Compare to the isotropic materials, one additional strain will be generated when the anisotropic materials are under stress. One more shear strain will be generated when the anisotropic materials under tension along the direction of x (or y), i.e., the additional shear strain γ_{xy} be caused by σ_x(or σ_y). When they are under shear stress, there is another two additional normal strains, i.e., the additional strain ε_x and $\varepsilon_y$be caused by τ_{xy}.

According to equations (8.136), (8.141) and (8.145), we have:

$$\gamma_{xy} = -m_x \frac{\sigma_x}{E_L}$$

$$\gamma_{xy} = -m_y \frac{\sigma_y}{E_L}$$

$$\varepsilon_x = -m_x \frac{\tau_{xy}}{E_L}$$

$$\varepsilon_y = -m_y \frac{\tau_{xy}}{E_L}$$

In the four equations above, m_x represents the shear strain in x-y direction that is caused by the normal stress σ_x in x direction. It also represents the elastic coefficient of normal strain in x direction which is caused by the shear stress τ_{xy} in x-y direction. Likewise, m_y represents the counterpart in y direction.

For every certain composite materials, $E_L$is a constant, so m_x and m_y directly reflect the size of shear strain that is caused by unit normal stress or the size of normal strain that is caused by unit shear stress under loading in any direction. It is an elastic coefficient as same as *E*, μ and G. The differences is that *E*, μ and G reflect linear relations between normal stress and normal strain or shear stress and shear strain, while m_x and m_y reflect linear relations between normal stress and shear strain or shear stress and normal strain. m_x and m_y are expressed by equation (8.137) and (8.142).

$$m_y = \left[\frac{E_L}{E_T} + \mu_{LT} - \frac{1}{2}\frac{E_L}{G_{LT}} - \left(1 + 2\mu_{LT} + \frac{E_L}{E_T} - \frac{E_L}{G_{LT}}\right)\sin^2\alpha\right]\sin 2\alpha \tag{8.142}$$

Analyzing (8.137) and (8.142), we can see that m_x and m_y have the following characteristics.

(1) When orthogonal elastic coefficient E_L,E_T,G_{LT} and μ_{LT} are known, we can get m_x and m_y of any α angle.

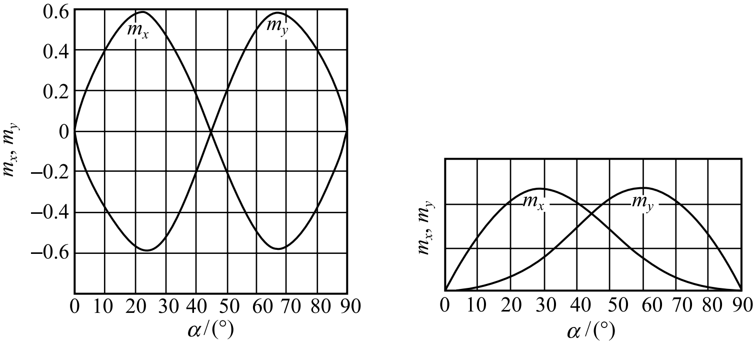
(2) m_x and m_y are also periodic functions of ply direction angle, with a period from 0° to 180°.

(3) m_x and m_y are anti-symmetric functions of α angle. It means $\alpha°$ and $-\alpha°$ have the same value with opposite sign and negative to each other. $\alpha° = 0$ is used as the anti-symmetry axis. Therefore for crossed $\pm\alpha$ ply laminates the two additional strains counteract with each other. If there are deviations in stacking layers, that is when plus angle is not equal to minus angle, then the additional strain will not be cancelled out completely. The residual additional strain will generate internal stress and that results in the deformation of products.

(4) m_x and m_y are functions of sin 2α. When $\alpha = 0°$ or 90°, $m_x = m_y = 0$ (positive axis condition). When composite materials under stress in longitude or latitude, normal stress will not cause additional shear strain and shear stress will not cause additional normal strain.

(5) For orthogonal composites with 1:1 balanced type, since $E_L = E_T$, when loading at $\alpha = \pm 45°$, $m_x = m_y = 0$. At this time, the curve of m_x and m_y changing with regard to direction angle is symmetric [Fig. 8.51(a)].

(6) For orthogonal composites reinforced by unidirectional cloth, since $E_L \neq \mathrm{E}_T$, when loading at $\alpha = \pm 45$, $m_x, m_y \neq 0$. At this time, the curve of m_x and m_y change with direction angle is dissymmetric [Fig. 8.51(b)].



(a) (b)

Fig. 8.51 m_x, m_y of orthogonal composites:

(a) 1:1 balanced type; (b) 7:1 unidirectional cloth.

8.7.5 Unique elastic system of unidirectional and orthogonal composite materials

1) Stress-strain relationship of isotropic material

For isotropic material, normal stress cause normal strain (elastic modulus E cause elongation in the forced direction and Poisson's ratio μ cause shortening in vertical direction of stress), and shear stress only cause angle strain.

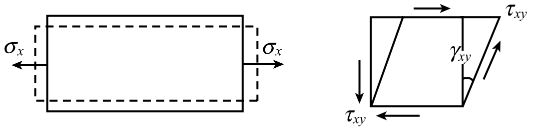
Under single σ_x [Fig. 8.52(a)], we get:

$$\varepsilon_x = \frac{\sigma_x}{E}$$

$$\varepsilon_y = -\mu\frac{\sigma_x}{E}$$

Under single τ_{xy} [Fig. 8.52(b)], we get:

$$\gamma_{xy} = \frac{\tau_{xy}}{G}$$



(a) (b)

Fig. 8.52 Stress-strain relationship of isotropic materials:

(a) normal stress; (b) shear stress.

Under in-plane stress, stress-strain relationship is given by:

$$\left\{\begin{array}{c}\varepsilon_x\\ \varepsilon_y\\ \gamma_{xy}\end{array}\right\}=\left\{\begin{array}{ccc}\dfrac{1}{E} & \dfrac{-\mu}{E} & 0\\ \dfrac{-\mu}{E} & \dfrac{1}{E} & 0\\ 0 & 0 & \dfrac{1}{G}\end{array}\right\}\left\{\begin{array}{c}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{array}\right\} \tag{8.147}$$

The relationship among three elastic coefficients is given by:

$$G=\frac{E}{2(1+\mu)}$$

2) Stress-strain relationship of orthoaxis composite materials

In condition of positive axis, since $m_x = m_y = 0$, like isotropic materials, normal stress only generates elongation of elastic modulus and contraction of Poisson's ratio and shear stress only generates angle strain of shear modulus. However, due to fiber′s directivity, elastic coefficient has suffix. Under plane stress (σ_L, σ_T, τ_{LT}), the stress - strain relationship is given by:

$$\left\{\begin{array}{c}\varepsilon_L\\ \varepsilon_T\\ \gamma_{LT}\end{array}\right\}=\left\{\begin{array}{ccc}\dfrac{1}{E_L} & \dfrac{-\mu_{TL}}{E_T} & 0\\ \dfrac{-\mu_{LT}}{E_L} & \dfrac{1}{E_T} & 0\\ 0 & 0 & \dfrac{1}{G_{LT}}\end{array}\right\}\left\{\begin{array}{c}\sigma_L\\ \sigma_T\\ \tau_{LT}\end{array}\right\} \tag{8.148}$$

There are totally five elastic coefficients E_L, E_T, G_{LT}, μ_{LT} and μ_{TL}, four of them are independent, which is expressed by:

$$\frac{\mu_{LT}}{E_L}=\frac{\mu_{TL}}{E_T}$$

3) Stress-strain relationship of off-axis composite materials

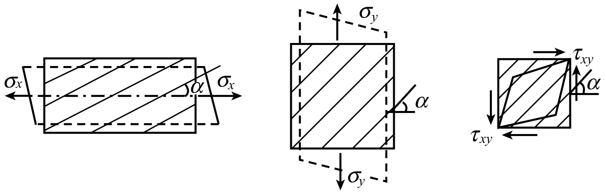
(1) Single stress function.

Single σ_x generates three strains [Fig. 8.53(a)], they are:

$$\varepsilon_x=\frac{\sigma_x}{E_x}$$

$$\varepsilon_y=-\mu_{xy}\frac{\sigma_x}{E_x}$$

$$\gamma_{xy}=-m_x\frac{\sigma_x}{E_L}$$



(a) (b) (c)

Fig. 8.53 Stress-strain relationship of off-axis composites:

(a) strain caused by σ_x; (b) strain caused by σ_y; (c) strain caused by τ_{xy}.

Single σ_y generates three strains [Fig. 8.53(b)], they are:

$$\varepsilon_y = \frac{\sigma_y}{E_y}$$

$$\varepsilon_x = -\mu_{yx}\frac{\sigma_y}{E_y}$$

$$\gamma_{xy} = -m_y\frac{\sigma_y}{E_L}$$

Single τ_{xy} generates three strains [Fig. 8.53(c)], they are:

$$\gamma_{xy} = \frac{\tau_{xy}}{G_{xy}}$$

$$\varepsilon_x = -m_x\frac{\tau_{xy}}{E_L}$$

$$\varepsilon_y = -m_y\frac{\tau_{xy}}{E_L}$$

(2) In-plane stress function.

Under in-plane stress (σ_x, σ_y, τ_{xy}), stress-strain relationship of composites is the integration expression of generalizd Hooke's law of composites under external load, which is shown:

$$\left\{\begin{array}{c}\varepsilon_x\\ \varepsilon_y\\ \gamma_{xy}\end{array}\right\} = \left\{\begin{array}{ccc}\dfrac{1}{E_x} & \dfrac{-\mu_{yx}}{E_y} & \dfrac{-m_x}{E_L}\\ \dfrac{-\mu_{xy}}{E_x} & \dfrac{1}{E_y} & \dfrac{-m_y}{E_L}\\ \dfrac{-m_x}{E_L} & \dfrac{-m_y}{E_L} & \dfrac{1}{G_{xy}}\end{array}\right\}\left\{\begin{array}{c}\sigma_x\\ \sigma_y\\ \tau_{xy}\end{array}\right\} \tag{8.149}$$

The number of elastic coefficients is increased to seven with increase of m_x and m_y, and modulus matrix is still symmetric matrix, so we get:

$$\frac{\mu_{xy}}{E_x} = \frac{\mu_{yx}}{E_y}$$

8.7.6 The strength criterion of composite materials

In orthoaxis coordinates system, if unidirectional laminate is applied under single stress, its ultimate stress is determined by experiment; usually we define these ultimate stresses as basic strengths of laminate. Under in-plane stress, unidirectional composites have five basic strengths: σ_{Lu} is longitudinal tensile strength; σ_{-Lu} is longitudinal compressive strength; σ_{Tu} is transverse tensile strength; σ_{-Tu} is transverse compression strength; τ_{LTu} is in-plane shear strength.

1) Maximum stress criterion

When any of stress components on the material orthoaxis reaches the basic strength, the material will be destroyed.

$$\left.\begin{aligned} &-\sigma_{-Lu} < \sigma_L < \sigma_{Lu} \\ &-\sigma_{-Tu} < \sigma_T < \sigma_{Tu} \\ &|\tau_{LT}| < \tau_{LTu} \end{aligned}\right\} \tag{8.150}$$

When inequality (8.150) is right, the material is safe. If any inequality in (8.150) is not met, the material will break.

Also when any of strain components on material orthoaxis reaches the ultimate strain, the material will be destroyed. This is the maximum strain criterion.

2) Tsai-Hill failure criterion

For composite materials under in-plane stress, i.e., under coactions of normal stress and shear stress, we can check strength on the basis of tensile (compressive) strength and edge shear strength by using Tsai-Hill failure criterion.

When in-plane stress function in x-y direction, there is:

$$\left(\frac{\sigma_x}{\sigma_{xu}}\right)^2 + \left(\frac{\sigma_y}{\sigma_{yu}}\right)^2 - \frac{\sigma_x\sigma_y}{\sigma_{xu}\sigma_{yu}} + \left(\frac{\tau_{xy}}{\tau_{xyu}}\right)^2 = 1 \tag{8.151}$$

When in-plane stress function in L-T direction, there is:

$$\left(\frac{\sigma_L}{\sigma_{Lu}}\right)^2 + \left(\frac{\sigma_T}{\sigma_{Tu}}\right)^2 - \frac{\sigma_L\sigma_T}{\sigma_{Lu}\sigma_{Tu}} + \left(\frac{\tau_{LT}}{\tau_{LTu}}\right)^2 = 1$$

For in-plane stress in x-y direction, we can use (8.131) to transform (σ_x, σ_y, τ_{xy}) to (σ_L, σ_T, τ_{LT}) firstly, and then use (8.125) to check it.

8.8 Basic mechanical properties of multi-directional composite materials

We previously have illustrated the basic mechanical properties of unidirectional and orthogonal composite materials, as well as how to estimate the basic mechanical properties of unidirectional or two-directional composite materials when they are loaded in any directions. In order to play characteristics of composite materials, ply direction is arbitrary. So we can stack plies in accordance with the demand of stress on products, for improving the bearing ability of the products.

The composite materials which are composed of layers in random directions, "multi-directional composite materials", are also called combination laminate. In practical application, the stress state of composites product is mostly the in-plane stress state, mainly bearing functions of tension, compression and edge shear stress. Therefore, the usually used multi-directional composite materials are composed of orthogonal ply along longitude-latitude and ±45° ply. The orthogonal ply of these multi-directional composites are mainly used for bearing tension and compression, while ±45° ply is mainly used for bearing the edge shear stress. The following examples will illustrate the label method of combination laminate stacking-ply.

$[0_5/90_2/45/-45_3]_\mathrm{S}$, i.e., $[0_5/90_2/45/-45_3/-45_3/45/90_2/0_5]_\mathrm{T}$. The down subscript S represents mirror symmetrical laminate, which means plies in the square bracket are combined with its mirror symmetry; the down subscript T represents asymmetric laminate, and the square bracket show all the ply in order. We may shorten the representation by combining plus ply and minus ply, for example, $[0/45/-45]_\mathrm{S} = [0/\pm45]_\mathrm{S}$. We also can use the multiple sign method, for example, $[0/90/0/90]_\mathrm{T}= [0/90]_{2\mathrm{T}}$, $[0/90/\pm45/0/90/\pm45/0/90/\pm45]_\mathrm{S}= [0/90/\pm45]_{3\mathrm{S}}$. $[(\pm30)_2/90/\overline{90}]_\mathrm{S}$ represents $[(\pm30)_2/90/90/90/(\pm30)_2]_\mathrm{T}$, i.e., $\overline{90}$ represents that 90° is monolayer in the middle of thickness.

8.8.1 Estimating mechanical properties of composite laminates

There are many fiber directions in composite laminates, so it is much complicated to estimate the mechanical properties of composite laminates using properties of fiber and matrix. In order to simplify the calculation, usually we estimate the properties using properties of unidirectional laminate. Generally, there are two steps to carry it.

There are two ways to get mechanical properties of unidirectional laminate at the first step. They are: ① estimating properties of the unidirectional laminate in L and T directions by performances of raw materials, then calculate the performance in x and y direction with angle α. This method brings much more accumulative error, and the actual performance of materials will not be fully equal to its theory predicted value. ② Determine the actual performance of the unidirectional laminate by experiment, which brings less errors.

Use the performance of the unidirectional laminate to evaluate the performance of composite laminate at the second step. The easier method and also rough estimation are the calculation using the rule of mixture.

1) Utilizing the rule of mixture to estimate the mechanical properties of multi-

directional composite laminates

Suppose the composite plate is composed of unidirectional laminate with n kinds of different forms. Use σ, E, τ and G to express average stress and average modulus of the composite laminate's entire section; use σ_i, E_i, τ_i and G_i to express stress and modulus of the i layer; F_i is the percentage of cross sectional area of the i layer.

According to the rule of mixture, we have:

$$\sigma = \sum_{i=1}^{n} \sigma_i F_i$$

$$E = \sum_{i=1}^{n} E_i F_i$$

$$\tau = \sum_{i=1}^{n} \tau_i F_i$$

$$G = \sum_{i=1}^{n} G_i F_i$$

Putting strength and modulus of the unidirectional laminate σ_{iu}, τ_{iu}, E_i, G_i and the percentage of the cross-sectional area F_i into the above equations, we will get the estimation value of composite laminate's strength and modulus.

The Following example illustrates utilizing the rule of mixture to estimate basic mechanical properties of the multi-directional composite plate.

[Example 8.2] There is a piece of glass cloth with 4:1 latitude and longitude fiber content ratio, with single laminate along its latitude and longitude (*L-T* direction); another piece of glass cloth with 1:1 latitude and longitude fiber content ratio, with single laminate crossed stacking in ±45° with L direction of the 4:1 cloth, these two kinds of single laminates made up composite laminates. The question is to evaluate the average tensile strength and the tensile elastic modulus of the composite laminates in L direction, and the average shear strength and shear elastic modulus of the composite plate in *L-T* direction.

Known: parameters of the 4:1 unidirectional laminate in *LT* direction are:

$$E_{4:1L} = 2.5 \times 10^5 \mathrm{kg/cm^2}$$

$$\sigma_{4:1Lb} = 5000\,\mathrm{kg/cm^2}$$

$$G_{4:1LT} = 2.9 \times 10^4\ \mathrm{kg/cm^2}$$

$$\tau_{4:1LTb} = 670\,\mathrm{kg/cm^2}$$

Known When the 1:1 unidirectional laminate crossed stacking in ±45° with L direction, its parameters along 4:1 unidirectional laminate in *L-T* direction are:

$$E_{1:145^\circ} = 1.02 \times 10^5\ \mathrm{kg/cm^2}$$

$$\sigma_{1:145^\circ b} = 1400\ \mathrm{kg/cm^2}$$

$$G_{1:145^0} = 7.03 \times 10^4\ \mathrm{kg/cm^2}$$

$$\tau_{1:145^\circ b} = 1300\ \mathrm{kg/cm^2}$$

When the percentage of laminate with ±45° ply is respectively 10%, 20%, 30%, 40% and 50%, calculate the average tensile strength and the tensile elastic modulus of the composite laminates in *L* direction, and the average shear strength and shear elastic modulus of the composite laminates in *L*-*T* direction.

Solution Applying the rule of mixture, the average tensile strength is calculated as follows.

$$\sigma_{Lb} = \sigma_{4:1Lb} \times F_{4:1} + \sigma_{1:145b} \times F_{1:1}$$

Substituting the known data into it, we get:

$$\sigma_{Lb} = 5000 \times \left\{\begin{array}{l} 90\% \\ 80\% \\ 70\% \\ 60\% \\ 50\% \end{array}\right. + 1400 \times \left\{\begin{array}{l} 10\% \\ 20\% \\ 30\% \\ 40\% \\ 50\% \end{array}\right. = \left\{\begin{array}{l} 4640 \\ 4280 \\ 3920 \\ 3560 \\ 3200 \end{array}\right. (\mathrm{kg/cm^2})$$

The average tensile elastic modulus can be calculated in following.

$$E_L = E_{4:1L} \times F_{4:1} + E_{1:145} \times F_{1:1}$$

Substituting the known data into it, we get:

$$E_L = 2.5 \times 10^5 \times \left\{\begin{array}{l} 90\% \\ 80\% \\ 70\% \\ 60\% \\ 50\% \end{array}\right. + 1.02 \times 10^5 \times \left\{\begin{array}{l} 10\% \\ 20\% \\ 30\% \\ 40\% \\ 50\% \end{array}\right. = \left\{\begin{array}{l} 2.35 \times 10^5 \\ 2.20 \times 10^5 \\ 2.06 \times 10^5 \\ 1.90 \times 10^5 \\ 1.76 \times 10^5 \end{array}\right. (\mathrm{kg/cm^2})$$

The average shear strength can be calculated in following:

$$\tau_{LTb} = \tau_{4:1LTb} \times F_{4:1} + \tau_{1:145b} \times F_{1:1}$$

Substituting the known data into it, we get:

$$\tau_{LTb} = 670 \times \left\{\begin{array}{l} 90\% \\ 80\% \\ 70\% \\ 60\% \\ 50\% \end{array}\right. + 1300 \times \left\{\begin{array}{l} 10\% \\ 20\% \\ 30\% \\ 40\% \\ 50\% \end{array}\right. = \left\{\begin{array}{l} 733 \\ 796 \\ 859 \\ 922 \\ 985 \end{array}\right. (\mathrm{kg/cm^2})$$

The average shear elastic module can be calculated in the following:

$$G_{LT} = G_{4:1LT} \times F_{4:1} + G_{1:145} \times F_{1:1}$$

Put the known data into it, thus we get:

$$G_{LT} = 2.9 \times 10^4 \times \left\{ \begin{array}{l} 90\% \\ 80\% \\ 70\% \\ 60\% \\ 50\% \end{array} \right. + 7.03 \times 10^4 \times \left\{ \begin{array}{l} 10\% \\ 20\% \\ 30\% \\ 40\% \\ 50\% \end{array} \right. = \left\{ \begin{array}{l} 3.31 \times 10^4 \\ 3.73 \times 10^4 \\ 4.14 \times 10^4 \\ 4.55 \times 10^4 \\ 4.97 \times 10^4 \end{array} \right. \quad (\mathrm{kg/cm^2})$$

What we have discussed above is the way to evaluate basic mechanical properties of the multi-directional composite laminates by utilizing the rule of mixture. It should be pointed out that when using the rule of mixture to calculate, the different values μ and m of each single board are not considered, so it brings about additional stress in the composite laminates; at the same time, since each monolayer has a certain thickness, it brings about moment in the composite laminates which is caused by the additional stress. The laminates would warp as a result. So, it is only a rough estimation of basic mechanical properties when we use the rule of mixture. It cannot reflect the real stress state of each monolayer in the composite laminates. The rough estimation of data cannot be for component design.

There are two relatively more accurate ways to do this:

(1) Materials mechanics method: considering different values μ and m of each monolayer laminate, we can deduce stress state equation and use it to evaluate the actual stress of each monolayer laminate in the composite laminate, then compare and check the strength.

(2) Finite element method: taking the performance of unidirectional laminate for known qualification, we utilize finite element method to calculate the stress distribution in frame of the composite laminates, and then design the stacking-ply.

A stress state equation of the composite laminate that is composed of two kinds of monolayer plates will be discussed later.

2) The stress state equation of composite laminate which is composed of two kinds of monolayer laminates

Suppose that there are two kinds of monolayer laminates which are separately represented by "I"and "II". And the longitude and latitude direction of the two kinds of monolayer laminates are separately L_{I}, T_{I} and L_{II}, T_{II}. The multi-directional laminate which is composed of these two kinds of monolayer laminates, each of them has many layers which are supposed to have thickness of t_{I} and t_{II} and the total thickness of t. This multi-directional laminate endures the external load σ_x, σ_y and τ_{xy}. Suppose there is an angle $+\alpha$ between L_{I} and x direction, an angle $-\beta$ between L_{II} and x direction. See Fig. 8.54. We will analyze the basic mechanical properties of the composite laminate in the following.

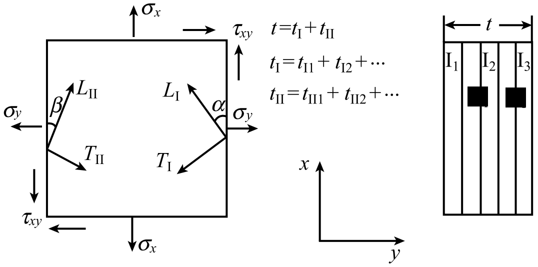


Fig. 8.54 Multi-directional laminate from two kinds of monolayer laminate.

The analysis process is like the basic mechanical properties of unidirectional and two-directional composite materials which we have discussed above, suppose the basic mechanical properties of the two kinds of monolayer laminates for known qualifications (use the previous formula to calculate, or measure it directly). We will use three basic hypothesis qualifications of basic mechanical properties analysis to discuss.

Known qualifications: ① three basic hypothesis; ② basic mechanical performances of each monolayer laminate in *L*-*T* direction which include strength parameters σ_{Lb}, σ_{Tb}, τ_{LTb} and elastic parameters E_L, E_T, G_{LT}, μ_{LT} and μ_{TL}; ③ strength parameters σ_{xb}, σ_{yb}, τ_{xyb} and elastic parameters E_x, E_y, G_{xy} and μ_{xy} of each monolayer laminate in x-y direction having an arbitrary angle α with *L*-*T* direction.

Questions to be solved: when the multi-directional laminate composed of two kinds of monolayer laminates is placed under loading in arbitrary x-y direction, how to evaluate the strength and modulus analysis formula?

Analysis and conclusion: according to the statement we have mentioned above, we will only analyze a special example, but the deduced formula has prevalent meanings.

(1) Base on the balance condition of static (stress state theory).

$$\begin{aligned}\sigma_x\cdot t&=\sigma_{\mathrm{I}x}\cdot t_{\mathrm{I}}+\sigma_{\mathrm{II}x}\cdot t_{\mathrm{II}}\\ \sigma_y\cdot t&=\sigma_{\mathrm{I}y}\cdot t_{\mathrm{I}}+\sigma_{\mathrm{II}y}\cdot t_{\mathrm{II}}\\ \tau_{xy}\cdot t&=\tau_{\mathrm{I}xy}\cdot t_{\mathrm{I}}+\tau_{\mathrm{II}xy}\cdot t_{\mathrm{II}}\end{aligned}\tag{8.152a}$$

or

$$\begin{aligned}\sigma_{\mathrm{II}x}&=(\sigma_x\cdot t-\sigma_{\mathrm{I}x}\cdot t_{\mathrm{I}})/t_{\mathrm{II}}\\ \sigma_{\mathrm{II}y}&=(\sigma_y\cdot t-\sigma_{\mathrm{I}y}\cdot t_{\mathrm{I}})/t_{\mathrm{II}}\\ \tau_{\mathrm{II}xy}&=(\tau_{xy}\cdot t-\tau_{\mathrm{I}xy}\cdot t_{\mathrm{I}})/t_{\mathrm{II}}\end{aligned}\tag{8.152b}$$

Similarly, there is also another set of equation for $\sigma_{\mathrm{I}x}$, $\sigma_{\mathrm{I}y}$ and $\tau_{\mathrm{I}xy}$, which is omitted here.

(2) Base on the condition of identical deformation (strain state theory).

$$\begin{aligned}\varepsilon_x &= \varepsilon_{\mathrm{I}x} = \varepsilon_{\mathrm{II}x}\\ \varepsilon_y &= \varepsilon_{\mathrm{I}y} = \varepsilon_{\mathrm{II}y}\\ \gamma_{xy} &= \gamma_{\mathrm{I}xy} = \gamma_{\mathrm{II}xy}\end{aligned}\tag{8.153}$$

(3) Base on the elastic hypothesis (generalized Hooke's law).
Here we consider the function of μ and m.
For the layer I, we have:

$$\begin{aligned}\varepsilon_{\mathrm{I}x} &= \frac{\sigma_{\mathrm{I}x}}{E_{\mathrm{I}x}} - \mu_{\mathrm{I}yx}\frac{\sigma_{\mathrm{I}y}}{E_{\mathrm{I}y}} - m_{\mathrm{I}x}\frac{\tau_{\mathrm{I}xy}}{E_{\mathrm{I}L}}\\ \varepsilon_{\mathrm{I}y} &= \frac{\sigma_{\mathrm{I}y}}{E_{\mathrm{I}y}} - \mu_{\mathrm{I}xy}\frac{\sigma_{\mathrm{I}x}}{E_{\mathrm{I}x}} - m_{\mathrm{I}y}\frac{\tau_{\mathrm{I}xy}}{E_{\mathrm{I}L}}\\ \gamma_{\mathrm{I}xy} &= \frac{\tau_{\mathrm{I}xy}}{G_{\mathrm{I}xy}} - m_{\mathrm{I}x}\frac{\sigma_{\mathrm{I}x}}{E_{\mathrm{I}L}} - m_{\mathrm{I}y}\frac{\sigma_{\mathrm{I}y}}{E_{\mathrm{I}L}}\end{aligned}\tag{8.154a}$$

For the layer II, we have:

$$\begin{aligned}\varepsilon_{\mathrm{II}x} &= \frac{\sigma_{\mathrm{II}x}}{E_{\mathrm{II}x}} - \mu_{\mathrm{II}yx}\frac{\sigma_{\mathrm{II}y}}{E_{\mathrm{II}y}} - m_{\mathrm{II}x}\frac{\tau_{\mathrm{II}xy}}{E_{\mathrm{II}L}}\\ \varepsilon_{\mathrm{II}y} &= \frac{\sigma_{\mathrm{II}y}}{E_{\mathrm{II}y}} - \mu_{\mathrm{II}xy}\frac{\sigma_{\mathrm{II}x}}{E_{\mathrm{II}x}} - m_{\mathrm{II}y}\frac{\tau_{\mathrm{II}xy}}{E_{\mathrm{II}L}}\\ \gamma_{\mathrm{II}xy} &= \frac{\tau_{\mathrm{II}xy}}{G_{\mathrm{II}xy}} - m_{\mathrm{II}x}\frac{\sigma_{\mathrm{II}x}}{E_{\mathrm{II}L}} - m_{\mathrm{II}y}\frac{\sigma_{\mathrm{II}y}}{E_{\mathrm{II}L}}\end{aligned}\tag{8.154b}$$

(4) Put the generalized Hooke's law and the balance condition of static into the condition of identical formation, eliminate $\sigma_{\mathrm{II}x}$, $\sigma_{\mathrm{II}y}$ and $\tau_{\mathrm{II}xy}$ (formula 8.152 b), we get:

$$\begin{aligned}A_{11}\sigma_{\mathrm{I}x} + A_{12}\sigma_{\mathrm{I}y} + A_{13}\tau_{\mathrm{I}xy} &= \frac{t}{t_{\mathrm{I}}\cdot t_{\mathrm{II}}}\left(\frac{\sigma_x}{E_{\mathrm{II}x}} - \mu_{\mathrm{II}yx}\frac{\sigma_y}{E_{\mathrm{II}y}} - m_{\mathrm{II}x}\frac{\tau_{xy}}{E_{\mathrm{II}L}}\right)\\ A_{21}\sigma_{\mathrm{I}x} + A_{22}\sigma_{\mathrm{I}y} + A_{23}\tau_{\mathrm{I}xy} &= \frac{t}{t_{\mathrm{I}}\cdot t_{\mathrm{II}}}\left(-\mu_{\mathrm{II}xy}\frac{\sigma_x}{E_{\mathrm{II}x}} + \frac{\sigma_y}{E_{\mathrm{II}y}} - m_{\mathrm{II}x}\frac{\tau_{xy}}{E_{\mathrm{II}L}}\right)\\ A_{31}\sigma_{\mathrm{I}x} + A_{32}\sigma_{\mathrm{I}y} + A_{33}\tau_{\mathrm{I}xy} &= \frac{t}{t_{\mathrm{I}}\cdot t_{\mathrm{II}}}\left(-m_{\mathrm{II}x}\frac{\sigma_x}{E_{\mathrm{II}L}} - m_{\mathrm{II}y}\frac{\sigma_y}{E_{\mathrm{II}L}} + \frac{\tau_{xy}}{G_{\mathrm{II}xy}}\right)\end{aligned}\tag{8.155a}$$

Similarly, eliminate $\sigma_{\mathrm{I}x}$, $\sigma_{\mathrm{I}y}$ and $\tau_{\mathrm{I}xy}$, get another equation:

$$A_{11}\sigma_{\mathrm{II}x} + A_{12}\sigma_{\mathrm{II}y} + A_{13}\tau_{\mathrm{II}xy} = \frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}}\cdot\left(\frac{\sigma_x}{E_{\mathrm{I}x}} - \mu_{\mathrm{I}yx}\frac{\sigma_y}{E_{\mathrm{I}y}} - m_{\mathrm{I}x}\frac{\tau_{xy}}{E_{\mathrm{I}L}}\right)$$

$$A_{21}\sigma_{\mathrm{II}x} + A_{22}\sigma_{\mathrm{II}y} + A_{23}\tau_{\mathrm{II}xy} = \frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}} \cdot \left(-\mu_{\mathrm{I}xy}\frac{\sigma_x}{E_{\mathrm{I}x}} + \frac{\sigma_y}{E_{\mathrm{I}y}} - m_{\mathrm{I}y}\frac{\tau_{xy}}{E_{\mathrm{I}L}}\right) \tag{8.155b}$$

$$A_{31}\sigma_{\mathrm{II}x} + A_{32}\sigma_{\mathrm{II}y} + A_{33}\tau_{\mathrm{II}xy} = \frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}} \cdot \left(-m_{\mathrm{I}x}\frac{\sigma_x}{E_{\mathrm{I}L}} - m_{\mathrm{I}y}\frac{\sigma_y}{E_{\mathrm{I}L}} + \frac{\tau_{xy}}{G_{\mathrm{I}xy}}\right)$$

Where

$$A_{11} = \frac{1}{E_{\mathrm{I}x}\cdot t_{\mathrm{I}}} + \frac{1}{E_{\mathrm{II}x}\cdot t_{\mathrm{II}}}$$

$$A_{12} = \frac{-\mu_{\mathrm{I}yx}}{E_{\mathrm{I}y}\cdot t_{\mathrm{I}}} - \frac{\mu_{\mathrm{II}yx}}{E_{\mathrm{II}y}\cdot t_{\mathrm{II}}}$$

$$A_{13} = A_{31} = -\frac{m_{\mathrm{I}x}}{E_{\mathrm{I}L}\cdot t_{\mathrm{I}}} - \frac{m_{\mathrm{II}x}}{E_{\mathrm{II}L}\cdot t_{\mathrm{II}}}$$

$$A_{21} = -\frac{\mu_{\mathrm{I}xy}}{E_{\mathrm{I}x}\cdot t_{\mathrm{I}}} - \frac{\mu_{\mathrm{II}xy}}{E_{\mathrm{II}x}\cdot t_{\mathrm{II}}}$$

$$A_{22} = \frac{1}{E_{\mathrm{I}y}\cdot t_{\mathrm{I}}} + \frac{1}{E_{\mathrm{II}y}\cdot t_{\mathrm{II}}}$$

$$A_{23} = A_{32} = -\frac{m_{\mathrm{I}y}}{E_{\mathrm{I}L}\cdot t_{\mathrm{I}}} - \frac{m_{\mathrm{II}y}}{E_{\mathrm{II}L}\cdot t_{\mathrm{II}}}$$

$$A_{31} = A_{13}$$

$$A_{32} = A_{23}$$

$$A_{33} = \frac{1}{G_{\mathrm{I}xy}\cdot t_{\mathrm{I}}} + \frac{1}{G_{\mathrm{II}xy}\cdot t_{\mathrm{II}}}$$

Suppose the stresses σ_x, σ_y and τ_{xy} which are caused by the external load are known. There are three unknown values $\sigma_{\mathrm{I}x}$, $\sigma_{\mathrm{I}y}$, $\tau_{\mathrm{I}xy}$ and $\sigma_{\mathrm{II}x}$, $\sigma_{\mathrm{II}y}$, $\tau_{\mathrm{II}xy}$ in equations (8.155a) and (8.155b) respectively. Since there are three equations in each equation group, the unknown numbers can be solved by simultaneous equations, i.e. when the composite laminate is under loading in any direction, the stress value of each monolayer laminate in its direction can be calculated. On the contrary, suppose the strength values of each monolayer laminate in any x-y direction are known, utilizing the above equations to get the strength values σ_{xb}, σ_{yb} and τ_{xyb} of the composite laminate which is under loading in x-y direction. After solving σ_x, σ_y and τ_{xy}, based on the condition of identical formation, we use ε_x, ε_y and r_{xy} to divide, and get calculation formula of E_x, E_y and G_{xy}. Equation group (8.155a) and (8.155b) are called the stress state equation of the composite laminates.

In practical application, the composite laminate is often under the action of single stress. For example, the composite is only loaded in x direction, σ_y and τ_{xy} are both “0”; or only under the action of two-directional stress, suppose there are

σ_x and τ_{xy}, while σ_y =0, the calculation formula can be simplified. Furthermore, the composite laminate is composed of two monolayer laminates. If L-T direction of one laminate is the same with the loading direction (x-y direction) of the composite laminate, then m_x and m_y of the ply is "0". Similarly, L-T direction of layer I is the same with loading direction of the composite laminate ($m_{\mathrm{I}x}$ =0, $m_{\mathrm{I}y}$ =0), and layer II is composite materials with 1:1 balance-type, arrange layer I ±45° angle with L-T ($m_{\mathrm{II}x}$ =0, $m_{\mathrm{II}y}$ =0), then the calculate formulae will be greatly simplified.

3) Application of the stress state equation of multi-directional composite laminate

From the discussion of directional equation in the previous section, mechanical properties of composite materials change with the loading direction. Under normal circumstance (along any loading direction), the extra normal stress will cause an additional shear strain, and the extra shear stress will cause an additional normal strain. Therefore, the composite laminate composed of such materials should avoid or reduce the additional stress to gain the best combination of layers as much as possible.

According to usage of composite material products, unidirectional cloth (or non-weft fabric) is often used to undertake the requirements of strength and stiffness in the main direction and the balanced cloth of 1:1 ply in ±45° is often used to undertake the requirements of shear and torsion. When a composite laminate made of both the above is loaded in the main direction, the m_x and m_y of the two layers are "0" which says no additional strain, so this kind of composite laminate is good to use. We take the composite laminate as example to explain application of the stress state equation in the following.

[Example 8.3] Now there is a product of GFRP which is composed of single-layer laminate I with 4:1 cloth and single-layer laminate II with 1:1 cloth. The warp (L direction) ply of 4:1 cloth is under loading along x direction; the warp (L direction) ply of 1:1 cloth is in ±45° with x direction. Fig. 8.55 shows the loading condition of this product.

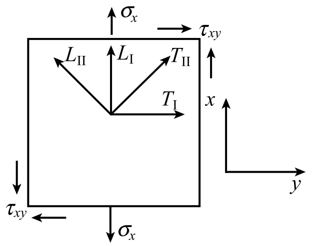


Fig. 8.55 The loading diagram of multi-directional laminate from 4:1 and 1:1 monolayer laminate.

We know that the composite laminate is under external load σ_x and τ_{xy}, σ_y =0.

The mechanical properties parameters of 4:1 single-layer laminate I are shown as follows:

$$E_{\mathrm{I}x} = E_{\mathrm{I}L} = 2.5 \times 10^5\ \mathrm{kg/cm^2}$$

$$E_{\mathrm{I}y} = E_{\mathrm{I}T} = 1.2 \times 10^5\ \mathrm{kg/cm^2}$$

$$G_{\mathrm{I}xy} = G_{\mathrm{I}LT} = 2.9 \times 10^4\ \mathrm{kg/cm^2}$$

$$\sigma_{\mathrm{I}x} = \sigma_{\mathrm{I}L} = 5000\ \mathrm{kg/cm^2}$$

$$\sigma_{\mathrm{I}y} = \sigma_{\mathrm{I}T} = 1600\ \mathrm{kg/cm^2}$$

$$\tau_{\mathrm{I}xy} = \tau_{\mathrm{I}LT} = 670\ \mathrm{kg/cm^2}$$

$$\mu_{\mathrm{I}xy} = \mu_{\mathrm{I}LT} = 0.2$$

$$\mu_{\mathrm{I}yx} = \mu_{\mathrm{I}TL} = 0.1$$

$$m_{\mathrm{I}x} = m_{\mathrm{I}L} = 0$$

$$m_{\mathrm{I}y} = m_{\mathrm{I}T} = 0$$

The mechanical properties parameters of 1:1 single-layer laminate II in L-T direction of single-layer laminate I are shown as follows:

$$E_{\mathrm{II}x} = E_{\mathrm{II}45^\circ} = 1.02 \times 10^5\ \mathrm{kg/cm^2}$$

$$\sigma_{\mathrm{II}x} = \sigma_{\mathrm{II}45^\circ} = 1400\ \mathrm{kg/cm^2}$$

$$E_{\mathrm{II}y} = E_{\mathrm{II}45^\circ} = 1.02 \times 10^5\ \mathrm{kg/cm^2}$$

$$\sigma_{\mathrm{II}y} = \sigma_{\mathrm{II}45^\circ} = 1400\ \mathrm{kg/cm^2}$$

$$G_{\mathrm{II}xy} = G_{\mathrm{II}45^\circ} = 7.02 \times 10^4\ \mathrm{kg/cm^2}$$

$$\tau_{\mathrm{II}xy} = \tau_{\mathrm{II}45^\circ} = 1300\ \mathrm{kg/cm^2}$$

$$\mu_{\mathrm{II}xy} = \mu_{\mathrm{II}45^\circ} = 0.44$$

$$\mu_{\mathrm{II}yx} = \mu_{\mathrm{II}45^\circ} = 0.44$$

$$m_{\mathrm{II}x} = m_{\mathrm{II}45^\circ} = 0$$

$$m_{\mathrm{II}y} = m_{\mathrm{II}45^\circ} = 0$$

Solution Based on the above conditions, calculate σ_{xb}, τ_{xyb} and E_x, G_{xy} of the composite laminate.

If thickness of single-layer laminate I is the same as that of single-layer laminate II, i.e., $t_{\mathrm{I}} = t_{\mathrm{II}} = t/2$, since $m_{\mathrm{I}x}, m_{\mathrm{I}y}, m_{\mathrm{II}x}$ and $m_{\mathrm{II}y}$ are all "0", σ_y =0, thus we have:

$$A_{11}\sigma_{\mathrm{I}x} + A_{12}\sigma_{\mathrm{I}y} + A_{13}\tau_{\mathrm{I}xy} = \frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}} \cdot \frac{\sigma_x}{E_{\mathrm{II}x}}$$

$$A_{21}\sigma_{\mathrm{I}x} + A_{22}\sigma_{\mathrm{I}y} + A_{23}\tau_{\mathrm{I}xy} = \frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}} \cdot \left(-\mu_{\mathrm{II}xy}\frac{\sigma_x}{E_{\mathrm{II}x}}\right)$$

$$A_{31}\sigma_{\mathrm{I}x} + A_{32}\sigma_{\mathrm{I}y} + A_{33}\tau_{\mathrm{I}xy} = \frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}} \cdot \frac{\tau_{xy}}{G_{\mathrm{II}xy}}$$

Or which is expressed with the laminate II, thus we have

$$A_{11}\sigma_{\mathrm{II}x}+A_{12}\sigma_{\mathrm{II}y}+A_{13}\tau_{\mathrm{II}xy}=\frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}}\cdot\frac{\sigma_x}{E_{\mathrm{I}x}}$$

$$A_{21}\sigma_{\mathrm{II}x}+A_{22}\sigma_{\mathrm{II}y}+A_{23}\tau_{\mathrm{II}xy}=\frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}}\cdot\left(-\mu_{\mathrm{I}xy}\frac{\sigma_x}{E_{\mathrm{I}x}}\right)$$

$$A_{31}\sigma_{\mathrm{II}x}+A_{32}\sigma_{\mathrm{II}y}+A_{33}\tau_{\mathrm{II}xy}=\frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}}\cdot\frac{\tau_{xy}}{G_{\mathrm{I}xy}}$$

In calculating strength of the composite laminate, firstly, we should work out the relationship between main stresses $\sigma_{\mathrm{I}x}$, $\sigma_{\mathrm{I}y}$ and $\tau_{\mathrm{I}xy}$ of each single-layer laminate and main stresses σ_x, σ_y and τ_{xy} of the composite laminate according to the stress state equation. Second, we check each layer's strength by strength criterion, the composite laminate is judged to be destroyed if one single-layer is broken.

Base on the premise, we take the known parameters into equations, and work out the relationship between main stress of each single-layer laminate and each main stress of the composite laminate. See Table 8.4.

Table 8.4 Coefficient of stress state equation of composite laminate with different thickness of 45°, which is composed of 4:1 fabric single-layer laminate I in *L*-*T* direction and 1:1 fabric single-layer laminate II in 45°

Thickness ratio of each layer	A_{11}	$A_{12}=A_{21}$	A_{13}	A_{22}	A_{23}	A_{31}	A_{32}
$t_{\mathrm{I}}=0.9t$ $t_{\mathrm{II}}=0.1t$	$10.4\times10^{-5}/t$	$4.57\times10^{-5}/t$	0	$10.7\times10^{-5}/t$	0	0	0
$t_{\mathrm{I}}=0.8t$ $t_{\mathrm{II}}=0.2t$	$5.56\times10^{-5}/t$	$2.36\times10^{-5}/t$	0	$5.94\times10^{-5}/t$	0	0	0
$t_{\mathrm{I}}=0.7t$ $t_{\mathrm{II}}=0.3t$	$4.02\times10^{-5}/t$	$1.63\times10^{-5}/t$	0	$4.45\times10^{-5}/t$	0	0	0
$t_{\mathrm{I}}=0.6t$ $t_{\mathrm{II}}=0.4t$	$3.33\times10^{-5}/t$	$1.29\times10^{-5}/t$	0	$3.84\times10^{-5}/t$	0	0	0
$t_{\mathrm{I}}=0.5t$ $t_{\mathrm{II}}=0.5t$	$3.01\times10^{-5}/t$	$1.10\times10^{-5}/t$	0	$3.65\times10^{-5}/t$	0	0	0

Thickness ratio of each layer	A_{33}	$\frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}}$	$\frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}}\cdot\frac{1}{E_{\mathrm{II}x}}$	$\frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}}\cdot\frac{-\mu_{\mathrm{II}xy}}{E_{\mathrm{II}x}}$	$\frac{t}{t_{\mathrm{I}}t_{\mathrm{II}}}\cdot\frac{1}{G_{\mathrm{II}xy}}$
$t_{\mathrm{I}}=0.9t$ $t_{\mathrm{II}}=0.1t$	$17.4\times10^{-5}/t$	$11.1/t$	$10.9\times10^{-5}/t$	$-4.79\times10^{-5}/t$	$15.81\times10^{-5}/t$
$t_{\mathrm{I}}=0.8t$ $t_{\mathrm{II}}=0.2t$	$10.7\times10^{-5}/t$	$6.25/t$	$6.12\times10^{-5}/t$	$-2.70\times10^{-5}/t$	$8.90\times10^{-5}/t$
$t_{\mathrm{I}}=0.7t$ $t_{\mathrm{II}}=0.3t$	$8.82\times10^{-5}/t$	$4.76/t$	$4.67\times10^{-5}/t$	$-2.05\times10^{-5}/t$	$6.78\times10^{-5}/t$
$t_{\mathrm{I}}=0.6t$ $t_{\mathrm{II}}=0.4t$	$8.32\times10^{-5}/t$	$4.17/t$	$4.08\times10^{-5}/t$	$-1.80\times10^{-5}/t$	$5.94\times10^{-5}/t$
$t_{\mathrm{I}}=0.5t$ $t_{\mathrm{II}}=0.5t$	$8.57\times10^{-5}/t$	$4.00/t$	$3.92\times10^{-5}/t$	$-1.73\times10^{-5}/t$	$5.69\times10^{-5}/t$

According to the Table 8.4, the relationship between main stress of the single-layer laminate and stress of the composite laminate are shown, find data at 50% of I and II , suppose strength of the composite laminate is calculated by the single-layer laminate, then

$$\sigma_{xb}=\sigma_{\mathrm{I}xb}/1.39=5000/1.39\approx 3597\ (\mathrm{kg/cm^2})$$

$$\tau_{xyb}=\tau_{\mathrm{I}xyb}/0.58=670/0.58\approx 1155\ (\mathrm{kg/cm^2})$$

At this time, stress of the single-layer laminate II is given by

$$\sigma_{\mathrm{II}x} = \sigma_{xb} \times 0.61 \approx 3597 \times 0.61 \approx 2194\ (\mathrm{kg/cm^2}) > 1400\ (\mathrm{kg/cm^2})$$

$$\tau_{\mathrm{II}xy} = \tau_{xyb} \times 1.41 \approx 1155 \times 1.41 \approx 1629\ (\mathrm{kg/cm^2}) > 1300(\mathrm{kg/cm^2})$$

According to the above data, if the strength of the composite laminate is calculated by strength of the single-layer laminate I, then the single-layer laminate II is destroyed earlier than the single-layer laminate I.

Suppose the strength of the composite laminate is calculated by the single-layer laminate II , then we get:

$$\sigma_{xb} = \sigma_{\mathrm{II}xb}/0.61 = 1400/0.61 \approx 2295(\mathrm{kg/cm^2})$$

$$\tau_{xyb} = \tau_{\mathrm{II}xyb}/1.41 = 1300/1.41 \approx 922(\mathrm{kg/cm^2})$$

At this time, the stress that single-layer laminate I bears is given by:

$$\sigma_{\mathrm{I}x} = 1.39\sigma_x \approx 2295 \times 1.39 \approx 3190(\mathrm{kg/cm^2}) < 5000(\mathrm{kg/cm^2})$$

$$\tau_{\mathrm{I}xy} = 0.58\tau_{xy} \approx 922 \times 0.58 \approx 535(\mathrm{kg/cm^2}) < 670(\mathrm{kg/cm^2})$$

By the above calculation, the external load bearing ability of the combination laminate which is consisted of single-layer laminates I and II is: $\sigma_x \leqslant 2295\mathrm{kg/cm^2}$; $\tau_{xy} \leqslant 922\mathrm{kg/cm^2}$, the data are lower than the previous calculated values by the rule of mixture method (Example 8.2).

The above calculations indicate that when estimating the load bearing ability of the composite laminate, we should make a comprehensive analysis of all stresses of the single laminate. This is another characteristic of mechanical properties of composite materials. In addition, although the combination laminate is under a state of single stress, an increase of the strength in the single direction not necessarily improves the strength of the composite laminate, because of the differences between μ and m, damages may occur in other directions. The effective measures is to choose different kinds of single-layers and ratio of single-layer (the content of single-layer), which should be taken into account in using composite materials.

We analyze E_x and G_{xy} of the above composite laminate in the following.

Since $E_x = \sigma_x/\varepsilon_x$, σ_x is known, according to the same deformation condition:

$$\varepsilon_x = \varepsilon_{\mathrm{I}x} = \varepsilon_{\mathrm{II}x}$$

$$\varepsilon_{\mathrm{I}x} = \frac{\sigma_{\mathrm{I}x}}{E_{\mathrm{I}x}} - \mu_{\mathrm{I}yx}\frac{\sigma_{\mathrm{I}y}}{E_{\mathrm{I}y}} - m_{\mathrm{I}x}\frac{\tau_{\mathrm{I}xy}}{E_{\mathrm{I}L}}$$

$$\varepsilon_{\mathrm{II}x} = \frac{\sigma_{\mathrm{II}x}}{E_{\mathrm{II}x}} - \mu_{\mathrm{II}yx}\frac{\sigma_{\mathrm{II}y}}{E_{\mathrm{II}y}} - m_{\mathrm{II}x}\frac{\tau_{\mathrm{II}xy}}{E_{\mathrm{II}L}}$$

Calculate by the single-layer laminate I, we have:

$$\sigma_{\mathrm{I}x} = 1.39\sigma_x = 1.39 \times 2295 \approx 3190\,(\mathrm{kg/cm^2})$$

$$\sigma_{\mathrm{I}y} = -0.09\sigma_x = -0.09 \times 2295 \approx -207(\mathrm{kg/cm^2})$$

$$\tau_{\mathrm{I}xy} = 0.58\tau_{xy} = 0.58 \times 922 \approx 535(\mathrm{kg/cm^2})$$

Take the given data into the equation of $\varepsilon_{\mathrm{I}x}$, we have:

$$\varepsilon_{\mathrm{I}x} = \frac{3190}{2.5 \times 10^5} - 0.1\frac{-207}{1.2 \times 10^5} - 0 \approx 0.0129$$

Calculate by the single-layer laminate II , we have:

$$\sigma_{\mathrm{II}x} = 0.61\sigma_x = 0.61 \times 2295 = 1400(\mathrm{kg/cm^2})$$

$$\sigma_{\mathrm{II}y} = 0.08\sigma_x = 0.08 \times 2295 \approx 184(\mathrm{kg/cm^2})$$

$$\tau_{\mathrm{II}xy} = 1.41\tau_{xy} = 1.41 \times 922 = 1300(\mathrm{kg/cm^2})$$

Take the given data into the equation of $\varepsilon_{\mathrm{II}x}$, we have:

$$\varepsilon_{\mathrm{II}x} = \frac{1400}{1.02 \times 10^5} - 0.44 \times \frac{184}{1.02 \times 10^5} \approx 0.0129$$

Take ε_x into the equation of E_x, we have:

$$E_x = \frac{\sigma_x}{\varepsilon_x} = \frac{2295}{0.0129} \approx 1.77 \times 10^5(\mathrm{kg/cm^2})$$

Since $G_{xy} = \tau_{xy}/\gamma_{xy}$, τ_{xy} is known, according to the same deformation conditions:

$$\gamma_{xy} = \gamma_{\mathrm{I}xy} = \gamma_{\mathrm{II}xy}$$

$$\gamma_{\mathrm{I}xy} = \frac{\tau_{\mathrm{I}xy}}{G_{\mathrm{I}xy}} - m_{\mathrm{I}x}\frac{\sigma_{\mathrm{I}x}}{E_{\mathrm{I}L}} - m_{\mathrm{I}y}\frac{\sigma_{\mathrm{I}y}}{E_{\mathrm{I}L}}$$

$$\gamma_{\mathrm{II}xy} = \frac{\tau_{\mathrm{II}xy}}{G_{\mathrm{II}xy}} - m_{\mathrm{II}x}\frac{\sigma_{\mathrm{II}x}}{E_{\mathrm{II}L}} - m_{\mathrm{II}y}\frac{\sigma_{\mathrm{II}y}}{E_{\mathrm{II}L}}$$

Calculate by the single-layer laminate I, we have:

$$\gamma_{\mathrm{I}xy} \approx \frac{535}{2.9 \times 10^4} - 0 - 0 \approx 0.0184$$

Calculate by the single-layer laminate II , we have:

$$\gamma_{\mathrm{II}xy} \approx \frac{1300}{7.02 \times 10^4} - 0 - 0 \approx 0.0185$$

Take γ_{xy} into the equation of G_{xy}, we have:

$$G_{xy} = \frac{\tau_{xy}}{\gamma_{xy}} \approx \frac{922}{0.0184} \approx 5.01 \times 10^4(\mathrm{kg/cm^2})$$

The results show that the elastic modulus calculated by the stress state equation is similar to the data calculated by the rule of mixture (Example 8.2).

8.8.2 Additional stress and coupling effect of the composite laminate

1) Additional stress of the composite laminate

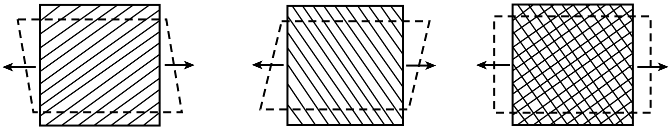
From the previous analysis, the multi-directional composite materials (composite laminate) will cause additional stress (also be called the interlaminar stress) under external load. There are two main reasons for the generation of additional stress.

(1) The additional stress is caused by different Poisson's ratios of each layer. Such as [0/90/±45]$_S$, although $m_x = m_y = 0$ of each single-layer, Poisson's ratio of them are different. Poisson's ratio of 0° layer is μ_{LT}=0.28, of 90° layer is μ_{TL} =0.07 and ±45° layer is μ_{45} =0.454. Under external loading, single-layers with different Poisson's ratio are forced to keep the same deformation and that will definitely cause additional stress between each layer.

(2) The additional stress is caused by the nonzero of additional strain coefficient m_x or m_y.

[Example 8.4] Suppose the two-layer laminate with crossed $\pm\alpha$ ply subject to off-axis normal stress σ_x.

Since unidirectional laminates of $+\alpha$ and $-\alpha$ have the equal additional strain coefficient with the opposite directions, they will generate additional shear strain with the opposite directions and the same value in individual deformation. When they are combined together, according to the same deformation principle, it will cause a pair of additional shear stresses to offset the additional shear deformation (Fig. 8.56). On the side of the board, additional shear stresses of upper board and lower board are equal in value and opposite in direction, which constitute a couple of force. The generated torque M_{xy} will bring about distorted deformation in board (shape from flat to saddle) (Fig. 8.57).



Upper board($+\alpha$ layer) Lower board($-\alpha$ layer) $\pm\alpha$ composite board

Fig. 8.56 The off-axis tensile deformation of $\pm\alpha$ composite laminate.

[Example 8.5] Suppose the laminate in example 8.4 subject to shear stress τ_{xy}.

Besides the same shear strains that are generated in each unidirectional plate, there are also the additional normal strains which are equal in value and opposite in x and y direction. After laminating, linear strain is offset according to the consistent deformation principle, and only shear strain is shown externally. Meanwhile,

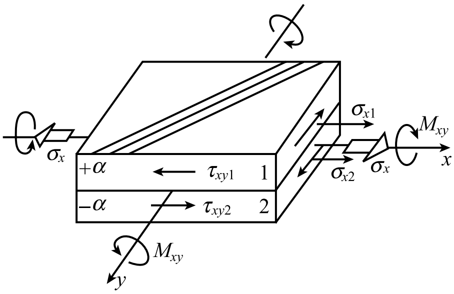


Fig. 8.57 The off-axis tensile inner force of $\pm\alpha$ composite laminate.

additional tensile stress and additional compression stress are generated. Additional normal stresses of upper board and lower board are equal in value and opposite in direction. Since additional stresses act in different planes, bending moment is formed in the thickness direction. Therefore, the synthetic bending moment M_x, M_y will cause bending deformations of laminates (arched) (Fig. 8.58).

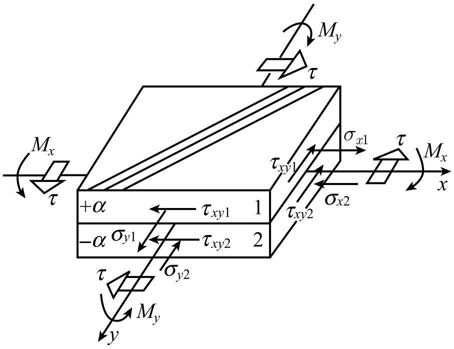


Fig. 8.58 The off-axis shear inner force of $\pm\alpha$ composite laminate.

2) Coupling effect

When the multi-directional composite laminate is placed under external loading, the warping or bending deformation caused by the additional stress are called the coupling effect. This is also the unique characteristic of composite materials. Additional stress and additional deformation phenomenon of the $\pm\alpha$ crossed ply is called the cross elastic phenomenon. The cross elastic phenomenon is studied from the standpoint of stress with additional stress and interlaminar stress, and studied from the standpoint of deformation with the coupling effect. Therefore, additional strain coefficient m_x or m_y is also called cross elastic coefficient.

3) Elimination of the coupling effect

Coupling effect brings about a negative impact on the manufacture of composites components. By using reasonable ply order (such as symmetric ply sequence) or increasing the number of layers we can eliminate or reduce the coupling effect. There are two kinds of ply-stacking sequences, which are the general stacking ply which is ±α layers in alternation; and mirror symmetric ply in which layers are symmetric with the central layer. Take four-sheet for example: when mirror symmetry $+\alpha/-\alpha/-\alpha/+\alpha$ combination plate under tension, the additional shear stress and torque are shown in Fig. 8.59. We see that the torque formed by additional shear stress of ply 1 and ply 2 and the torque formed by ply 3 and ply 4 are equal in value and opposite in direction, so the total torque is zero. It means that the coupling effect is offset. When mirror symmetric composite plates are under shear stress, the additional stress and bending moment are shown in Fig. 8.60. We saw that bending moments caused by additional normal stresses are also offset.

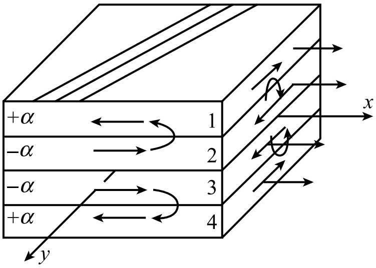


Fig. 8.59 The tensile inner force chart of mirror symmetric composite laminate.

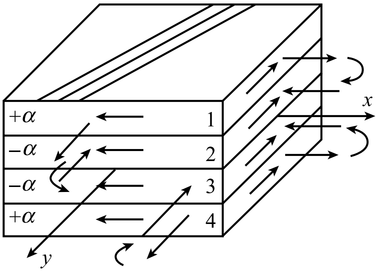


Fig. 8.60 The shear inner force chart of mirror symmetric composite laminate.

The general ply $+\alpha/-\alpha/+\alpha/-\alpha$ composite laminate under tension, the additional shear stress and torque are shown in Fig. 8.61. Compared to the two-sheet laminate in Fig. 8.57, if the total thickness of composite laminate is the same, the stress direction and value will not change. Now let's study the torque M_{xy} on the cross-section. The torque of four-sheet laminates is the sum of torques in two directions, its value is just reduced to 1/2 torque of the two-sheet. That is, when the number of layers doubles, the coupling effect reduces to half. Following this trend, the larger the number of layers, the smaller the coupling effect. When the composite laminate is under shear stress, the additional normal stress and bending moment are shown in Fig. 8.62. Compared to the two-sheet in Fig. 8.58, if the total thickness of composite laminate remains the same, total bending moment on cross-section become half on two-sheet, the coupling effect is reduced by half. In short, with the increase in layer number, heterogeneous degree of composite laminate in thickness direction decreases. The more material becomes homogeneous, the lower the coupling effect is.

The effect of ply sequence on the coupling effect also depends on type of load. For example, when four-ply laminate under the bending load, the mirror symmetrical laminate has the same torque directions which are caused by additional shear stress, so the coupling effect cannot be eliminated (Fig. 8.63). Torques are formed by additional shear stress of the general ply laminate are equal to value and opposite in direction, which can be offset. Therefore, the coupling effect can be eliminated (Fig. 8.64).

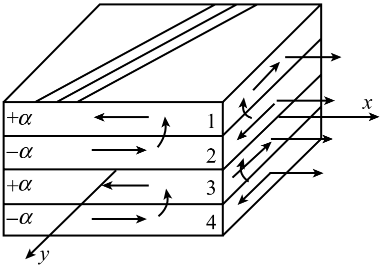


Fig. 8.61 Chart of inner force of the general stacking ply composites under tension.

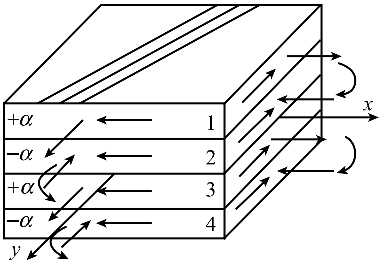


Fig. 8.62 Chart of inner force of the general stacking ply composites under shear.

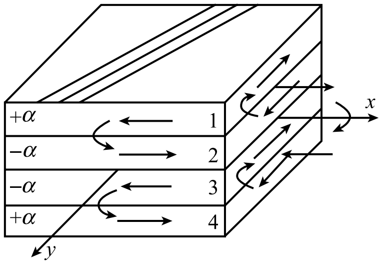


Fig. 8.63 Chart of inner force of the mirror sysmmetric composite laminate under bending.

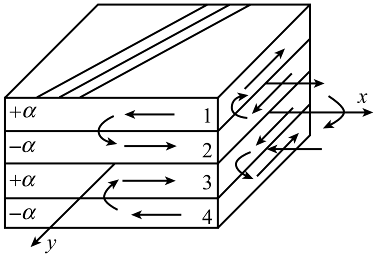


Fig. 8.64 Chart of inner force of the general stacking ply composites under bending.

When 1:1 orthogonal ply composite laminate is under tension in 45°, $m_x = m_y = 0$, the coupling effect is not generated.

If there are tensile stress, shear stress and bending stress in external loading at the same time, $\pm\alpha$ four-ply laminate is not able to form a balanced structure, at least seven layers is needed. Seven-ply $[+\alpha/-\alpha/-\alpha/0/+\alpha/+\alpha/-\alpha]_T$ and eight-ply $[+\alpha/-\alpha/-\alpha/+\alpha/-\alpha/+\alpha/+\alpha/-\alpha]_T$ are all balanced structures in tension, shearing and bending.

It is noticed that using reasonable order for ply-stacking, we can avoid bending and distortion phenomenon of the composite laminate, i.e., the coupling effect can be offset. Unfortunately, the additional stress (interlaminar stress) cannot be eliminated.

Exercises

1. Why should we conduct a micromechanics analysis of composite materials? What is the basic hypothesis of micromechanics?

2. What is the relationships among resin content w_m, resin volume fraction V_m, fiber mass content w_f and fiber volume fraction V_f?

3. Volume fraction of glass fiber and epoxy resin in glass fiber composites is measured by burn ablation, here are the results: mass of empty crucible =47.6504g; mass of crucible and composites =50.1817g; mass of crucible and composites after ablation =49.4476g. Please calculate the mass percentage and volume percentage of glass fiber and epoxy resin (density of glass fiber is 2.5 g/cm^3, density of resin is 1.2 g/ cm^3, void content is 0).

4. Calculate theoretical density ρ_c of composite materials by w_m, ρ_f and ρ_m in the previous question. If the practical density of composite material is 1.86 g/cm^3, please calculate void content of the material.

5. The unidirectional composite material is loaded in the direction that is parallel to the fiber direction, please calculate values of σ_f/σ_m and σ_f/σ_L when V_f is at 10%, 25%, 50%, 75% respectively $(E_f$ = 400GN/m^2, E_m = 3.2GN/m$^2)$.

6. A composite pull pole with section area is 10cm^2, behaviors of its component are shown in follows:

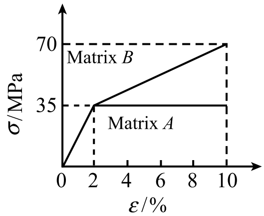
Material	ρ(g/cm^3)	$w_m(\%)$	E(GN/m^2)	σ_u(GN/m^2)
Matrix	1.27	35	3.5	0.06
Fiber	2.54	65	70	1.4

(1) Calculate the biggest load to be born when both components undamaged.

(2) Calculate the biggest load to be born by the pole.

(3) Draw the stress-strain curve of composites and its components.

7. Two kinds of unidirectional glass fiber composite materials which are made of matrix A and matrix B (V_f=50%). σ-ε curve of the glass fiber is straight, E_f is 70GN/m^2, the limit rupture strength is 2.8GN/m^2. σ-ε curves of these two matrixes are shown in the following picture. If loading in the direction parallel to the fiber direction, calculate the stress born by the composites when strain is 1% and 4% respectively.



8. A glass fiber composite material, properties of the fiber and the matrix are: σ_{fu}= 1.6×10^{4}kg/cm^2, E_f=7×10^{5}kg/cm^2, ρ_f=2.55g/cm^3, σ_{mu}=500 kg/cm^2, E_m=3.5×10^4 kg/cm^2, ρ_m=1.37. Specifications of glass cloth is:

	Strand count β_0/plied number N	Weave density (end/cm)
Longitude	80/8	18
Latitude	80/6	12

Ignore strength loss caused by weaving, calculate values of E_L, E_T, σ_{Lu}, σ_{Tu} of the composite when glue content (w_m) is 25%.

9. How to estimate longitudinal tensile stress, modulus and strength of unidirectional fiber composites?

10. What are the main factors that influence longitudinal tensile strength and modulus of unidirectional continuous fiber composite materials?

11. How to estimate the main Poisson ration μ_{LT} of the unidirectional composites?

12. What are $V_{fmin}$and V_{fcr}?

13. Deduce and estimate transverse tensile modulus of the unidirectional composites by using the equal strain hypothesis or the equal stress hypothesis.

14. What are stress concentration factor SCF and strain magnification factor SMF? What are the main factors that influence them?

15. What are the main factors that influence transverse tensile strength and modulus of the unidirectional fiber composites?

16. What are the characters of uniaxial tension stress-strain curve of the bidirectional orthogonal composite material? What is the reason?

17. What are factors that influence longitudinal compression strength of the unidirectional composite material? How to measure longitudinal compression strength?

18. What are in-plane shear and interlaminar shear respectively?

19. How to measure G_{LT} and τ_{LT} of composite material? What factors do the in-plane shear strength and modulus of the unidirectional fiber composites depend on?

20. List eleven basic mechanical properties parameters of the unidirectional fiber composites for composite design.

21. Prepare composite material by ten layers of 7:1 unidirectional glass cloth, if w_m=30%, calculate thickness of composite material h_c .

Given: parameters of glass cloth

	Strand count β_0/plied number N	Weave density (end/cm)
Longitude	80/14	24
Latitude	80/4	12

22. Bending strength of composite material in previous question (Q21) is σ_{Fu}= 600 MPa, if w_m% increases from 30% to 35% and the failure load is unchanged, calculate the bending strength $\sigma'_{Fu.}$

23. Why can the three point bending test be used for testing bending strength and also interlaminar shear strength? What are their different requirements? Make an illustration by deducing.

24. Apply the three point bending test to measure bending properties of composites, what is the requirement for $1/h$ of sample? Why?

25. What is stress transformation formula or matrix? What is strain transformation formula or matrix?

26. How to estimate strength and elastic coefficient of the off-axis composite material?

27. Why does outer skin of airplane usually use the ±45° ply?

28. Specify deformation of composite material when loading in random direction according to analysis of stress and strain.

29. What are additional strain parameters m_x and m_y? What's its physical essence and what are the characters?

30. What is the formula of the generalized Hooke's law which reflects relationships of stress-strain of composites under in-plane stress in arbitrary direction? Compared with on-axis and isotropic composite materials, what's the difference between number of elastic coefficient and deformation under stress?

31. How to judge whether composite material is damaged or not under in-plane stress?

32. How to represent ply order of composite laminates?

33. How to estimate mechanical properties of multi-directional fiber composite materials?

34. When preparing composite material products, what's the result if there is a large deviation in fiber ply direction? What if the order of ply is wrong?

35. What is the coupling effect? How to understand this concept?

36. What's the reason for warpage in composite laminate? How to avoid it?

37. Why do we usually use symmetrical $\pm\alpha$ angle layers for fiber composite materials?

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9

Other mechanical properties of composite materials

9.1 Impact, fatigue, creep, environmental effect, fracture and damage of composites

In the last chapter, we learned conventional mechanical properties of composite materials under short-time load. In practical applications, though, there are other issues to be dealt with such as impact load, dynamic load, and also creep, environmental effect, damage, fracture, and so on.

Therefore in this chapter we discuss impact property, fatigue performance, persistent strength and creep, environmental effect, fracture toughness and damage of composite materials.

9.1.1 Impact property of composite materials

Composite materials are to withstand impact load in many applications. Sometimes, even very small impact energy will seriously reduce the static strength of composite materials, influencing component reliability; and sometimes an attempt to improve the tensile property would lead to the decline of impact property at the same time. Among composite materials, fiberglass and Kevlar fiber composite materials have high impact property, while carbon fiber composite materials which are widely used in the structure, have low impact properties, so it is necessary to understand the impact property and energy-absorbing mechanism of composite materials.

1) Impact test method

The impact toughness can be determined by measuring the needed energy to break a standard specimen, which is one of the most common methods to evaluate the impact properties. Charpy and Izod impact tests are developed for isotropic materials, the former is under simple supported beam load, the latter is under cantilever load. After impact damage, the bob's energy loss can be read in the dial. This energy divided by the cross-sectional area of the sample gives the impact toughness or impact strength. The dimension of the value is force/length. Toughness data obtained in such test is only the qualitative results to some extent. The reasons are:

(1) Energy loss bob impact caused includes energy absorbed in both material damage and fracture, and energy loss consumed in the testing machine, flying-out power of fracture fragments and acoustic energy, etc.

(2) It gives only one general result and no further information about how the damage is incurred and what form of failure it is. Different materials have different fracture forms, but they might get the same impact strength. For isotropic materials, the form of damage is simple, these two impact test method can be well done. For composite materials, as a result of the complex damage phenomenon, these two impact tests are insufficient to provide complete data that reflects the impact properties of composite materials. Specific fracture mode determines the different mechanism of energy absorption on the course of the impact, and fracture mode and energy absorption are affected by various test parameters, such as fiber orientation, the sample size and the impact rate, etc. In order to better understand the impact performance of materials, new equipments have been developed such as Charpy tester with recording devices and drop hammer impact test machine. In the tester, bob or support is equipped with load sensors and recording instruments, the shape of impact edge can be changed, and the size of the effective impact energy can be adjusted by change the mass of hammer, the height of the drop can be regulated to meet different rates of the impact. In the oscilloscope show the P-t (load-time) curve and E-t (energy-time) curve of impact process (Fig. 9.1).

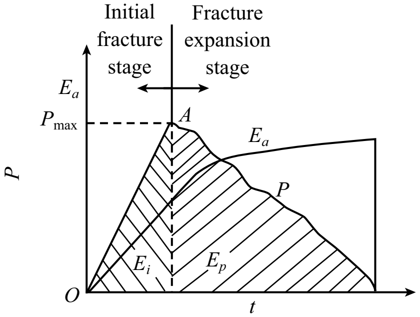

Fig. 9.1 Load-time and energy-time curve in the impact process.

P-t curve can be divided into two different regions, the initial fracture area and fracture expansion area. In the initial stage of the fracture, load growth only stores elastic strain energy in the samples and causes no macro-damage. At the end (A) of the initial stage reaching the critical load $(P_{\max})$, the composite specimen might be having tensile failure or shear failure, depending on the relative value of the tensile strength and interlaminar shear strength. At this point, the fracture expansion is in the manner of a sudden brittle fracture, or continuous gradual manner to absorb the energy under a higher load. The area under the curve reflects the energy absorbed, from the curve we can know the initial energy (E_i) and the expansion energy (E_p), the total impact energy (E_t) is the sum of E_i and E_p. For high-strength brittle materials, E_i is high, and E_p is low; and for low-strength ductile materials, E_i is low and E_p is high. Two materials may have the same total impact energy, so only knowing the value of E_t is not enough for the interpretation of the impact fracture characteristics. We define $DI = E_p/E_i$, it is called the toughness index. High DI value shows that the material has high toughness.

The energy E that specimen absorbs at any time is given by the following formula:

$$E = \int PV\mathrm{d}t \tag{9.1}$$

In the formula, P and V express the instantaneous load and speed respectively. However the energy E_a from energy-time curve is the product of impulse (the area under the load-time curve) and the initial impact velocity V_0.

$$E_a = V_0 \int P\mathrm{d}t \tag{9.2}$$

In reality, the speed of punch (V) will reduce in the process of contacting specimen. To get the true energy the specimen absorbed, we should amend E_a. Similarly, we use the product of the average speed of punch $\overline{V}$ and impulse to replace the right side of the formula (9.1), that is,

$$E = \overline{V} \int P\mathrm{d}t \tag{9.3}$$

In the formula, $\overline{V} = \frac{1}{2}(V_0 + V_f)$; V_f is the speed at specific moment when we calculate E. According to the principle of impulse and momentum, we have:

$$\frac{\overline{V}}{V_0} = 1 - \frac{E_a}{4E_0} \tag{9.4}$$

Where E_0 is the maximum effective impact energy, defined according to the following formula:

$$E_0 = \frac{1}{2}mV_0^2 \tag{9.5}$$

Here m is the mass of the drop hammer. Synthesize (9.2), (9.3) and (9.4), we have:

$$E = E_a\left(1 - \frac{E_a}{4E_0}\right) \tag{9.6}$$

The formula (9.6) is the modified formula when we calculate the true energy from E_a on the oscilloscope.

2) Energy absorption mechanism and failure mode

The various energy absorption mechanisms and failure modes discussed here is not just applicable to impact damage, but of universal significance. When a solid under static load or impact load, there are two kinds of energy absorption mechanisms: ① form new surface; ② material deformation.

Material deformation happens firstly; if the energy provided is large enough, crack may generate and expand; and in the crack expansion process, material deformation also exits on the crack front. Brittle materials will produce only a small amount of deformation, accompanied by little energy absorption. Ductile materials have large plastic deformation, and the energy absorbed is also large. Visibly, the total energy the materials absorbs (or toughness) can increase by adding the crack path of the separation process or by increasing the capacity of material deformation. To improve toughness in the composite material we can use the component which can absorb large energy to replace the component which has less energy absorption. For example, the introduction of glass fiber into carbon fiber composites can make hybrid fiber composite materials which have high toughness. However, for a given matrix and reinforcing material, the design of composite materials with high toughness requires a good understanding of the fracture process and related energy absorption mechanism.

The damage of fiber composite material can be thought of originating from small internal inherent defects in materials, which could be the broken fiber, matrix crack and interface debonding. It is a crack expansion process, which can be described by the crack tip model in the Fig. 9.2. A series of partial destruction may arise during the fracture process of fiber composites. In certain distance of crack front, the fibers are intact. In high-stress area near the crack tip, fiber is damaged, but damage is not necessarily along the crack plane. The fibers next to surface of the crack might pull out from the matrix. The debonding between fiber and the matrix may also be caused by the stress near the crack tip before fracture. When the brittle fiber and ductile matrix bond very well, the crack will almost certainly be blocked by the fibers in front of the crack tip. That builds a bridge in the matrix, makes the matrix material necking and breaks the material completely

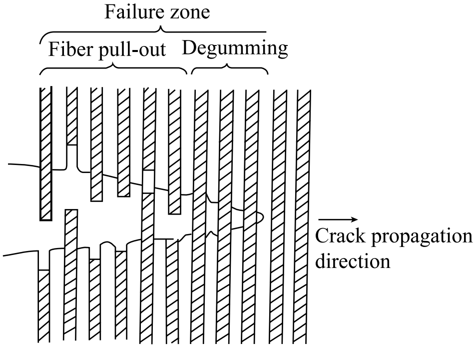

Fig. 9.2 The crack tip model of fiber composites.

in a ductile manner. In addition to this failure mechanism, when the crack arrive at two layer interface of laminated composite, it might branch and expand along the layer interface, resulting in delamination cracks. In the following, we discuss the failure mechanisms respectively, at the same time we will discuss influencing factors of energy absorption accompanied by each mechanism.

(1) Fiber damage.

Whenever the crack has to propagate perpendicularly to the fiber, and laminates completely separated, the fiber damage will eventually happen. Fiber breaks when the strain reaches its fracture strain. Brittle fiber (such as graphite fiber) has a low fracture strain, so its energy absorption is low. For fiber tensile fracture, the required energy per unit area of composite materials can be given by the following formula:

$$u = \frac{V_f \sigma_{fu}^2 l}{6E_f} \tag{9.7}$$

Where, V_f is the fiber volume fraction; σ_{fu} is the fiber's ultimate strength; E_f is the modulus of fiber; l is the fiber's length.

We must mention that, although fibers make up the bulk of composite materials' high strength, the fiber breakage only contributes to a small proportion of total energy absorption. It has been observed from experiments that the number of fiber breakage is with little impact on the total impact energy. However, it should be remembered that the fiber has a very significant impact on the failure mode, thereby also affects the total impact energy.

(2) Matrix deformation and cracking.

The total energy from matrix damage is spent in matrix deformation and cracking. Thermosetting resins are brittle materials, and the energy of matrix deformation is very small. This differs from metallic matrix which can produce large plastic deformation and thus could have a great contribution to the overall impact energy. The power from matrix deformation is proportional to the product of the power (U_m) from per unit volume of the matrix from deformation to the damage and matrix volume forming unit area of crack surface. For per unit area of composite material, the energy of matrix deformation is given by:

$$u = \frac{(1 - V_f)^2}{V_f} \cdot \frac{\sigma_{mu} d_f}{4\tau} U_m \tag{9.8}$$

Where, σ_{mu} is the tensile strength of matrix; d_f is the fiber's diameter; τ is the interface's shear stress.

The energy absorbed in matrix cracking is equal to the product of specific surface energy and new surface area. In actual composite materials, crack branches, resulting in larger crack area, which is an effective way to improve toughness.

(3) Fiber debonding.

In fracture process, because cracks propagate in parallel to the fiber (debonding crack), the fiber separates with the matrix. In the process, chemical bond and secondary bond between fiber and matrix is destroyed, and at the same time new surface forms. It happens when the fibers are strong and interfaces are weak. If debonding has a large range, fracture energy increases in evidence. Reducing interface strength will enable large-scale debonding or delamination, thereby increasing impact energy. Debonding power per unit area of composite materials is shown in follows:

$$u = \frac{V_f \sigma_{fu}^2 y}{4E_f} \tag{9.9}$$

Here y is the debonding length.

(4) Fiber pull-out.

When brittle or non-continuous fibers embedded in tough matrix, fiber pull-out will happen. Fiber breakage is in its own weak cross section, which does not necessarily coincide with the main fracture surface of composite materials. Stress concentration in the matrix, caused by fiber fracture, is relaxed due to matrix yielding, and therefore prevents matrix crack, while the crack may join breakage of other fiber. In this case, it fractures in the manner of fiber pull-out from the matrix, rather than in the fracture plane of composite material again. Especially in such a case, the fiber pull-out really exists, where the distance between fracture surfaces of these fibers and the main crack surface is within a small range (less than half the critical fiber length l_c). The pull-out energy per unit area is given by:

$$u = \frac{V_f \sigma_{fu} l_c}{12} \tag{9.10}$$

The differences between fiber debonding and fiber pull-out are: when matrix cracks do not expand transversely, fiber debonding happens; for fiber pull-out, crack initiated by fibers breakage cannot afford to extend into tough matrix. Fiber pull-out is usually accompanied by the elongation deformation of matrix, and such deformation is non-existent in fiber debonding. Their similarities are that the destruction occurred at the interface between fiber and matrix, and they both enhance the fracture energy significantly.

(5) Delamination crack.

The cracks expanding through a layer of laminates, when the crack tip reaches the fiber in the adjacent layer, it may be restrained. This process is similar to matrix crack suppressed in the interface between fiber and matrix. Because high shear stress in the matrix of neighboring crack tip, crack may branch, and begin to expand in parallel to the interface layer. This is called delamination cracks. If such a crack exits, the fracture energy absorption is high. In bending test, Charpy and Izod impact test for laminated composites, there are always delamination cracks, especially when the porosity is large, interlaminar shear damage happens firstly.

Energy absorption mechanisms of composite materials are discussed above, from which we can see clearly that the effects of the material parameters on the tensile and impact properties may be independent to each other. For example, lowing interfacial strength is harmful to tensile strength, but it improves impact strength. High-modulus fiber composites, because of the small fiber fracture strain, absorb lower energy than the low-modulus glass fiber composites, and are more brittle.

3) Influencing factors on impact properties of composite material

The influencing factors on impact properties of composite materials include two aspects: test parameters and material properties. Test parameters include impact velocity, weight of punch hammer, edge forms, span-height ratio and supporting conditions, and so on. Material properties, including fiber type, matrix toughness, fiber volume fraction and interfacial bonding conditions, etc. Now that the mechanisms of energy absorption are discussed, it is not difficult to understand the impact of materials properties on the impact property. Different fibers properties, different matrix toughness and different interface strength, will lead to different failure modes, which greatly affect the impact property of composite materials.

Table 9.1 shows Charpy impact properties of non-notched specimens of different fiber epoxy composite materials. As can be seen, the differences between the three fibers only leads to the different propagation energy U_p (propagation energy per unit area $U_p = E_p/bh$). The initial fracture energies have little differences. S-GF/epoxy composite materials and KF/epoxy composite materials have mostly higher impact toughness than the high-strength CF/epoxy composite material.

Table 9.1 Charpy impact properties of non-notched specimens of different fibers/epoxy composite materials

Impact property / Material	$P_{\max}$ (kN)	$U_i(E_i/bh)$ (kJ/m^2)	$U_p(E_p/bh)$ (kJ/m^2)	$U_t(U_i+U_p)$ (kJ/m^2)	DI
High-strength CF/epoxy	129	43	66	109	1.5
S-GF/epoxy	13.4	70	708	778	10.1
KF/epoxy	7.9	40	632	672	15.8

Interface strength affects the impact properties greatly, because it strongly influences the failure mode of composite materials. The interface situation can be changed by different methods of surface treatment on glass cloth. Unsaturated polyester and epoxy resin are used as matrix materials, and short beam shear strength is taken as a measure of interface strength. The interface strength of polyester laminate has a significant change due to the different coupling agent on fiber surface; and for epoxy laminate, interface strength does not change so much, because epoxy resin can also form a strong adhesive surface with fiber even in the absence of coupling agent. The results of Charpy impact test of polyester and epoxy laminates are shown in the Figs 9.3 and 9.4. As can be seen, the initial fracture energy of the two laminates U_i increases with the shear strength. For the epoxy laminate, the propagation energy and the total impact energy increase with the interface strength. And for the polyester laminate, the propagation energy and the total impact energy have a minimum value. At the case of interface shear strength greater than a certain limit, the total impact energy increases with the shear strength. Lower than this limit, the total impact energy reduces with the shear

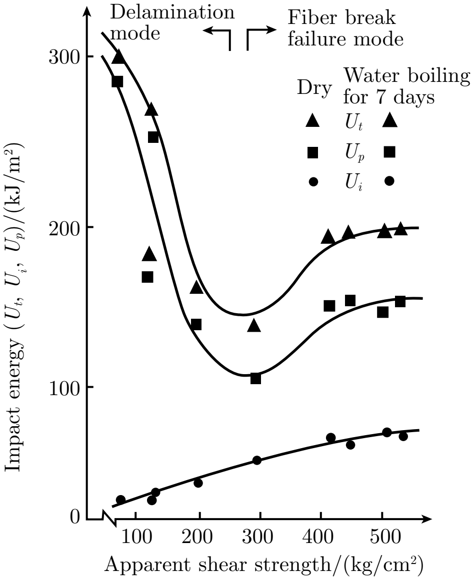

Fig. 9.3 The influence of interface strength on impact properties of glass fiber/polyester composites.

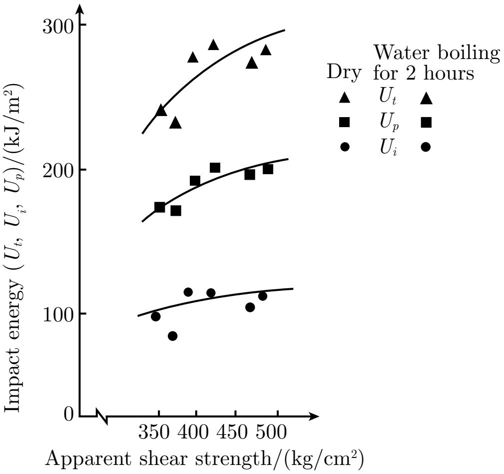

Fig. 9.4 The influence of interface strength on impact properties of glass fiber/epoxy of composites.

strength. Because below this limit the main failure mode is delamination, above the limit fiber damage is a major failure mode. When interface bonds weakly, initial fracture energy required is small, but after the initial damage, delamination occurs, which absorbs large energy. In the propagation stage, the sample carries a small load, but absorbs much energy. For the epoxy laminates, there is no weak interfacial adhesion, too low for delamination to happen, so the impact energy will always increase with the shear strength.

From above, the approaches to improve the impact toughness of composite materials are: ① matrix toughening; ② suitable interface strength; ③ use hybrid fiber composite materials, such as mixing carbon fiber with glass fiber or Kevlar fiber.

9.1.2 Fatigue performance of composite materials

Materials under alternating load, even if the highest stress is lower than the static strength limit of material, but after a certain loading period, it breaks down as well. That is to say, fatigue strength is always lower than its static strength, which is for all materials, including metals, plastics and composite materials. In practice, fatigue load is often inevitable, so people should not only understand static strength of materials, but also should better grasp its fatigue properties, as the basis for design.

1) Character of fatigue properties of composite materials

Designer and researcher of materials have paid much attention to fatigue property of composite materials for its increasing development of application, and a great deal of research works have been carried out. Although having not yet established the similar specific design criteria with metal fatigue, we had a fundamental understanding on many characters in the fatigue process of composite materials. Substantial research works shown that continuous unidirectional fiber reinforced composite materials have excellent fatigue resistance in the fiber direction, because for unidirectional composite materials, the fatigue load was mainly undertaken by the fibers with the same direction to the load. Fig. 9.5 shows the comparison of fatigue properties of some unidirectional fiber composite materials and aluminum alloy, from which we know that, for the high-modulus fiber reinforced composite materials, such as aramid, boron and carbon fiber reinforced composite materials, their fatigue performance is far superior to aluminum alloy and glass fiber composite materials. For carbon fiber or boron fiber epoxy composite materials, tension-tension fatigue S-N curve is far higher than other structural materials, including glass fiber composite materials, and the influence of temperature is not significant. This shows that at the stress level slightly lower than the static strength, the sample can reach a higher cycle number.

In practical applications, composite materials are usually used in the form of

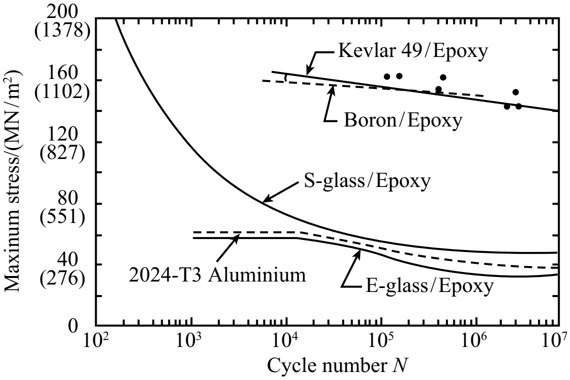

Fig. 9.5 Fatigue properties of some unidirectional fiber composites and aluminum alloy.

multilayer laminates to adapt to the multiaxial stress in structure. Because of the different strength of each layer, at early stage of the fatigue process (about 10% of the life) the transverse crack damage begins to appear. With the fatigue cycle increasing, a corresponding increase in crack length and quantity continues. There also appears delamination, interface debonding, fiber breakage or buckling, etc. These damages, accounting for a very broad scope of fatigue life, do not affect using the material or structure safely. Metal material is different, once cracks, it will soon fracture. In the fatigue process of composite materials damages occur at the early stage, but they expand slowly, until 90% of fatigue life rapid fracture occurs, and the ultimate destruction can be identified in advance, so composite materials have excellent damage safety.

There is a fatigue limit for metallic material, i.e., metallic material can bear unlimited cycle if it does not break under 10^7 cycle, and thus the maximum stress (S) corresponding to $N = 10^7$ in the S-N curve is called fatigue limit. But composite materials have not yet been recognized as having such nature, so the maximum stress S corresponding to $N = 10^7$ cycles is called conditional fatigue limit.

Temperature rising is another feature of fatigue performance of composites, and sometimes it is high to 40∼50°C. Temperature rising will undermine the performance of the matrix material so that the fatigue life decreases. Temperature rising is related to the test frequency and specimen's thickness.

2) The influencing factors on fatigue properties of composite material

The result of fatigue test can be usually shown in the form of stress to cycle number curve (S-N curve). Ordinate is the amplitude of the stress expressed by the ordinary ruler, and abscissa is the cycle number to damage of sample under fixed stress, using logarithmic coordinates. For all materials, the position and shape of S-N curve may be different, and the materials with higher position and slow drop show the excellent fatigue performance. The S-N curve of composites will be affected by a variety of materials and test parameters, such as: ① the type of matrix material; ② the type of reinforcing material; ③ fiber orientation and lay up sequence; ④ V_f ; ⑤ interfacial properties; ⑥ load type; ⑦ average stress; ⑧ test frequency; ⑨ environmental conditions. Here we do not discuss them in detail.

9.1.3 Mechanical properties of composite materials under long-term static load

The mechanical properties under long-term static load include: strength problem - persistent strength; deformation problem-creep.

1) Persistent strength of composite materials

Under a long period of static load and maintaining a certain period without failure, the maximum static load the material can bear is called as the persistent strength; and under a long period of certain static load and without failure, the longest time the material can withstand is called as persistence.

The persistent strength of composite materials is much lower than strength under short-term load, Table 9.2 shows the persistent strength of several glass fiber reinforced plastics under static bending load. As can be seen, different matrix materials have different ability to maintaining strength. Its essence is that matrix has different main-chain strength, different crosslinking density and different crosslinking bond strength. This can be explained by the residual deformation when material failure happened under a long period of load. The residual deformation is irreversible plastic deformation, reflecting the damage level of the main chain and cross-linked bond of adhesive under long-term load. Residual deformation under long-term load can be estimated by the residual deformation under short-term static load (fracture elongation) when specimen breaks. Their relationship is shown in follows:

$$\varepsilon' = \varepsilon'_0(1+t)^n \tag{9.11}$$

Here, ε' expresses the residual deformation under long-term static load when specimen breaks; ε'_0 expresses the residual deformation under short-term static load, when specimen with same material breaks; t expresses the time under long-term static load; n is the parameter depending on experimental conditions, the type of reinforcing material, in particular the type of matrix material.

Table 9.2 Persistent strength of several FRP under static bending load

FRP varieties	Static bending strength (MPa)		Persistent strength / Original strength
	Short-term tests	1000 hours loading	
Polyester FRP	350～430	230～280	65%
Epoxy FRP	450～520	280～330	62%～64%
Phenolic FRP	540～580	330	57%～62%
Silicone FRP	220	110	50%

The persistent strength of composite materials depends primarily on the matrix material, so its influencing factors primarily refer to the influencing factors on the matrix material. Temperature increases, the persistent strength of composite material declines. Humidity (water), on the one hand, plasticizes matrix material or makes main chain of matrix hydrolyze and fracture, and on the other hand, reduces the strength of glass fiber, thus affects the persistent strength of composite materials. For example, arrangement direction of the fiber and fiber type affect magnitude of matrix load in the composite material, and thus the persistent strength of composite materials.

2) Creep properties of composite materials

Under long-term static load, the phenomenon that the load remains unchanged and deformation continues to develop, is known as creep. Metallic materials at room temperature above the yielding point, or at high temperature below the yielding point, will produce creep phenomena caused by irreversible plastic deformation. For composite materials, the deformation will also continue to increase at room temperature and under the long-term invariable static load. Such deformation is usually recoverable, thus belongs to elastic deformation. The reason lies in the fact that the matrix is a viscoelastic polymer material. This shows that the creep properties of composite materials depend mainly on the relaxation properties of the matrix, and the greater cross-linking density of the matrix, the lower flexibility of main chain, the more unobvious creep characteristics.

We see from the above analysis that creep of composite materials has the following characteristics: ① creep of carbon fiber composite materials are lower than that of glass fiber reinforced plastic; ② creep phenomenon is the most unobvious along the fiber direction under the tensile load; ③ tension along arbitrary angle α with the fiber, creep phenomenon becomes clear, most obvious along the 45° direction; ④ creep under lasting bending load is more obvious than creep under sustained tensile load; ⑤ higher temperature, more significant creep phenomenon of composite materials.

Because of the persistent strength of composite materials under long-term static load less than the short-term static strength and the existence of apparent creep phenomenon, which must be taken into account in the design of composite material components.

9.1.4 Environmental effect on the properties of composite materials

Composite materials are all used in a certain environment, so it is important to understand the change in properties of materials under a variety of environmental conditions, such as exposure to water, steam or corrosive media, low temperature and high temperature, a variety of conditions in long-term physical and chemical stability test. In general, under these adverse environmental conditions, the performance of composite materials will reduce. This is because environmental factors affect the properties of fiber, matrix and interface, which are discussed below, respectively.

1) Fiber strength

There exist defects or cracks in materials inevitably. Under stress and chemical corrosion, such crack will extend, and when reaching the stress state of the maximum critical crack, the material will destroy. The decrease of fiber strength in this way is called stress corrosion. For glass fibers, water infiltrates along the surface micro-cracks into its interior, resulting in chemical and physical effects. Main chain of SiO_2 is broken by chemical effects, and physical role reduces intermolecular forces, so that the strength of glass fiber will decline significantly. We need to point out that the surface treatment agent can produce the protective physical effect on the fiber surface, so as to prevent fibers from being attacked by chemical media.

2) Matrix effect

(1) Aging at high temperature.

Generally speaking, organic polymer materials at high temperature are unstable, and they undergo a chemical decay process from pyrolysis. If the pyrolysis reaction sustains long enough, or very fast, the material will destruct essentially, and the matrix material is decomposed into volatile gas. This tempestuous pyrolysis reaction seriously affects the integrity of composite materials, and restricts the using temperature of composite materials. Temperature and time are two parameters affecting the pyrolysis process, and matrix decomposition will cause the stiffness and strength of composites declining significantly. It can be seen that the highest using temperature of composite materials is usually dominated by the thermal stability of the matrix.

(2) Viscoelasticity.

Many properties of composite materials, such as transverse tensile property of unidirectional composites, interlaminar shear strength, performance of short-fiber composite material, are mainly dominated by the matrix properties, and even small change of the matrix performance will reflect in the performance of composite materials. Polymer matrix material has a clear viscoelasticity, at the temperature far from matrix pyrolysis, the properties of matrix material such as modulus may decline much, and thus affecting the performance the matrix dominates, so that the application of composite materials is restricted. The closer to the glass transition temperature is, the more obvious stress relaxation and creep are, and the greater drop in modulus is. It shows that heat resistance of composite materials is determined by the heat resistance of matrix material.

(3) Infiltration.

Water or other chemical media through the infiltration into polymer matrix have two functions on the matrix. One is physical. The medium molecule penetrates into the interspace of macromolecular chains by diffusion, breaks the macromolecular secondary bond, and causes matrix swelling. In fact, this phenomenon is exactly matrix plasticization where the chemical medium serves as the plasticizer and the absorption of chemical medium is equivalent to the increase of the ambient temperature. The glass transition temperature of matrix after swelling decreases, modulus decreases. The greater hygroscopic capacity is, the greater it declines. Whether chemical media or water swelling matrix depend largely on whether their molecular polarity or solubility is close to each other. The other function is chemical, which is the chemical reaction between the medium molecule and macromolecule, such as oxidation, hydrolysis, and so on, the main chain ruptures, thus reducing the strength of the matrix material. Whether this happens depends largely on the special groups in the macromolecular chain. For example, the ester of unsaturated polyester can be hydrolyzed, and hydrolysis is more easily carried out particularly in alkaline aqueous solutions. Chemical cleavage can lead to irreversible performance loss. Increasing molecular chain stiffness and degree of crosslinking will effectively prevent the infiltration of media, reduce the performance deterioration. If combining temperature and chemical media role, the deterioration of material properties will be accelerated.

3) Interface effect

Good interfacial bond can avoid media or water from infiltrating into composite material through capillary action along the interface defects, thereby undermining the fiber, matrix and interface further. When using coupling agent to treat glass fiber, the fiber and matrix will link to each other by the chemical bonds, which greatly enhances the resistance of glass fiber reinforced plastics in boiling water.

9.1.5 Fracture toughness and damage of composite materials

1) Fracture toughness

Fracture toughness characterizes the capacity of resistance against crack to expand at the existence of defects in materials. It can usually be indicated by the critical stress strength factor K_c or critical strain energy release rate G_c. Both of them are material constants and can be obtained through experiments.

For an infinite plate, of which center has a penetration crack with length of $2a$, the tensile stress σ is vertical to cracks, the degree of stress within a small area near the crack tip can be expressed by the stress intensity factor K.

$$K = \sigma\sqrt{\pi a} \tag{9.12}$$

It is related to the crack length a and the stress σ, and increase with the external stress or crack length increasing. K_c is the critical value of K, when $K \geqslant K_c$, unstable crack propagation occurs. So K_c can be used to evaluate the ability to resist crack unstable propagation (fracture toughness), which is a constant for a given material.

The released energy of crack propagation per unit area is called the energy release rate G, which is the driving force for crack propagation.

$$G = \frac{\pi\sigma^2 a}{E} \tag{9.13}$$

Crack resistance, including the surface energy consumption forming new surface, and the work of the crack tip plastic deformation. G increases with the increase of applied stress or crack length; when G increases to the critical value G_c, unstable crack propagation occurs, G_c is called the critical strain energy release rate. It is also a material constant, the greater G_c, the greater energy required for the unstable crack propagation, the greater capacity to resist the unstable crack propagation. The relationships between K and G, K_c and G_c are given by:

$$G \cdot E = K^2 \tag{9.14}$$

$$G_c \cdot E = K_c^2 \tag{9.15}$$

For isotropic materials, the theory above (fracture mechanics) is quite successful for the study on the destruction of materials and the design of components.

The fracture mechanics theory of isotropic material is used into anisotropic composite materials. Over the years some progress has been made, but researchers fail to achieve the anticipative success because of the unique failure mechanism of composite materials. In the design of composite material components, damage mechanics is more appropriate than fracture mechanics, because there is no main crack but only damage area in composite materials.

Fracture toughness of composite materials is much higher than the fiber or the matrix itself. For CF/epoxy or polyester: the fracture surface energy for unidirectional fiber composite γ_F (half of G_c) is about 100kJ/m^2, and for the glass fiber and graphite fiber fracture surface energy are 4kJ/m^2 and 50∼100J/m^2, respectively, the fracture surface energy of resin less than 500J/m^2.We can see G_c of composite materials is 2∼3 orders of magnitude higher than the matrix, which naturally draws great interest. Composite materials have excellent fracture toughness and fatigue performance, and provide great reliability for the structure application. Difference to homogeneous materials is summarized in Table 9.3.

From the Table 9.3, we see the fracture toughness of composite materials is directly related to the mechanism of energy absorption in crack propagation process, so the influencing factors of fracture toughness of composite materials include fiber strength, modulus and V_f, fiber diameter, interfacial strength, matrix toughness, crack direction and ply-stacking mode, etc.

2) Damage factor

Actual composite materials are multi-ply laminates with many weak points.

Table 9.3 Main differences between composite materials and homogeneous materials

Item	Homogeneous material	Composite material
Crack propagation direction	Crack propagation direction collinear to crack plane, non-branching and changing direction, that is, "self-similar" crack propagation	Generally no "self-similar" crack propagation, only with the exception of unidirectional laminate under transverse tension
Crack propagation length	Can easily detect the crack propagation length. For elastic-plastic materials, crack tip produces plastic zone, use a_{eff} to amend: $a_{eff} = a + \gamma_y$	Since non-self-similar crack growth, so can not determine crack propagation length. There exists damage similar to plastic zone at crack tip
Crack propagation mechanism	Crack propagation resistance $R = 2\gamma_F = 2(\gamma_s + \gamma_p)$ $G > R$, Crack propagates automatically	In the damage zone exists in a wide range of energy absorption mechanism: fiber breakage, matrix crack, interface disbonding, fiber pull-out, etc. $\gamma_F = \dfrac{\partial S}{\partial a} = \dfrac{\partial(S_f + S_m + \gamma_i)}{\partial a}$
γ_F, G_c	γ_F, G_c is material constant, unrelated to the crack location and loading direction	It is a multi-parameter function, such as the direction and location, depending on the energy absorption mechanism of the crack propagation process, so G_c is a variable
Relationship between G and K	Since crack propagation direction collinear to crack plane, relationship between G and K can be expressed as $G \cdot E = K^2$	Since the crack expansion is not self-similar, so $K = \sigma\sqrt{\pi a}$ and $G \cdot E = K^2$ are not related

There are various forms of damage from the initial tension to the final fracture, such as transverse cracks, delamination, longitudinal cracks, fiber breakage, etc. With damage increasing progressively, material properties reduce gradually, such as consecutive decline of stiffness. Substantial damage exits before the main macro crack appears. Damage expansion accounts for 80%$\sim$90% of the total life, while the formation and propagation of the main macro crack only account for 10%$\sim$20% of the total life; and much damage does not lead to the main macrocrack described in fracture mechanics, but rather soften and loose, resulting in the collapse. We see that influence of these damages on the mechanical properties is not less than the main macro crack. In the end, the early eighties form another branch of solid mechanics - damage mechanics, which evolves by introducing a damage variable into the continuum mechanics. In this theory damage as the void that uniformly distributed in a continuous medium, is a composite material with the void as the second phase. According to the rule of mixture, the elastic modulus $E(w)$ of continuum damage medium:

$$E(w) = E_0(1 - w) + E_V \cdot w \tag{9.16}$$

Where, w is the percentage of voids in materials; E_0 is the elastic modulus of materials without damage; E_V is the elastic modulus of void, and when $E_V = 0$, we get:

$$w = 1 - \frac{E(w)}{E_0} \tag{9.17}$$

Where, w is defined as damage factor, is a variable, so is also called damage variable. The materials with micro-void are generally regarded as continuous media containing a micro-damage field, and the formation growth, diffusion and coalescence of such micro-damage are taken as a damage evolution process. Fracture problem of composites is in fact the process of the damage formation and its development. This justifies the effort researchers have spent in damage mechanics and using damage tolerance design for the design of composite components is more in line with the practice.

9.2 The basic mechanical properties of sandwich structure composite

We discuss mechanical properties of a single material or the composites in the previous chapter. In practice, especially in the aviation industry, we often use sandwich structure composed of the facesheet and lightweight core so as to reduce weight and increase stiffness. Thus, further analysis is needed to study the mechanical properties of such structure. To simplify the analysis, we hypothesize that composite facesheet and core are both isotropic materials, and discuss only the mechanical properties of sandwich structure under a single load, namely tension, compression, bending and shear. Similar to analysis on unidirectional composite materials in the previous chapter, the analysis of mechanical properties of sandwich structures will still be based on three basic assumptions. The assumptions are the same in words. The only difference is that we take facesheet and core as an essential component of sandwich structure, that is, we treat the basic mechanical properties of facesheet and core as known parameters. Three basic assumptions are also put forward for facesheet and core, for example the integration assumption is that the deformation of facesheet and core is the same to that of sandwich material. Based on these assumptions, we can discuss strength, modulus, deformation, stiffness and other basic mechanical properties of sandwich structure.

9.2.1 The tensile properties of sandwich structure

The tensile properties of sandwich structure panel can be discussed respectively at direction along the plate surface (plate surface) and perpendicular (normal) to plate surface.

1) Tension along plate surface

Tension along plate surface is shown in Fig. 9.6. Three basic assumptions here are: ① integration assumption: the consistent deformation of core and facesheet;

② elasticity assumption: deformations of sandwich structure, core and facesheet are all obey Hooke's law; ③ equal initial stress assumption: the initial stresses of core and facesheet are both zero or equal, that is, they load at the same time.

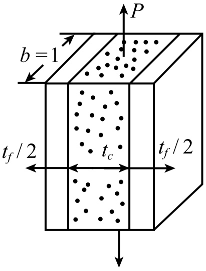

Fig. 9.6 The tension of sandwich panel along plate surface.

(1) Stress and strength.

Based on static equilibrium:

$$\sum P_L = 0, P_L = P_f + P_c$$

Videlicet:

$$\sigma \cdot F = \sigma_f \cdot F_f + \sigma c \cdot F_c$$

Here, σ, σ_f, σ_c express separately the tensile stress of sandwich structure, facesheet and core; F, F_f, F_c express the area of cross section of sandwich panel, facesheet and core, respectively. We have:

$$F = b \cdot t = b \cdot (t_f + t_c) = F_f + F_c, \quad F_f = b \cdot t_f, \quad F_c = b \cdot t_c$$

t, t_f, t_c express the section height of sandwich panel, facesheet and core, respectively.

After transformation, stress relationship is:

$$\sigma_L = \sigma_f A_f + \sigma_c A_c = \sigma_f A_f + \sigma_c(1 - A_f) \tag{9.18a}$$

Here, A_f, A_c respectively express the percentage of cross section area of facesheet and core. We have:

$$A_f = F_f/F, \quad A_c = F_c/F = 1 - A_f$$

The estimation formula of tensile strength along plate surface can be calculated by substituting the stress in formula (9.18a) with the strength of facesheet and core, respectively:

$$\sigma_{Lu} = \sigma_{fu} A_f + \sigma_{cu}(1 - A_f) \tag{9.18b}$$

(2) Modulus, deformation and stiffness.

According to the consistent deformation assumption, we have $\varepsilon_L = \varepsilon_f = \varepsilon_c$, Substitute them into (9.18a), and apply Hooke's Law:

$$E = \frac{\sigma}{\varepsilon} = \frac{\sigma_f}{\varepsilon_f} \cdot A_f + \frac{\sigma_c}{\varepsilon_c}(1 - A_f) = E_f \cdot A_f + E_c \cdot (1 - A_f) \tag{9.19}$$

We see that the tensile stress, strength and modulus along plate surface of sandwich structure obey the rule of mixture.

Tensile deformation is given by:

$$\varepsilon = P/EF \tag{9.20}$$

Here EF is called the tensile stiffness (H), which expresses a measure of the ability of sandwich structure to resist the tensile deformation under load along plate surface.

$$H = EF = E_f F_f + E_c F_c = E_f b t_f + E c b t_c \tag{9.21}$$

(3) Discussion.

According to the hypothesis of consistent deformation $\varepsilon_f = \varepsilon_c$, we have:

$$\frac{\sigma_f}{\sigma_c} = \frac{E_f}{E_c} \tag{9.22}$$

We see that the tensile stress along plate surface distributes according to the modulus of constitutive material in the sandwich structure.

$$\frac{P_f}{P_c} = \frac{E_f \cdot F_f}{E_c \cdot F_c} = \frac{E_f \cdot t_f}{E_c \cdot t_c} \tag{9.23}$$

That is, load ratio of the facesheet and core shows direct proportion of their each stiffness or distributes according to product of the material modulus and loading area.

Because of $E_f \gg E_c$, modulus, stiffness, stress, load along plate surface of sandwich structure are mainly dominated by the facesheet.

2) Tension perpendicular to plate surface

Tension perpendicular to plate surface is shown in Fig. 9.7.

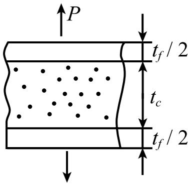

Fig. 9.7 The tension of sandwich panel perpendicular to plate surface.

(1) Stress and strength.

In accordance with static equilibrium $\sum P_N = 0$, we have:

$$P_N = P_f = P_c$$

Because of the same loading area, the relationship of stress is given by:

$$\sigma_N = \sigma_f = \sigma_c \tag{9.24}$$

Actually the tensile strength perpendicular to the plate surface is determined mainly by the bond strength (σ_{fcu}) between the facesheet and core as well as the tensile strength (σ_{cu}) of the core. These two strengths are both low, so the carrying capacity of tension perpendicular to plate surface is small. Therefore, generally sandwich structure should not be used in such load.

(2) Modulus.

According to the deformation conditions, and the fact that the facesheet and core are connected in series, we have:

$$\varepsilon_N \cdot t = \varepsilon_f \cdot t_f + \varepsilon_c \cdot t_c$$

According to elasticity assumptions and $\sigma_N = \sigma_f = \sigma_c$, we have:

$$E_N = \frac{\sigma_N}{\varepsilon_N} = \frac{\sigma_f \cdot t}{\varepsilon_f \cdot t_f + \varepsilon_c \cdot t_c} = \frac{\sigma_c \cdot t}{\varepsilon_f \cdot t_f + \varepsilon_c \cdot t_c}$$

Because

$$\varepsilon_f = \sigma_f / E_f, \varepsilon_c = \sigma c / E_c$$

We have

$$E_N = \frac{E_f \cdot E_c \cdot t}{E_c \cdot t_f + E_f \cdot t_c} \tag{9.25a}$$

Because

$$E_f \gg E_c, t_c > t_f$$

The tensile elastic modulus (E_N) perpendicular to plate surface can be approximately expressed by:

$$E_N \approx \frac{E_N \cdot t}{t_c} \tag{9.25b}$$

That is, when tensile perpendicular to the plate surface, the elastic modulus of sandwich panel depends mainly on the tensile modulus of the core materials.

9.2.2 Compressive properties of sandwich structure

Compressive properties of sandwich panel can be analyzed in compression along and perpendicular to plate surface.

1) Longitudinal compression

Compression along the plate surface or longitudinal compression is shown in the Fig. 9.8.

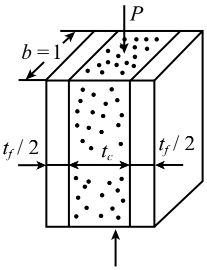

Fig. 9.8 The longitudinal compression of sandwich panel.

Longitudinal compression has two kinds of destructive ways, compression failure and compression instability. But owing to its larger size cross-section, sandwich structure usually has enough stiffness, so compression failure mostly happens in longitudinal compression. After degumming of adhesion layer between facesheet and core, unstable failure often happens. The analysis process of longitudinal compression is similar to the tension along plate surface. Only load, stress, deformation and others have the reversed symbol.

Stress relationship for compression:

$$\sigma_{-L} = \sigma_{-f} A_f + \sigma_{-c}(1 - A_f) \tag{9.26a}$$

Strength formula for compression:

$$\sigma_{-Lu} = \sigma_{-fu} A_f + \sigma_{-cu}(1 - A_f) \tag{9.26b}$$

Modulus formula for compression:

$$E_{-L} = E_{-f} A_f + E_{-c}(1 - A_f) \tag{9.27}$$

Load distribution relationship for compression:

$$\frac{P_{-f}}{P_{-c}} = \frac{E_{-f} \cdot t_f}{E_{-c} \cdot t_c} \tag{9.28}$$

Compressive deformation:

$$\varepsilon_{-} = \frac{P}{E_{-f} \cdot t_f \cdot b + E_{-c} \cdot t_c \cdot b} \tag{9.29}$$

Compressive stiffness:

$$H_{-} = E_{-} \cdot F = E_{-f} \cdot F_f + E_{-c} \cdot F_c \approx E_f \cdot t_f \cdot b \tag{9.30}$$

The meaning of symbol is the same to the along plate surface tension, but here are compression parameters.

2) Compression perpendicular to plate surface

Compression perpendicular to plate surface is shown in Fig. 9.9.

For compression perpendicular to plate surface, the performance of sandwich

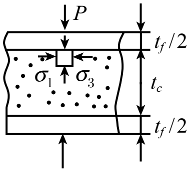

Fig. 9.9 The compression of sandwich panel perpendicular to plate surface.

panel depends primarily on the compressive strength and modulus of the sandwiched core, but it is different from the compressive performance of the pure core. Since under the compressive load (P_{-N}), the sandwiched core will produce deformation in the L and T direction, but they are constrained by the facesheet, so in fact the sandwiched core is subject to compressive stress in three directions, and its compressive strength is higher than that of a single compressive state.

By the maximum shear stress theory, failure condition of the sandwiched core in the three direction compression:

$$\tau_{\max} = \frac{\sigma_1 - \sigma_3}{2} \geqslant \tau_{cu} \tag{9.31a}$$

Suppose the core is isotropic material, then $E_1 = E_3$.

So

$$\frac{\sigma_1}{\varepsilon_1} = \frac{\sigma_3}{\varepsilon_3} \quad \sigma_3 = \sigma_1 \cdot \frac{\varepsilon_3}{\varepsilon_1} = \mu_{13} \cdot \sigma_1$$

Substitute in the above formula (9.31a):

$$\tau_{\max} = \frac{1 - \mu_{13}}{2}\sigma_1 \geqslant \tau_{cu} \tag{9.31b}$$

Compressive strength:

$$\sigma_{-Nu} = \frac{2\tau_{cu}}{1 - \mu_{13}} \tag{9.32}$$

When the core is affected by a single stress, $\sigma_3 = 0, \sigma_1' \geqslant 2\tau_{cu}$, the material fails. Here the compressive strength is $2\tau_{cu}$, which is less than the actual strength (σ_{-Nu}) of sandwich structure under the perpendicular compressive load.

The elastic modulus (E_{-N}) under the perpendicular compressive load is similar to that under the perpendicular tensile load. Only the parameters used are different, namely,

$$E_{-N} = \frac{E_{-fN} \cdot E_{-cN} \cdot t}{E_{-cN} \cdot t_f + E_{-fN} \cdot t_c} \approx \frac{E_{-cN} \cdot t}{t_c} \tag{9.33}$$

That is, under the perpendicular compressive load, the elastic modulus of sandwich panel depends primarily on the compressive modulus of core material.

9.2.3 The bending properties of sandwich structure

Here we only discuss the three-point bending performance under concentrated load in the center of simply supported beam, and the load is shown in Fig. 9.10.

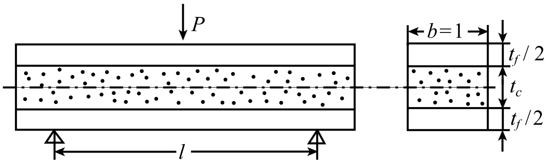

Fig. 9.10 Three point-bending of sandwich beam.

1) Stress and strength

In the load condition, there are two stresses existed in the sandwich panel, one is the normal stress caused by bending moment, and the other is the shear stress induced by shear load.

The maximum bending moment (in the center of the beam):

$$M_{\max} = \frac{Pl}{4}$$

The maximum shear load (invariant):

$$Q_{\max} = \frac{P}{2}$$

According to materials mechanics, and the normal stress at the point which is the distance Z away from neutral layer:

$$\sigma_F = \frac{MZ}{J} \tag{9.34}$$

J is the inertia moment of beam, for solid rectangular cross-section beam:

$$J = \frac{bh^3}{12} \tag{9.35}$$

For sandwich structure plate, we analyze the inertia moment of facesheet and core respectively at first. According to the definition of the inertia moment, inertia of the facesheet (J_f) is given by:

$$J_f = 2b\int_{\frac{t_c}{2}}^{\frac{t_c}{2}+\frac{t_f}{2}} Z^2 \mathrm{d}Z = \frac{bt_f}{4}\left[\left(t_c + \frac{t_f}{2}\right)^2 + \frac{t_f^2}{12}\right] \tag{9.36a}$$

In general, total thickness of facesheet is small and $b = 1$, so we find the inertia of the facesheet to be approximately:

$$J_f \approx \frac{t_f}{4}\left(t_c + \frac{t_f}{2}\right)^2 \tag{9.36b}$$

The inertia moment of the core:

$$J_c = 2b\int_0^{\frac{t_c}{2}} Z^2 \mathrm{d}Z = \frac{bt_c^3}{12} \tag{9.37}$$

Since $E_f \gg E_c$, the ability of the core sandwich to bear bending moment is very low. σ_F in the core is small, while the value in the facesheet is great. Its distribution is shown in Fig. 9.11.

By neglecting the bending moment borne by the core, we assume that bending moment is solely born by the facesheet; and because of thinner facesheet, we assume that normal stress is uniformly distributed in the plate. So

$$\sigma_F = \frac{MZ}{J} \approx \frac{MZ}{J_f}$$

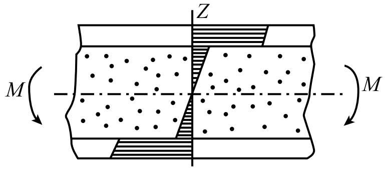

Fig. 9.11 The normal stress distribution of sandwich structure beam.

Taking the action point of average stress into account, the distance (Z) away from the axial line is:

$$Z = \frac{\frac{t_f}{2} + t_c}{2} = \frac{t_f + 2t_c}{4}$$

Substitute the relevant parameters in the formula above, the bending normal stress of sandwich structure:

$$\sigma_F = \frac{M}{\frac{t_f}{2}\left(t_c + \frac{t_f}{2}\right)} \tag{9.38a}$$

Substitute the maximum bending moment in the formula above, the bending strength of sandwich structure:

$$\sigma_{Fu} = \frac{\frac{P_{\max} l}{4}}{\frac{t_f}{2}\left(t_c + \frac{t_f}{2}\right)} = \frac{P_{\max} l}{t_f(2t_c + t_f)} \tag{9.38b}$$

Here, $P_{\max}$ is the concentrated load (P) when bending failure happens.

In cross-section of the sandwich structure, the shear stress distributes in a parabola (Fig. 9.12). Shear stress on the edge is the smallest, zero; shear stress in neutral layer is largest, $\tau_{\max}$; shear stress in the facesheet sharply increases, changes slightly in the core inside, can be approximated as constant.

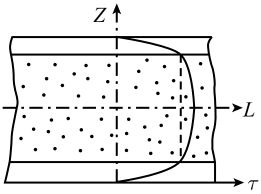

Fig. 9.12 The internal shear stress distribution of sandwich panel.

Because

$$\tau_{ZL} = \frac{Q}{t \cdot b} \tag{9.39a}$$

$$t_f \ll t_c \qquad b = 1 \text{ (unit width)}$$

Therefore, the shear stress of the sandwich structure is given by:

$$\tau_{ZL} = \frac{Q}{tb} \approx \frac{P}{2t_c} \tag{9.39b}$$

The shear strength of sandwich structure is given by:

$$\tau_{ZLu} \approx \frac{P_{\max}}{2t_c} \tag{9.39c}$$

The shear stress on the sandwiched core is bigger than that of the facesheet and the shear strength of core is lower than that of the facesheet, so here $P_{\max}$ is referred to the concentrated load (P) when core shear failure or bonding layer shear failure occurs.

We can see from the analysis above that, in the three-point bending case, to determine the strength of sandwich panel, we should not only check the bending strength, but also the shear strength. Whether the facesheet bending failure (tensile and compressive failure), or core shear failure occurs, depends on the relative size of the load at that time, which further depends on the span-height ratio of the beam. Similar to the bending case of unidirectional fiber composites, there is critical span-height ratio. To determine bending properties of sandwich structure, the span-height ratio must be greater than the critical span-height ratio.

2) Deformation, stiffness, modulus

(1) Deformation.

There are two parameters to measure the bending deformation of the beam: the deflection (δ) and rotation angle (θ). Here we only discuss the deflection (δ). For a solid simply supported beam, the maximum bending deformation δ includes δ_b caused by the bending moment and δ_s induced by shear load under the concentrated load (P) at the center of beam.

$$\delta_b = \frac{Pl^3}{48E_fJ} \tag{9.40}$$

$$\delta_s = \frac{Pl}{4Gt} \tag{9.41}$$

$$\delta = \delta_b + \delta_s \tag{9.42a}$$

From the above formula, under the constant external load, the stiffness parameters to decide the bending deformation can be seen as follows.

The stiffness parameter (D) to resist deformation of the bending moment $D = EJ$.

The stiffness parameter (U) to resist deformation of the shear load $U = Gt$.

It is proved that for the solid beam of the common materials, when the beam span (l) is five times bigger than the thickness ($l > 5t$), $\delta_b \gg \delta_s$. So usually the bending deformation of solid beam (δ) is approximated with $\delta_b(\delta \approx \delta_b)$. In fact, for carbon fiber composite materials, only when $l > 40 \sim 100t$, for FRP $l > 16 \sim 20t, \delta$ can be approximately equal to δ_b.

For the sandwich structure, because of the low shear modulus of the core, in general the shear deformation (δ_s) should not be omitted in the bending. The total deformation (δ):

$$\delta = \delta_b + \delta_s = \delta_{fb} + \delta_{fs} + \delta_{cb} + \delta_{cs} \tag{9.42b}$$

Where, δ_{fb} is the bending deflection of facesheet; δ_{fs} is the shear deflection of facesheet; δ_{cb} is the bending deflection of core; δ_{cs} is the shear deflection of core.

Usually, the shear deflection (δ_{fs}) of facesheet and the bending deflection of core (δ_{cb}) are smaller and can be omitted, so

$$\delta \approx \delta_{fb} + \delta_{cs} \tag{9.42c}$$

At the case of simply-supported sandwich structure beam under concentrated load at the beam center:

$$\delta_{fb} = \frac{Pl^3}{48E_f J_f} \tag{9.43}$$

$$\delta_{cs} = \frac{Pl}{4G_c t_c} \tag{9.44}$$

While

$$J_f \approx \frac{t_f}{4}\left(t_c + \frac{t_f}{2}\right)^2$$

So

$$\delta_{fb} = \frac{Pl^3}{48E_f \cdot \dfrac{t_f}{4}\left(t_c + \dfrac{t_f}{2}\right)^2} = \frac{Pl^3}{3E_f t_f (2t_c + t_f)^2} \tag{9.45}$$

Transformation from the above formula (9.45):

$$Pl = \delta_{fb} \cdot \frac{3E_f t_f (2t_c + t_f)^2}{l^2} \tag{9.46}$$

Substitute the above formula (9.46) to the formula (9.44), we get:

$$\delta_{cs} = \frac{3}{4} \times \frac{E_f t_f (2t_c + t_f)^2}{l^2 G_c t_c} \times \delta_{fb} \tag{9.47}$$

So

$$\delta \approx \delta_{fb} + \delta_{cs} = \left[1 + \frac{3}{4} \times \frac{E_f t_f (2t_c + t_f)^2}{l^2 G_c t_c}\right] \times \delta_{fb} \tag{9.48}$$

According to the formula (9.48), for sandwich structure, only at his time:

$$\frac{3}{4} \times \frac{E_f t_f (2t_c + t_f)^2}{l^2 G_c t_c} \ll 1, \quad \delta \approx \delta_{fb}$$

Then the beam span requires:

$$l^2 \gg \frac{3}{4} \times \frac{E_f t_f (2t_c + t_f)^2}{G_c t_c} \tag{9.49}$$

The experimental results show that only when $l > 100t$ the bending deflection (δ_{fb}) of facesheet can approximately replace the deflection of the entire sandwich structure.

(2) Stiffness, modulus.

Since the total bending deflection (δ_b):

$$\delta_b = \delta_{fb} + \delta_{cb} = \frac{Pl^3}{48E_f J_f} + \frac{Pl^3}{48E_c J_c} = \frac{Pl^3(E_f J_f + E_c J_c)}{48E_f J_f E_c J_c} \tag{9.50}$$

While

$$\delta_b = \frac{Pl^3}{48E_F J}$$

So the total bending stiffness (D) of sandwich structure:

$$D = E_F J = \frac{E_f J_f E_c J_c}{E_f J_f + E_c J_c} \tag{9.51a}$$

The bending modulus (E_F):

$$E_F = \frac{E_f J_f E_c J_c}{(E_f J_f + E_c J_c) J} \tag{9.51b}$$

Because

$$J = \frac{t^3}{12}$$

$$J_f = \frac{1}{12}(t^3 - t_c^3) \approx \frac{t_f}{4}\left(t_c + \frac{t_f}{2}\right)^2$$

$$J_c = \frac{t_c^3}{12}$$

Substitute the above relationship to the formula (9.51b), we get:

$$\begin{aligned} E_F =& \frac{E_f \cdot \frac{1}{12}(t^3 - t_c^3) \times E_c \cdot \frac{t_c^3}{12}}{\left[E_f \cdot \frac{1}{12}(t^3 - t_c^3) + E_c \cdot \frac{t_c^3}{12}\right] \times \frac{t^3}{12}} \\ &= \frac{E_f(t^3 - t_c^3) \times E_c \cdot t_c^3}{[E_f(t^3 - t_c^3) + E_c \cdot t_c^3] \cdot t^3} \\ &= \frac{E_f \cdot t_f \times E_c \cdot t_c}{E_f \cdot t_f + E_c \cdot t_c \cdot \frac{4}{3}\left(\frac{t_c}{t + t_c}\right)^2} \times \frac{t_c^3}{t^3} \end{aligned} \tag{9.51c}$$

Also for the total shear deflection (δ_s):

$$\delta_s = \delta_{fs} + \delta_{cs} = \frac{Pl}{4G_f t_f} + \frac{Pl}{4G_c t_c} = \frac{(G_f t_f + G_c t_c)Pl}{4G_f t_f G_c t_c} \tag{9.52}$$

While

$$\delta_s = \frac{Pl}{4Gt}$$

So the total shear stiffness of sandwich structure (U):

$$U = Gt = \frac{G_f t_f G_c t_c}{G_f t_f + G_c t_c} \tag{9.53a}$$

The shear modulus (G):

$$G = \frac{G_f t_f G_c t_c}{(G_f t_f + G_c t_c)t} \tag{9.53b}$$

9.2.4 The shear properties of sandwich structure

In the sandwich panel, because of the low shear strength of the sandwiched core, the shear strength is an important indicator of sandwich structure. For shear on sandwich panel, there are three ways, namely: longitudinal shear, vertical plate shear and interlaminar shear.

1) Longitudinal shear (L-T shear, edge shear)

L-T shear is shown in Fig. 9.13.

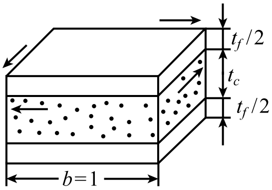

Fig. 9.13 The edge shear of sandwich panel.

(1) Edge Shear stress and shear strength.

According to static equilibrium conditions, we have:

$$Q_{LT} = Q_f + Q_c$$

Namely

$$\tau_{LT} \cdot F = \tau_f \cdot Ff + \tau_c \cdot F_c$$

While

$$F = b \cdot t = t; \quad F_f = b \cdot t_f = t_f; \quad F_c = b \cdot t_c = t_c$$

So shear stress (τ_{LT}):

$$\tau_{LT} = \tau_f \cdot \frac{t_f}{t} + \tau_c \cdot \frac{t_c}{t} = \tau_f A_f + \tau_c(1 - A_f) \tag{9.54a}$$

The shear strength is given by:

$$\tau_{LTu} = \tau_{fu} A_f + \tau_{cu}(1 - A_f) \tag{9.54b}$$

(2) Shear modulus and shear stiffness.
In accordance with consistent deformation conditions $\gamma_{LT} = \gamma_f = \gamma_c$
Because

$$G = \frac{\tau}{\gamma}$$

So the shear modulus:

$$G_{LT} = G_f A_f + G_c(1 - A_f) \tag{9.55}$$

The shear stiffness:

$$N = GF = G_f(t - t_c)b + G_c t_c b \tag{9.56a}$$

Also because $G_f \gg G_c$, so

$$N \approx G_f t_f b \tag{9.56b}$$

(3) Discussion.
Similar to longitudinal tension, because $\gamma_{LT} = \gamma_f = \gamma_c$. So stress ratio:

$$\frac{\tau_f}{\tau_c} = \frac{G_f}{G_c} \tag{9.57}$$

While:

$$\tau_f = \frac{Q_f}{t_f b} \qquad \tau_c = \frac{Q_c}{t_c b}$$

So load ratio:

$$\frac{Q_f}{Q_c} = \frac{G_f t_f}{G_c t_c} \tag{9.58}$$

It shows that, the shear load ratio of the facesheet and core is equal to ratio of the product of their respective shear modulus and thickness. Also $G_f \gg G_c$, so the facesheet plays a major role in carrying shear load.

2) Vertical plate shear (transverse shear)

Vertical plate shear is shown in the Fig. 9.14. Short beam bending shear is in this case, the shear force vertical to the plate, which is mainly born by the core material. Shear strength, modulus and others have the same relationship formula to the bending properties in the discussion of section 9.2.3. Because shear stress always appears in pairs, shear in vertical plate of the sandwich panel also causes interlaminar shear.

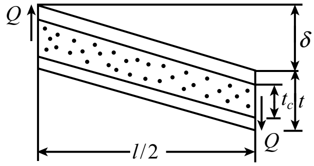

Fig. 9.14 The vertical plate shear of sandwich panel.

3) Interlaminar shear

Interlaminar shear is shown in the Fig. 9.15. Shear load is parallel to the facesheet. Here, the shear stress of the sandwiched core is the same to that of the facesheet.

$$\tau_{LZ} = \tau_f = \tau_c = \frac{Q}{bl} \tag{9.59}$$

Interlaminar shear damage includes shear failure of bonding adhesive and sandwiched core, so the interlaminar shear strength is shear strength of bonding adhesive (τ_{fcu}) or shear strength of sandwiched core (τ_{cu}).

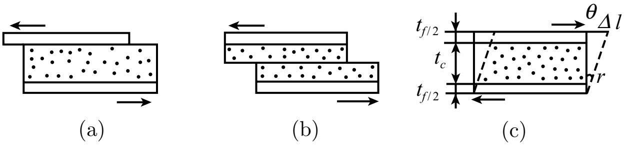

Fig. 9.15 The interlaminar shear of sandwich panel: (a) adhesive shear failure; (b) sandwiched core shear failure; (c) interlaminar shear deformation.

From the deformation relationship, we have:

$$\gamma_{LZ} = \frac{\Delta l}{t} = \frac{t - t_c}{t}\gamma_f + \frac{t_c}{t}\gamma_c$$

While

$$G = \frac{\tau}{\gamma}$$

So

$$\frac{1}{G_{LZ}} = \frac{A_f}{G_f} + \frac{1 - A_f}{G_c} \tag{9.60a}$$

Namely

$$G_{LZ} = \frac{G_f \cdot G_c \cdot t}{G_c t_f + G_f t_c} \tag{9.60b}$$

Because

$$G_f \gg G_c \qquad t_c > t_f$$

So

$$G_{LZ} \approx \frac{G_f t_c}{t_c} \tag{9.60c}$$

The interlaminar shear modulus of the sandwich panel mainly depends on the interlaminar shear modulus of sandwiched core materials.

Exercises

1. How to characterize impact properties of composite materials? Why do we say the term “the impact strength” is not precise?

2. Why is it said that the impact toughness data from the traditional impact test method are only qualitative characterization to some extent?

3. Discuss the main failure modes and energy absorption mechanism of composite materials.

4. Discuss the main influencing factors on the impact toughness of composite materials and the way to improve the impact toughness.

5. Why can suitable interface strength lead to the highest impact strength for composite materials?

6. Please understand some basic concepts, terminology and expression way of the fatigue properties: the cycle character (R), the stress amplitude (S), the average stress, S-N curve, fatigue limit, and so on.

7. What characteristics the fatigue properties of composite materials have? What difference from metal materials in failure mode and mechanism of energy absorption?

8. What are the main influencing factors on the fatigue properties of composite materials? How?

9. What is persistent strength and persistence of composite materials? What characteristics does the creep of composites have?

10. What is the fracture toughness? What are the common methods to measure fracture toughness of composite materials?

11. Discuss the fracture and damage process of unidirectional fiber composite materials in longitudinal tension.

12. Why is damage mechanics more suitable for composite materials than fracture mechanics? What is the damage factor?

13. Please analyze the impact of hygrothermal environmental conditions on properties of composite materials, and how to improve its moisture and heat resistance.

14. What characteristics do the mechanical properties of sandwich structure composites have? How to use it rationally?

15. Please discuss separately the failure modes of sandwich structure under tension, compression, bending and shear load, and describe the main influencing factors on these properties.

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10

High frequency dielectric properties of composites and radome

10.1 High frequency dielectric properties of glass fiber composites

In aviation industry, composites are used not only as structure material, but also as electric insulating materials. These insulating materials are made of glass fiber, aramid fiber, high-silica fiber and quartz fiber. Most importantly, they are irreplaceable materials to make radome because of their high frequency dielectric properties and good mechanical properties.

At present, the composites to make radome are mainly FRP and FRP honeycomb sandwich structure. In high frequency electric field, electrical properties of dielectric material are determined by the relative dielectric coefficient $\varepsilon/\varepsilon_0$ and dielectric loss tangent tanδ (dielectric loss for short).

FRP is made of glass fiber reinforced material and matrix adhesive, so the high frequency dielectric properties of FRP mainly depend on properties and ratio of these two materials.

10.1.1 Resin

In FRP of radome, many kinds of resins are used among thermoplastic and thermoset, though the most popular choices are modified phenolic resin, epoxy resin, unsaturated polyester resin including DAP resin, and modified silicone. Giving consideration to strength and electric properties requirements of FRP, the resin matrices used will have certain amount of polarity groups in their molecular structures, so under an electric field, they suffer dipole relaxation polarization and loss. $\varepsilon/\varepsilon_0$ and tanδ vary according to different group polarity and crosslinking density in molecule. In addition, $\varepsilon/\varepsilon_0$ and tanδ are greatly affected by temperature and frequency. Table 10.1 shows high dielectric properties of several common resins. Fig.10.1 and Fig.10.2 show temperature and frequency's impact on $\varepsilon/\varepsilon_0$ and tanδ of amine curing epoxy resin. As each kinds of resins have many types, these data in Table 10.1 are just for reference. In Fig. 10.1 and Fig. 10.2, in the frequency of $10^2 \sim 10^{10}$Hz, dielectric coefficient decreases with the increase of frequency and increases with the increase of temperature, while tanδ increases with the increase of frequency. Unfortunately, there is no regular law with the change of temperature. Within the scale of $10^2 \sim 10^7$Hz, at a special temperature, tanδ reaches minimum and then increases rapidly. With an increase of frequency, the temperature at the minimum of tanδ increases. However, at 10^{10}Hz, there is no any minimum between 20∼160°C. Tanδ only increases with the increase of temperature within 20∼90°C. There is no significant change any more above 90°C. This variation rule may be related to dipole relaxation polarization of the resin under electric field.

Table 10.1 High frequency dielectric properties of several common resins(10^{10}Hz)

Resin	$\varepsilon/\varepsilon_0$	tanδ
Phenolic resin	4.5∼5.0	0.015∼0.030
Epoxy resin	3.7	0.019
Unsaturated polyester resin	2.8∼4.0	0.006∼0.026
Silicone resin	3.0∼5.0	0.003∼0.050

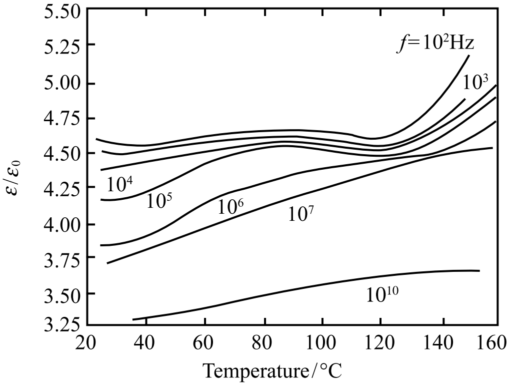


Fig. 10.1 Temperature's impact on dielectric coefficient of amine cured epoxy resin in different frequency.

10.1.2 Glass fiber

Glass fiber is another main component of FRP, which is an amorphous ion structure. Its dielectric properties are related to alkali content. As alkali metal is univalent, the silicone dioxide lattice structure will become loose after we introduce alkali metal into it. Under the electric field, ion relaxation polarization and loss occur. There is also large ion conductance. Therefore dielectric loss of glass depends on its composition. For example, A-glass contains many alkalis, so it has the highest dielectric coefficient and dielectric loss because of its high conductivity, while D-glass has low $\varepsilon/\varepsilon_0$ and tanδ. Table 10.2 shows properties of several glass fiber reinforcing materials for radar cover.

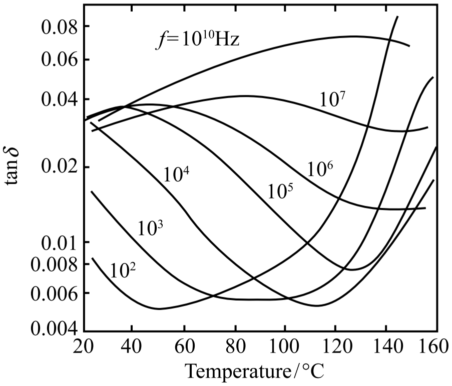


Fig. 10.2 Temperature's impact on dielectric loss of amine cured epoxy resin in different frequency.

Table 10.2 The properties of several glass fiber reinforced materials

Glass	Density (g/cm^3)	Tensile strength (MPa)	Elastic modulus (GPa)	Dielectric coefficient at 9.375GHz	Dielectric loss at 9.375GHz
E-glass	2.54	3500	73.5	6.13	0.0039
S-glass	2.49	4660	86.8	5.21	0.0068
D-glass	2.16	2450	52.5	4.00	0.0026
High silica glass	2.2	875~1750	72.5	3.78	0.0002

$\varepsilon/\varepsilon_0$ and tanδ of glass fiber are related to temperature and frequency, which fits general law of the dielectric containing dipole relaxation polarization. But the impact of temperature is outstanding. Fig.10.3 and Fig.10.4 show temperature effects on the $\varepsilon/\varepsilon_0$ and tanδ. It is obvious that D-glass has better high frequency dielectric properties than E-glass. So in overseas, D-glass is used as reinforcing material in radar cover, but domestically, E-glass is the main reinforcing material.

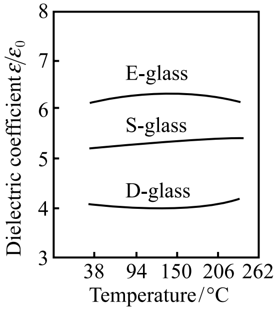


Fig. 10.3 Relationship of dielectric coefficient of glass fiber and temperature (10GHz).

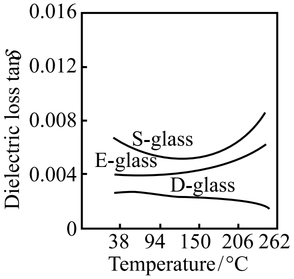


Fig. 10.4 Relationship of dielectric loss of glass fiber and temperature (10GHz).

10.1.3 Resin content

The dielectric properties of FRP are made of different dielectric properties' resin and glass fiber. They are related to resin content besides fiber and resin. Fig.10.5 shows the effect of resin content on dielectric properties of TAC polyester/E-glass cloth laminate. The dielectric coefficient of composites can be estimated by the formula as follows:

$$\ln\varepsilon = V_f \ln\varepsilon_f + (1 - V_f)\ln\varepsilon_m \tag{10.1}$$

Where, ε, ε_f, ε_m stand for dielectric coefficient of composite, fiber and matrix; V_f stands for fiber volume fraction.

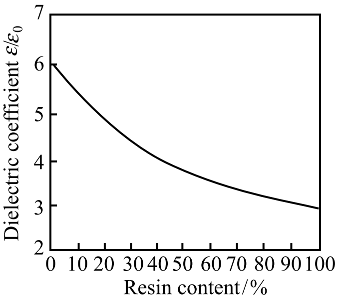


Fig. 10.5 Resin content's impact on dielectric coefficient of TAC polyester/E-glass cloth laminate (9.375GHz).

10.1.4 Porosity

Void content of FRP has great effect on dielectric coefficient. Fig.10.6 shows the effect of void content on dielectric coefficient of polyester/glass cloth laminate. It is obviously linear relationship between void content and dielectric coefficient. That is to say the more the void content, the less the dielectric coefficient.

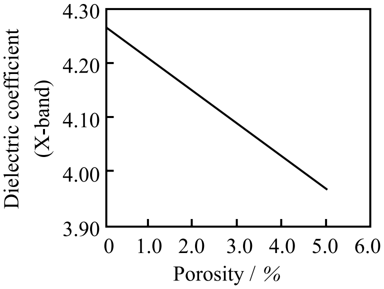


Fig. 10.6 Void content's impact on dielectric coefficient of polyester/E-glass cloth laminates (resin content 35%).

Besides component properties, resin content and porosity, ε and $\tan\delta$ of FRP are related to post treatment temperature and time, glass fiber surface treatment, water content of FRP. With the increase of post treatment temperature or time, resin has higher crosslinking density but lower ε and tanδ. High water content can obviously decrease the dielectric properties of FRP. Especially with more void content, wet and rainwater are very bad for radar cover. So it is necessary to paint waterproof protection on radar cover.

Table 10.3 and 10.4 show dielectric properties of several FRP and honeycomb sandwiched core materials.

Table 10.3 Dielectric properties of several FRP

Resin Types	Test condition	dielectric coefficient ε	dielectric loss tanδ
307 Polyester	10^6Hz	3.4~3.6	0.015~0.016
DAP Resin	10^6Hz, RT	4.1	0.013
	10^6Hz, 180°C	4.2	0.014
	10^{10}Hz, RT	3.85~4.0	0.017
Phenolic-acetal(X98.1)	10^{10}Hz, RT	3.2~5.0	0.020
SC-13	10^{10}Hz, RT	4.25~4.50	0.01~0.02

Table 10.4 Dielectric properties of several honeycomb core materials(10^{10}Hz)

Adhesive type	Side length of honeycomb (mm)	Adhesive content (%)	Curing technology	ε	tanδ
X98.1	4.5	24	100°C/4h +145°C/3h	1.06	0.0025
	5.0	29.3		1.05	0.0015
	6.0	26		1.04	0.0012
A*varnish	4.5	58.7	100°C/0.5h +150°C/1h	1.09	0.0059
	5.0	54.6		1.08	0.0051
	6.0	52		1.07	0.0030
307 polyester	4.5	55	60°C/2h +80°C/4h	1.10	0.0020
	5.0	54		1.08	0.0019
	6.0	56.6		1.06	0.0016
DAP	5.0	47	100°C/2h +150°C/2h	1.056	0.0025
	6.0	55		1.041	0.0013

10.2 Radome

10.2.1 Introduction

1) Radar antenna

Those radars equipped on modern aircraft are called airborne radar. Its function is to emit electromagnetic wave with certain frequency by antenna and to use electromagnetic wave propagation character to achieve the objective of exploring target, ranging, locating and controlling weapon to attack target.

Antenna is an equipment emitting and receiving electromagnetic wave. As radar antenna has to rotate to scan surrounding, it is called scanner, too.

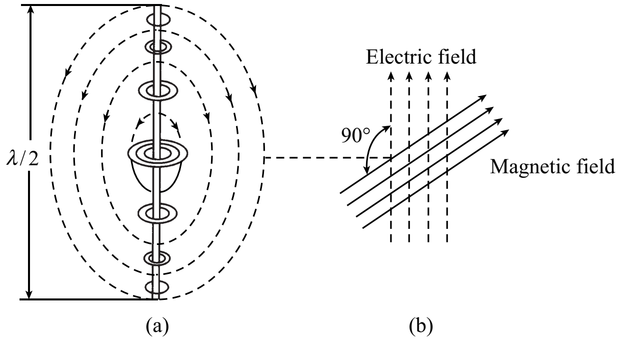
Radar antenna is made of radiator (feed), metal reflector and transmission line. Radiator is used to radiate and receive electromagnetic wave. It is installed on reflector's focal point to make electromagnetic wave into certain shape and narrow directional beam radiation. Transmission line is used to transfer high-frequency energy from transmitter to radiator or from antenna to receiver.

There are many kinds of antennas, such as horn antenna, slot antenna, dielectric antenna, and so on. Half-wave oscillators is the simplest form of antenna radiator, which is a conductor with the length less than 0.5λ(generally 0.47λ). λ is the wavelength of electromagnetic wave. Symmetric half-wave oscillators are also called dipole, which is an important element of many ultrahigh frequency antennas.

Fig.10.7(a) shows the electromagnetic fields nearby oscillator and those far from it. The radiator will launch electromagnetic wave in all around directions if there is no reflector. In order to concentrate energies of radar electromagnetic wave to a spiculate beam to confirm the direction and distance of target, it is necessary to use reflector. The narrower the beam, the better quality the radar image is. Fig. 10.8 shows antennas with different shapes of reflector. Spiculate degree of beam depends on the ratio of reflector size and wavelength. The bigger the reflector, the shorter wavelength and the narrower beam there are. Big antenna is not allowed in airborne radar, so it is better to use centimeter wave.

Far away from oscillator, electromagnetic wave has always some polarization. The polarization of wave is the orientation of electric field intensity pattern with time (the way with the distance change). As long as wave propagation is free without reflection and refraction, in place far away from oscillator the power line is parallel to the oscillator, but the magnetic line is perpendicular to the oscillator [Fig. 10.7(b)].

Generally, electromagnetic wave polarization is determined by direction of electric field. The plane composed of electric field E and electromagnetic wave propagation direction is called polarized plane. When dipole is perpendicular to ground, power line is on the vertical polarized plane. So its electromagnetic wave is vertical polarization wave. When dipole is parallel to ground, its polarized plane is



(a) (b)

Fig. 10.7 Electromagnetic field: (a) near and (b) far from oscillator.

horizontal, so its electromagnetic wave is horizontal polarization wave.

2) Radome

When putting radar antenna on the plane, it is necessary to fix radar antenna protection cover (i.e., radome) to prevent big aerodynamic load and bad influence on flight control. Airborne radome includes all kinds of microwave antenna protection cover, beacon response antenna protection cover, IFF (identification of friend or foe) antenna protection cover, and so on.

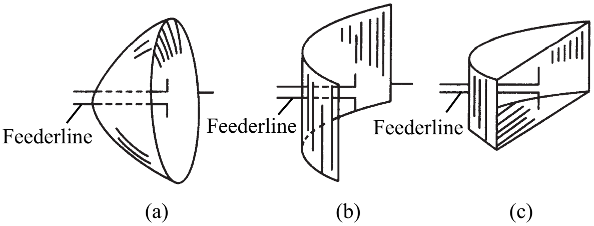


Fig. 10.8 Reflector's antenna with: (a) parabolic and (b) (c) parabolic cylinder.

Radome is usually made of FRP or other materials which can be penetrated by electromagnetic wave. Radome can significantly reflect and absorb electromagnetic wave, which cause energy loss that would decrease radar's detection range. If there is strengthening rib on radome, electromagnetic wave diffraction will occur. Reflection and diffraction can cause antenna directional graph distortion. Strong reflection may cause signal to disappear. In order to make high quality radar cover, design must follow the electric and mechanical requirements and manufacturing technology must be strictly controlled besides choosing good dielectric properties material.

There are many kinds of radome, which are classified in follows:

(1) Radome can be classified to conical, cylindrical and semi-ellipse or hemispherical by the shape.

(2) Radome can be classified to monolayer radome, double layer radome and multiplayer radome (sandwich structure cover) by the structure (Fig.10.9).

① Monolayer radome. This kind of cover is made of materials with big dielectric coefficient. This kind of material has high strength but heavy and bigger dielectric loss. It is suitable for small antenna radar cover.

② Double layer radome. This kind of cover is made of materials with small dielectric coefficient such as foam. It has smaller dielectric loss. This kind of cover is two layers by using of different density of foam, which suits low speed vehicle.

③ Multilayer radome. Multilayer radome is usually sandwich structure cover. Its surface sheet is of high strength and dielectric coefficient material. Core layer is light and small dielectric coefficient material. This kind of cover is light but high strength and stiffness. It also has good electrical performance but manufacturing technology is relatively complicated. According to requirements of electric performance, usually it is made in odd number of layers, such as three layers, five layers, and so on. A three-layer cover is a common one, which suits single antenna and incident angle of electromagnetic wave that is less than 70°. When there are more antennas in the cover or incident angle of electromagnetic wave is 0°~75°or broader, it is better to use multilayer cover. The simplest form of multilayer cover is double-A type of five-layer cover or called C type cover. When wider frequency band electromagnetic wave goes through radome, there must be more layers. To avoid complicated manufacturing technology, it is possible to add dielectric layer containing metal in cover wall (such as add metallic strip in dielectric) and meanwhile decrease the number of layers. Besides, when cover is too big, metal skeleton can be used to support cover wall for increasing cover strength. To avoid lightning strike, metallic strip can be used to bleed-off electrostatic. But these measures might affect electric performance of radome.

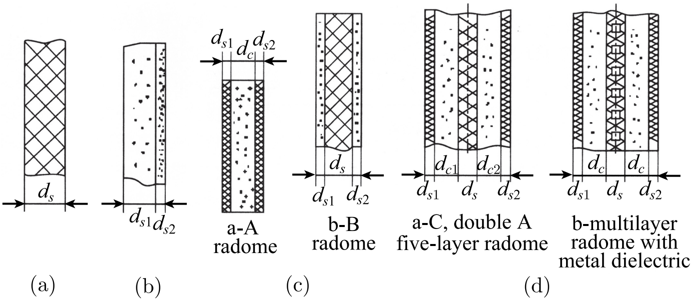


Fig. 10.9 Classification schematic diagram of radome according to its structure: (a) monolayer radome; (b) double layer radome; (c) three-layer radome; (d) multilayer radome.

(3) Radome can be classified to normal incidence radome and streamline radome by electric performance.

① Normal incidence radome. When parallel electromagnetic wave beam projects to radome, incident angle of electromagnetic wave is less than 30° on every working point of cover wall wherever antenna is. This kind of radome is called normal incidence radome. It is shown in Fig. 10.10.

② Streamline radome. When electromagnetic wave beam projects to radome, incident angle of electromagnetic wave is more than 30°, or incident angle of electromagnetic wave on working region of cover wall changes in a wider range 0° ~70° or more with direction of antenna. This called streamline radome. Fig.10.11 shows it.

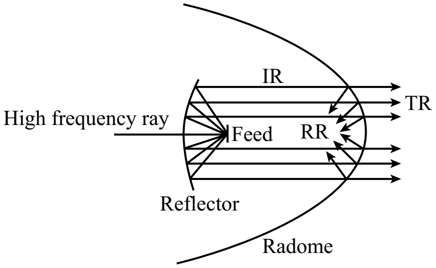


Fig. 10.10 Schematic diagram of normal incidence radome: IR-incident ray; RR-reflected ray; TR-transmitted ray.

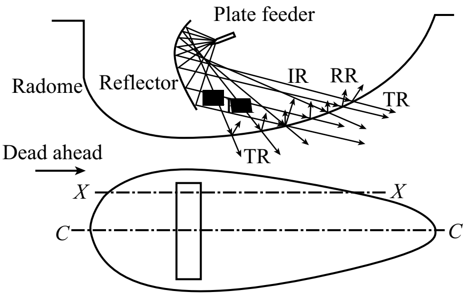


Fig. 10.11 Schematic diagram of streamline radome: IR-incident ray; RR-reflected ray; TR-transmitted ray.

For normal incidence radome, if reflected ray might go back along incident ray, this will damage working performance of radar equipment, even cause signal to disappear. For streamline radome, it is necessary to avoid large disordered reflection of electromagnetic wave to cause directivity graph distortion. So in order to make radar's normal operation, it's better to make sure that power reflection coefficient of radome is at the minimum and power penetration coefficient is at the maximum. Power penetration coefficient of any point on radome is the ratio of permeation power and incident power, while power reflection coefficient is the ratio of reflection power and incident power. The ratio is represented by$|T|^2$and$|R|^2$ respectively, which are important indices for evaluating electric performance of radome.

10.2.2 Electric performance of normal incidence radome

For normal incidence radome, incident angle of electromagnetic wave on every point of cover wall is less than 30°. In this case, $|T|^2$ and $|R|^2$are close to that of normal incidence (incident angle is 0°), on which incident angle has little effect. So every point of normal incidence radome has the same electric performance. Speaking to permeation power, it can be forecasted by the plate made of the same material in normal incidence of electromagnetic wave. Therefore permeation property of every normal incidence cover can be predicted by electric properties of the same dielectric material plate when it is normally incident. In the same way, electric performance of any sandwich structure radome can be approximately judged according to corresponding performance of same material plate.

1) Normal incidence lossless plate

Assuming that electromagnetic wave is normally incident upon lossless plate. Electromagnetic wave totally permeates radome except for some reflection. That is

$$|T|^2 = 1 - |R|^2 \tag{10.2}$$

According to electromagnetic wave reflection and transmission theory, power reflection coefficient$|R|^2$ can be calculated by this formula.

$$|R|^2 = \frac{4r_{ab}^2 \sin^2 \phi}{(1 - r_{ab}^2)^2 + 4r_{ab}^2 \sin^2 \phi} \tag{10.3}$$

In which, r_{ab} is amplitude reflection coefficient of front surface, i.e., the ratio of reflection wave amplitude and incident wave amplitude.

$$r_{ab} = \frac{n-1}{n+1} = \frac{\sqrt{\dfrac{\varepsilon}{\varepsilon_0}} - 1}{\sqrt{\dfrac{\varepsilon}{\varepsilon_0}} + 1} \tag{10.4}$$

ϕ is phase angle:

$$\phi = 2\pi \frac{d}{\dfrac{\lambda_0}{n}} = 2\pi \cdot \frac{d}{\lambda_s} \tag{10.5}$$

$$n = \sqrt{\frac{\varepsilon}{\varepsilon_0}}$$

In the formula (10.3), (10.4) and (10.5), d is plate thickness; λ_0 is wavelength of electromagnetic wave in free space, n is refractive index; ε_0 is dielectric coefficient of free space, almost 1; $\dfrac{\varepsilon}{\varepsilon_0}$ is relative dielectric coefficient; λ_s is wavelength of electromagnetic wave in dielectric material, $\lambda_s = \dfrac{\lambda_0}{n}$; $\dfrac{d}{\lambda_s}$ is plate thickness which is equivalent to several wavelengths in dielectric material. So $\dfrac{\phi}{2\pi}$ is called electrical thickness of plate.

According to the formula (10.2), when material and ε are determined, r_{ab} is determined. $|R|^2$ is the function of sin 2ϕ.

Obviously, when $\phi = N\pi$ (N=0,1,2,3$\cdots\cdots$ arbitrary integer):

$$\sin^2\phi = 0, \quad |R|^2 = 0$$

Then, d can be calculated by this formula (10.6):

$$d = \frac{N}{2}\cdot\frac{\lambda_0}{n} = N\cdot\frac{\lambda_s}{2} \tag{10.6}$$

That is, when plate thickness is half-wavelength or in dielectric material its integral multiple, power reflection coefficient $|R|^2$ is equal to 0.

If $\phi = \left(N + \frac{1}{2}\right)\pi$ (N=0,1,2,3$\cdots\cdots$ arbitrary integer):

$$\sin^2\phi = 1, \quad |R|^2 = \max$$

$$|R|^2_{\max} = \frac{4r_{ab}^2}{(1 + r_{ab}^2)^2} = \frac{(n^2 - 1)^2}{(n^2 + 1)^2} \tag{10.7}$$

$$d = \left(N + \frac{1}{2}\right)\cdot\frac{1}{2}\cdot\frac{\lambda_0}{n} = (2N + 1)\cdot\frac{\lambda_s}{4} \tag{10.8}$$

That is, when plate thickness is one forth of wavelength $\frac{\lambda_s}{4}$ or odd times of $\frac{\lambda_s}{4}$, such as $\frac{3\lambda_s}{4}$, $\frac{5\lambda_s}{4}$, $\frac{7\lambda_s}{4}$, and so on, power reflection coefficient $|R|^2$ is the maximum.

According to electromagnetic wave theory, from Fig.10.12 we can see that when electromagnetic wave is normally incident upon dielectric material plate, some electromagnetic wave reflects on front surface. The others go into plate. Some of them reflect again on back surface, some of which go back to front surface and superpose with the original reflection wave; others reflect over and over again within the plate. It is supposed that reflection wave of front and back surface are equal but in opposite direction. According to superposition principle, these two waves must be countacted so that the total reflection wave goes to 0. Otherwise

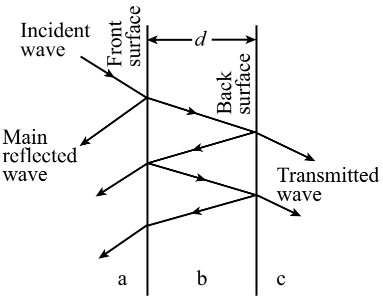


Fig. 10.12 Inner reflection of medium.

reflection will get big. Electromagnetic wave reflection theory affirms it. That is amplitude reflection coefficients of two surfaces are equal but in opposite direction, and for extra-thin plate, amplitude of mixed reflection tends to be 0.

When thickness of dielectric material plate is one forth of wavelength 1/4 λ_s, reflection wave from back surface will go one more half wavelength than that from front surface, so the phase are same. For this thickness, $\frac{3\lambda_s}{4}$, $\frac{5\lambda_s}{4}$, and so on $\left(\text{odd times of}\frac{\lambda_s}{4}\right)$, reflection should be the maximum. But for plate that thickness is $\frac{\lambda_s}{2}$ or integral multiple, electromagnetic wave phase is opposite, so mixed reflection tends to be 0.

Fig. 10.13 shows curves between $|R|^2$ and d/λ_0 in the different $\varepsilon/\varepsilon_0$. Table 10.5 shows the different half-wave thickness (shows as cm) corresponding to several λ_0 and $\varepsilon/\varepsilon_0$. From the Table 10.5, in practical application if wavelength is longer (10~25 cm), radome looks thicker. It's better at 1~3 cm.

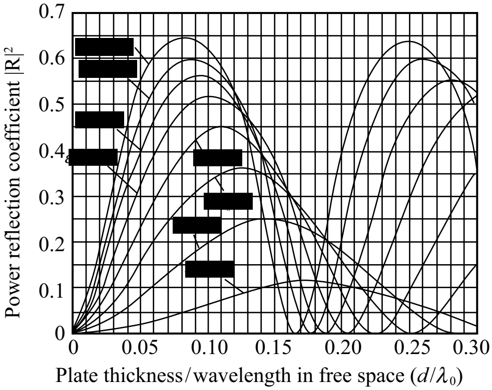


Fig. 10.13 Relation curve between $|R|^2$ and d/λ_0 for lossless plate in normal incidence.

Table 10.5 Half wavelength thickness $\lambda_s/2$ under normal incidence

$\varepsilon/\varepsilon_0$	d/λ_0	λ_0 (cm)			
		25	10	3	1
10	0.158	3.95	1.58	0.47	0.158
4	0.250	6.25	2.50	0.75	0.250
2	0.354	8.84	3.54	1.06	0.354

When making radar cover, it is impossible to make products with thickness of exact half wavelength. The maximum thickness tolerance allowed depends on the biggest power reflection coefficient allowed. The bigger the allowed $|R|^2$ is, the bigger half wavelength thickness tolerance is, which is shown in the formula (10.9). Partial results are shown in the Table 10.6.

$$|R|^2 \approx \left[\left(\frac{\varepsilon}{\varepsilon_0} - 1\right)\pi \cdot \frac{\Delta d}{\lambda_0}\right]^2 \tag{10.9}$$

Table 10.6 Half wavelength thickness tolerance of homogeneous plate

$\varepsilon/\varepsilon_0$	$\frac{\Delta d}{\lambda_0}$		
	$\|R\|^2$=0.01	$\|R\|^2$=0.02	$\|R\|^2$=0.04
2	0.033	0.047	0.069
4	0.011	0.015	0.022
10	0.0044	0.005	0.007

From Table 10.6, the lower the dielectric coefficient is, the bigger thickness tolerance is. This result can be obviously seen in Fig. 10.13. So only when wavelength is bigger, can we use material with bigger dielectric coefficient. When λ_0 is small (1∼3 cm), we must use material with small dielectric coefficient to get possible thickness tolerance.

From Fig.10.13, the largest reflection of lossless plate (tanδ=0) in normal incidence drops fast with the decrease of dielectric coefficient. Table 10.7 shows the largest power reflection coefficient of plates with dielectric coefficient less than 2, which is calculated by the formula (10.7).

Table 10.7 Power reflection coefficient of low dielectric coefficient plate

$\varepsilon/\varepsilon_0$	$\|R\|^2$maximum
1.7	0.067
1.6	0.053
1. 5	0.040
1.4	0.028

From the Table 10.7, if $\varepsilon/\varepsilon_0 \leqslant 1.5$ then $|R|^2$ maximum $\leqslant 0.04$. If the allowed largest power reflection coefficient of radome is 0.04, for $\varepsilon/\varepsilon_0 = 1.5$ plate, arbitrary thickness can be used and we can choose thickness of plate according to strength and stiffness. In fact, dielectric material is not lossless. The thicker the plate is, the more the absorption will be. This makes permeation energy of electromagnetic wave to get small even if reflection is getting small.

2) Normal incidence lossy plate

When electromagnetic wave is normally incident upon lossy dielectric plate or radome, some electromagnetic wave energies are absorbed except for some reflection. So $|T|^2 = 1 - |R|^2-$permeation loss (absorption),$|T|^2 < 1 - |R|^2$. Besides, even for half wavelength lossless plate, because the reflection wave from back surface goes at least twice in the plate before superposing with the first reflection wave from front surface, its amplitude wave will be smaller than that of first reflection wave, so they can not completely counteract. So for lossy material with integral multiple thickness of half wavelength, reflection can be expected to reach minimum though not 0.

For lossy plate, when tan$\delta \ll 1$, its refractive index n can be calculated by the formula (10.10).

$$n = \sqrt{\frac{\varepsilon}{\varepsilon_0}}\left(1 + \frac{\tan^2\delta}{8}\right) \tag{10.10}$$

From the formula (10.10), when $\varepsilon/\varepsilon_0$ is invariant, the bigger the tanδ, the bigger the n is, the smaller $\lambda_s \left(\frac{\lambda_0}{n}\right)$ is. Therefore, half wavelength thickness of lossy plate is slightly less than that of lossless plate.

Permeation loss of half wavelength thickness lossy plate can be calculated by the formula (10.11) (after deduction of $|R|^2$, residual incidence wave power is 100%).

$$1 - |T|^2 \approx \frac{\frac{\varepsilon}{\varepsilon_0} + 1}{2\sqrt{\frac{\varepsilon}{\varepsilon_0}}} N\pi \tan\delta \tag{10.11}$$

For a half wavelength thickness plate, if $\varepsilon/\varepsilon_0$= 4 and tan$\delta$= 0.015, according to calculation of the formula (10.11), permeation loss is almost caused by absorption, whose loss is 5% of incident power. If $\varepsilon/\varepsilon_0$= 4 and tan$\delta$= 0.1 permeation is only 64% of incident power, the other 36% are almost absorbed by the dielectric material. As absorption coefficient is the value as $\frac{d}{\lambda_0}$ for index, for material $\varepsilon/\varepsilon_0$= 4 and tan$\delta$= 0.015, when $\frac{d}{\lambda}$= 0.025 or $\frac{d\sqrt{\frac{\varepsilon}{\varepsilon_0}}}{\lambda_0}$= 0.05, absorption loss is less than 1% but reflection loss is 5%. Even tan$\delta = 0.1$ absorption is only 5%. Therefore, for radar cover of longer wavelength, thin-wall structure is benefit for increasing permeation ratio.

3) Sandwich structure radome

The purpose of using sandwich structure radome is to decrease permeation loss and satisfy the requirement of strength and stiffness.

Sandwich structure radome usually uses FRP as facesheet and honeycomb or foam as core layer. Dielectric coefficient of facesheet is usually 3.5~4.5. Dielectric coefficient of core is 1.1~1.7. For wavelength between 1cm and 10cm, electrical thickness of facesheet of normal incidence radome is usually less than 0.1cm.

When sandwich structure is symmetric structure, i.e., there are the same material and same thickness of facesheet, in order for power reflection coefficient of sandwich structure to be equal 0 (assuming tanδ=0), the relationship of the best thickness between thin facesheet and core is nearly:

$$(d_c)_N = \frac{N\lambda_0}{2\sqrt{a_c}} = -2d_s\left(\frac{a_s - 1}{a_c - 1}\right) \tag{10.12}$$

In which, $(d_c)_N$ is core thickness of N-order sandwich structure; a_c is relative dielectric coefficient of core material, $a_c = \varepsilon_c/\varepsilon_0$; a_s is relative dielectric coefficient of facesheet material, $a_s= \varepsilon_s/\varepsilon_0$; d_s is facesheet thickness of sandwich structure.

If facesheet thickness changes, core thickness should change correspondingly; otherwise it will make power reflection coefficient get big.

Adhesive (glue film) thickness between the facesheet and core must be considered. If adhesive thickness is at the allowed tolerance of layer thickness, there will be little effect on power reflection coefficient. Otherwise, it's better to decrease practical facesheet thickness to reduce reflection to minimum.

Permeation loss of sandwich structure can be calculated by the formula (10.13).

$$\frac{|T_0|^2 - |T_1|^2}{|T_0|^2} \approx 4Q_s + 2Q_c \tag{10.13}$$

In which

$$Q_s = \frac{\pi d_s \sqrt{a_s}}{\lambda_0} \tan\delta_s$$

$$Q_c = \frac{\pi d_c \sqrt{a_c}}{\lambda_0} \tan\delta_c$$

Where, $\tan\delta_s$ is dielectric loss of facesheet; $\tan\delta_c$ is dielectric loss of core; $|T_0|^2$ is permeation power of lossless sandwich plate; $|T_1|^2$ is permeation power of loss sandwich plate made of the same materials.

10.2.3 Electrical performance of streamline radome

Radomes of all radar equipments used on the ground and shipborne and some on the plane belong to normal incidence radome. Those radomes on high-speed aircraft must be geometrically shaped into streamline in order to reduce aerodynamic drag (see the nasal conical radome shown in Fig.10.11). When using this kind of radar cover, the range of incident angle, which electromagnetic wave projects from antenna to radome, is close to $0^\circ \sim 70^\circ$ or more. Polarized plane of electromagnetic wave projected on cover wall may be parallel to incident plane, also may be vertical or any angle with incident plane.

Incident plane is the plane that made of incident line of the electromagnetic wave projected on radome and normal line of this point. Polarized plane is composed of electric field direction and electromagnetic wave propagation direction. Vertical polarization is that polarized plane is vertical to incident plane, and the electromagnetic wave is called vertical polarized wave (electric field vector is vertical to incident plane). Parallel polarization is that polarized plane is parallel with incident plane, and the electromagnetic wave is parallel polarized wave (electric field vector is in the incident plane).

See Fig.10.11, when feed is horizontal polarization, the electromagnetic wave is projected on c-c profile of radome whose polarized plane will be vertical to incident plane, as the incident plane is coincided with c-c plane. On x-x profile, the polarization of electromagnetic wave which antenna projects on radome wall at big incident angle is compound. The polarized direction has an arbitrary angle with incident plane, which can be decomposed into parallel and vertical polarized wave.

Because streamline radome has a big range of incident angle and the possibility that reflection wave directly reflects back to antenna is small, the influence of reflection is not as serious as that of normal incidence radar cover. But in order to permeate more power and decrease possible directivity graph distortion caused by reflection, it's still desirable to decrease reflection at large incident angle range. Besides, at any point of working area on streamline radome, incident angle of electromagnetic wave can have a large variation, so it's impossible for every point in whole incident angle range to have the best performance. Satisfying with dielectric properties, mechanical properties and aerodynamic configuration is ok.

1) Lossless plate at any incident angle

When the incident electromagnetic wave at any angle θ_0 goes upon lossless plate, its power reflection coefficient $|R|^2$ can be calculated by the formula of normal incidence.

$$|R|^2 = \frac{4r_{ab}^2 \sin^2 \phi}{(1 - r_{ab}^2)^2 + 4r_{ab}^2 \sin^2 \phi}$$

$$r_{ab} = \frac{n-1}{n+1} = \frac{\sqrt{\dfrac{\varepsilon}{\varepsilon_0}} - 1}{\sqrt{\dfrac{\varepsilon}{\varepsilon_0}} + 1}$$

But here the equivalent refractive index or equivalent relative dielectric coefficient are needed to replace n or $\varepsilon/\varepsilon_0$.

For parallel polarization, the equivalent relative dielectric coefficient is given by:

$$\frac{\varepsilon_{11}}{\varepsilon_0} = \frac{\left(\dfrac{\varepsilon}{\varepsilon_0}\right)^2}{1 + \dfrac{\left(\dfrac{\varepsilon}{\varepsilon_0} - 1\right)}{\cos^2 \theta_0}} \tag{10.14}$$

For vertical polarization, the equivalent relative dielectric coefficient is given by:

$$\frac{\varepsilon_{\perp}}{\varepsilon_0} = 1 + \frac{\dfrac{\varepsilon}{\varepsilon_0} - 1}{\cos^2 \theta_0} \tag{10.15}$$

In which, $\varepsilon/\varepsilon_0$ is relative dielectric coefficient of medium (cover wall); θ_0 is incident angle of electromagnetic wave.

$$\phi = \frac{2\pi d}{\lambda_0}\sqrt{\frac{\varepsilon}{\varepsilon_0} - \sin^2\theta_0}$$

That is

$$\frac{\phi}{2\pi} = \frac{d}{\lambda_0}\sqrt{\frac{\varepsilon}{\varepsilon_0} - \sin^2\theta_0} \tag{10.16}$$

ϕ is not related with polarization. Therefore for a certain thickness plate, electrical thickness decreases with the increase of incident angle when incident angle changes.

Fig 10.14 shows the relationship between amplitude reflection coefficient r_{ab}, power reflection coefficient $|R|^2$ and incident angle θ_0. Obviously, to all the incident angles, reflection of parallel polarization wave is smaller than that of vertical polarization wave.

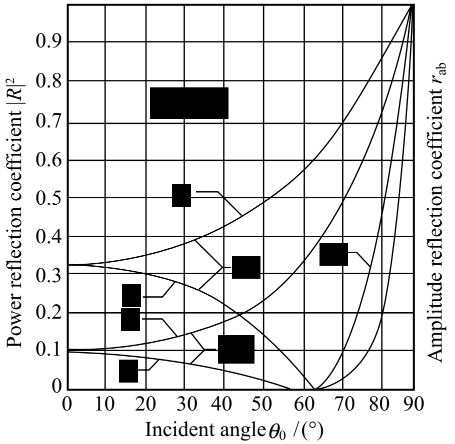


Fig. 10.14 The relationship of amplitude reflection coefficient r_{ab} and power reflection coefficient $|R|^2$ with incident angle θ_0: A-vertical polarization; B-parallel polarization.

(1) Lossless plate under vertical polarization.

① Approxiate half wavelength thickness plate.

Fig.10.15 shows changes of power reflection coefficient $|R|^2$ with different incident angles for lossless plate under vertical polarization whose dielectric coefficient is $4\varepsilon_0$ and thickness is near half wavelength. The thickness of half wavelength plate is $0.25\lambda_0$ when $\varepsilon = 4\varepsilon_0$. At beginning, reflection increases slowly with the increase of incident angle for this plate. When incident angle increases to 30°, $|R|^2$ is still smaller than 1%. After that, it increases rapidly. When incident angle increases to 60°, $|R|^2$ is up to 20%.

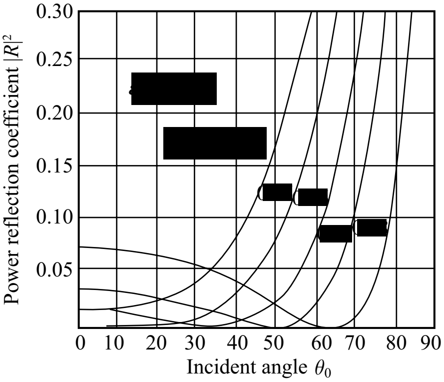


Fig. 10.15 The relationship of power reflection coefficient $|R|^2$ with incident angle θ_0 for lossless plate under vertical polarization.

When thickness is 4% bigger than half wavelength (d= $0.26\lambda_0$), $|R|^2$ is 1% under normal incidence ($\theta_0 = 0°$). Reflection slowly reduces with the increase of incidence angle. $|R|^2$ decreases to 0 when $\theta_0 = 33°$, and then it begins to increase rapidly. The power reflection coefficient of the plate is the same when incident angle is 45° and 0°. So this plate can be used to the case in which the largest reflection power is 1% and incident angle range is between 0° and 45°.

In the same way, to decrease reflection loss of incident wave when incident angle is between 0°and 63°, it's possible to use the plate, whose thickness is 8% more than half wavelength ($d = 0.27\lambda_0$). In this incident angle range the largest reflection power is 3%. When incident angle is 50° the reflection is 0. To those thickness is 12% more than half wavelength ($d = 0.28\lambda_0$), the reflection is less than 7% when incident angle is between 0°and 77°.

When plate thickness is less than half wavelength such as $d = 0.24\lambda_0$, its reflection is more than that of half wavelength plate. This result fits all the dielectric coefficients. Therefore the correction half wavelength plate is thicker than practical half wavelength.

Because

$$\phi = \frac{2\pi d}{\lambda_0}\sqrt{\frac{\varepsilon}{\varepsilon_0} - \sin^2\theta_0}$$

When $\phi = \pi, |R|^2 = 0, d = \dfrac{\lambda_0}{2\sqrt{\dfrac{\varepsilon}{\varepsilon_0} - \sin^2\theta_0}}$; if $\theta_0 > 0°$, value in radical sign is less than $\sqrt{\dfrac{\varepsilon}{\varepsilon_0}}$ in order to make $\phi = \pi$, d must increase.

Assume that the best thickness of radome is the one whose reflection can decrease to the minimum at any incident angle when there is an incident angle range.

This reflection minimum is called the maximum power reflection coefficient of minimum limit. Table 10.8 expresses the best correction half wavelength thickness and the maximum power reflection coefficient of minimum limit of lossless plate under vertical polarization when ε is $2\varepsilon_0$ and $4\varepsilon_0$. It can be seen in the first four rows that maximum power loss caused by reflection increases with increase of the incident angle range. It can also be seen between the first row and the last two rows that maximum reflection loss increases when incident angle with given range is larger.

② thickness tolerance of correction half wavelength plate.

Table 10.8 shows that to the whole incident angle range it's possible to keep reflection relatively small if the thickness can be made exactly to the specified value. This is true even under vertical polarization and bigger incident angle. Practically, wall thickness of radome cannot perfectly keep to a certain value. Thickness tolerance exists and must be considered.

Table 10.8 Best thickness and maximum power reflection coefficient of minimum limit of lossless plate under vertical polarization

Dielectric coefficient ε	Incident angle range (°)	Best d/λ_s	Maximum power reflection coefficient$\lvert R\rvert^2$
$2\varepsilon_0$	40	0.535	0.006
	60	0.590	0.032
	0~70	0.630	0.058
	0~80	0.672	0.084
	20~60	0.594	0.032
	40~80	0.673	0.062
$4\varepsilon_0$	0~40	0.516	0.006
	0~60	0.536	0.026
	0~70	0.551	0.048
	0~80	0.565	0.089
	20~60	0.538	0.023
	40~80	0.566	0.053

Assume that incident angle is between 0° and 70°, and power reflection loss is less than 10%, which is the basis of thickness tolerance calculation. From every equal power reflection curves of some dielectric coefficient, we can read directly the wall thickness allowed and the tolerance for power reflection loss 10%. For example, from Fig 10.16, we can get the allowed thickness range of the plate with dielectric coefficient $2.7\varepsilon_0$, whose $\dfrac{d_1}{\lambda_0}$ upper limit is 0.393, $\dfrac{d_2}{\lambda_0}$ lower limit is 0.350 and tolerance is $\pm\dfrac{d_1 - d_2}{2\lambda_0} = \pm 0.021$. Table 10.9 shows upper limit, lower limit and tolerance of several plate with different dielectric coefficient in the same way.

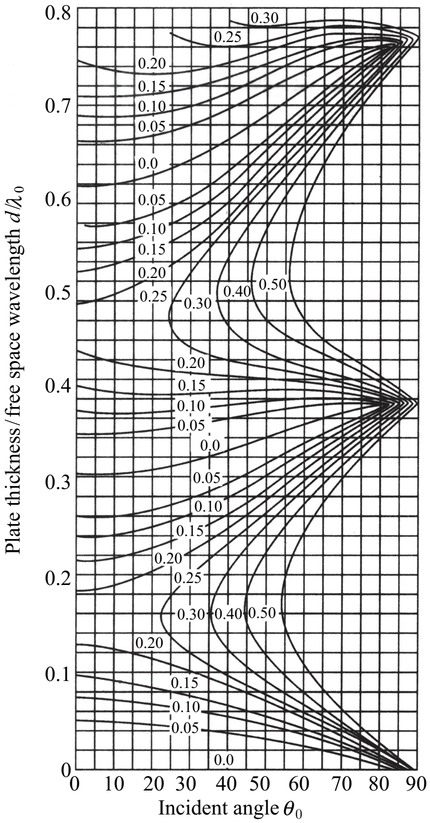


Fig. 10.16 The equal power reflection curve (vertical polarization, $\varepsilon = 2.70\,\varepsilon_0$).

Table 10.9 Correction half wavelength thickness and tolerance of lossless plate under vertical polarization(reflection power<10%, incident angle range 0°~70°)

$\frac{\varepsilon}{\varepsilon_0}$	$\frac{d_1}{\lambda_0}$	$\frac{d_2}{\lambda_0}$	$\frac{d_1 - d_2}{2\lambda_0}$
1.7	0.587	0.505	0.041
2.2	0.444	0.407	0.019
3.7	0.290	0.288	0.001
10.0	0.169	0.160	0.005
10.0	0.327⁽¹⁾	0.326⁽¹⁾	0.0005⁽¹⁾

Note: (1) thickness and tolerance of second-order(N=2).

③ Reflection of low dielectric coefficient plate.

For normal incident radar cover, if using low dielectric coefficient material, we may choose any thickness as long as medium absorption is neglected. This is because the maximum power reflection coefficient is low. But for streamline radome vertical polarization wave projects on the wall at a large incident angle, its equivalent dielectric coefficient becomes large and leads to large reflection. For example, dielectric coefficient is $1.7\varepsilon_0$, when θ_0 at 0°$\sim$30°, the biggest $|R|^2$ is 0.06. While dielectric coefficient is $1.7\varepsilon_0$, when θ_0 is 70°, the equivalent dielectric coefficient becomes $7.0\varepsilon_0$, the corresponding biggest $|R|^2$ is 0.56. Obviously, for the vertical polarization of streamline radar cover, in order to avoid too much reflection at a big incident angle, the thickness of cover wall must be strictly controlled even if the cover is made of low dielectric coefficient material.

Reflection properties of homogeneous plate at vertical polarization are summarized as follows:

① Plate thickness is half wavelength, then the $|R|^2$ is always small when incident angle is between 0° and 30°. While incident angle is more than 30°, $|R|^2$ increases quickly. It is shown that electrical performance of every point on normal incidence radome is the same, which is approximately equal to the electrical performance of the plate made of the same material at normal incidence.

② The minimum reflection loss depends on incident angle range. The bigger range leads to the bigger reflection loss.

③ In order to make the reflection minimum at a certain incident angle range, thickness must be a little thicker than half wavelength.

④ The minimum reflection loss increases with the increase of the half wavelength number in plate when incident angle range is given. For example, first-order reflection loss is bigger than that of zero-order, and second-order is bigger than that of first-order.

⑤ Half wavelength thickness tolerance decreases with the increase of dielectric coefficient of material at given incident angle range.

⑥ $|R|^2$ of radome made of low dielectric coefficient material increases quickly with the increase of incident angle range, and its thickness must be strictly controlled.

(2) Lossless plate of parallel polarization.

Fig. 10.17 shows equal power reflection curves under parallel polarization when dielectric coefficient is $2.7\varepsilon_0$. Table 10.10 and Table 10.11 show best thickness and half wavelength tolerance of different dielectric coefficient materials.

Plate reflection properties between parallel and vertical polarization are summarized as follows:

① With the same $\varepsilon/\varepsilon_0$ and incident angle range, amplitude reflection coefficient r_{ab} of parallel polarization is lower than that of vertical polarization (Fig.10.14), so $|R|^2$ of parallel polarization of correction half wavelength lossless plate is lower than that of vertical polarization (see Table 10.8 and Table 10.10).

② Correction half wavelength thickness tolerance of parallel polarization is bigger than that of vertical polarization (see Fig.10.17, Table 10.9 and Table 10.11).

③ $|R|^2$ of low dielectric coefficient material under parallel polarization also increases with the increase of incident angle.

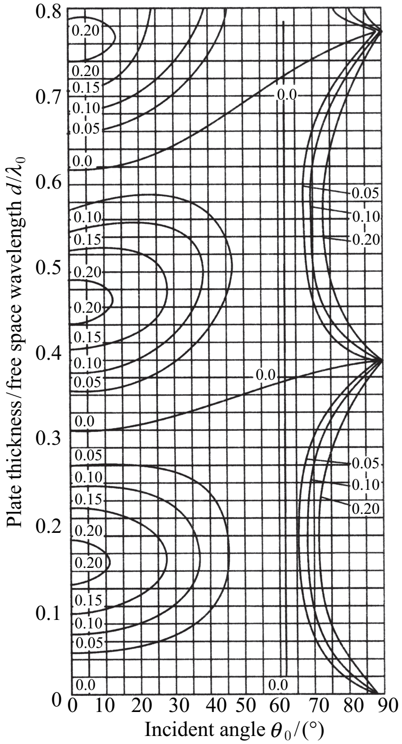


Fig. 10.17 The equal power reflection curve (parallel polarization, $\varepsilon = 2.70\ \varepsilon_0$).

Table 10.10 Best thickness and maximum power reflection of minimum limit of lossless plate under parallel polarization

Dielectric coefficient ε	Incident angle range (°)	Best d/λ_s	Maximum power reflection coefficient $\vert R\vert^2$
$2\varepsilon_0$	0∼40	0.521	0.002
	0∼60	0.525	0.003
	0∼70	0.582	0.029
	0∼80	0.648	0.073
	20∼60	0.541	0.002
	40∼80	0.675	0.013
$4\varepsilon_0$	0∼40	0.506	0.001
	0∼60	0.511	0.003
	0∼70	0.516	0.006
	0∼80	0.541	0.036
	20∼60	0.514	0.005
	40∼60	0.559	0.009

2) Lossy plate at any incident angle

Mentioned above, dielectric loss of material has effect on both reflection and permeation under normal incidence. If tanδ is small, it has little effect on both reflection, while permeation energy decreases greatly. Formula (10.17) is an approximate formula of permeation power for correction half wavelength thickness lossy plate.

$$|T|^2_{\text{loss}} \approx A_N^2 \left(\frac{1 - r_{ab}^2}{1 - A_N^2 r_{ab}^2} \right)^2 \tag{10.17}$$

Here, r_{ab} can be calculated by equivalent dielectric coefficient of parallel or vertical polarization (see formula 10.14, formula 10.15 and formula 10.4).

Table 10.11 Correction half wavelength thickness and tolerance of lossless plate under parallel polarization(reflection power<10%, incident angle range 0° ∼70°)

$\dfrac{\varepsilon}{\varepsilon_0}$	$\dfrac{d_1}{\lambda_0}$	$\dfrac{d_2}{\lambda_0}$	$\dfrac{d_1 - d_2}{2\lambda_0}$
1.7	0.722	0.401	0.160
2.2	0.444	0.311	0.067
3.7	0.290	0.232	0.029
3.7	0.549(1)	0.502(1)	0.024(1)
10.0	0.169	0.147	0.011
10.0	$0.327^{(1)}$	$0.306^{(1)}$	$0.011^{(1)}$

Note: (1) thickness and tolerance of second-order(N=2).

A_N is the decrease of amplitude as electromagnetic wave passes front and back surface of lossy plate. It has no relation with polarization. For low loss dielectric plate, we have:

$$A_N = \mathrm{e}^{\frac{\pi N \tan\delta}{2} \cdot \frac{\frac{\varepsilon}{\varepsilon_0}}{\frac{\varepsilon}{\varepsilon_0} - \sin^2\theta_0}} \tag{10.18}$$

In formula (10.18), $A_N = A$ when N=1.

According to the formula (10.17), permeation loss ($\varepsilon/\varepsilon_0$= 4, tan$\delta$= 0.02) of correction half wavelength plate can be calculated (see Table 10.12). From the Table 10.12 we see that absorption power increases quickly with the increase of incident angle under vertical polarization, especially when incident angle is very big. While in parallel polarization, absorption power increases little with the increase of incident angle. Variable range depends on dielectric coefficient and dielectric loss of material. When incident angle is 70°, permeation loss caused by absorption is almost 3 times of that under normal incidence.

Table 10.12 Permeation loss of correction half wavelength plate($\varepsilon/\varepsilon_0$ = 4, tanδ= 0.02)

Incident angle	$\dfrac{d}{\lambda_0}$	Permeation loss	
		Vertical polarization	Parallel polarization
0°	0.250	0.08	0.08
60°	0.277	0.14	0.08
75°	0.286	0.23	0.11

3) Streamline sandwich radome

Streamline radome on aircraft usually uses sandwich structure in order to satisfy the mechanical properties of light, strong and rigid and electric property of low permeation loss. For example, radome shown in Fig. 10.11 has good permeation property to parallel and vertical polarization wave within the wide range of incident angle.

In the same incident angle range, permeation property of parallel polarization is better than that of vertical polarization. For a certain radome, it must have good permeation property under parallel polarization if it has good property at a certain incident angle under vertical polarization.

The best thickness and tolerance of radome facesheet and sandwiched core is designed under vertical polarization for the minimum permeation loss according to dielectric properties ($\varepsilon/\varepsilon_0$ and tanδ) of chosen facesheet and sandwiched core material, incident angle range, and the allowed maximum power reflection coefficient.

Design requirements must be strictly followed for quality control during the process of manufacturing radome. Any factors changing $\varepsilon/\varepsilon_0$ and tanδ, deviation from the designed thickness and tolerance of facesheet and sandwiched core can significantly affect the permeation property of radar cover.

Facesheet thickness of sandwich structure must be as thin as possible under the premise of meeting the need of structure thickness and rigidity. After determining the thickness of facesheet, we must find the best thickness of sandwiched core to reduce the power reflection coefficient to the minimum. For lossless sandwich plate with any incident angle, the best thickness of sandwiched core can be obtained by equal power reflection curves. For example, if facesheet thickness $\frac{d_s}{\lambda_0}$ is 0.040, dielectric coefficient of facesheet a_s is 3.7, dielectric coefficient of sandwiched core a_c is 1.4 and the equal power reflection curve under vertical polarization is shown in Fig.10.18. From Fig.10.18, when the allowed maximum power reflection coefficient is 0.10 and $N = 1$, the best $\frac{d_c}{\lambda_0}$ is 0.254 and incident angle range is between 0° and 65°. While N=2, $|R|^2$=0.10, the best $\frac{d_c}{\lambda_0}$ is 0.635, but the incident angle range decreases to 0°∼35°.

Table 10.13 shows the effect of facesheet thickness of lossless sandwich plate on reflection under vertical polarization and 0° ∼ 70° incident angle range. Table 10.13 also shows that with the increase of facesheet thickness, the maximum power reflection coefficient increases significantly even using the best sandwiched core thickness.

In practical production, both facesheet thickness and core thickness have some changes in sandwich plate made of the same material by the same method. Supposed both of them change at the same time, this change may cause mutual compensation or accumulation of reflection power. Besides, change of dielectric coefficient of material may cause the change of electrical thickness of plate (or radar cover), which changes $|R|^2$. And the increase of tanδ will increase radome absorption of electromagnetic wave and increase permeation loss.

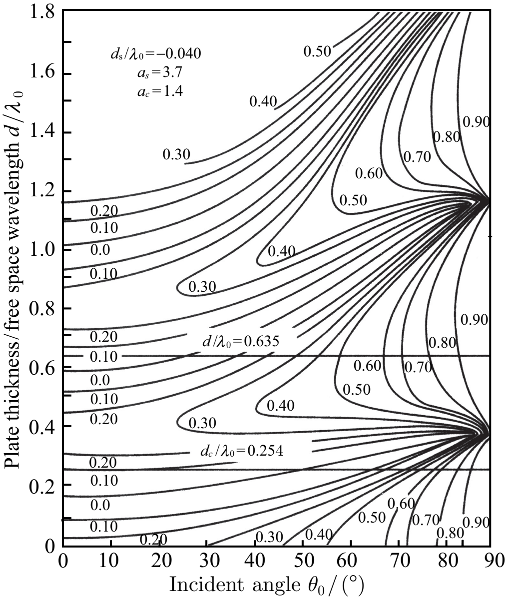


Fig. 10.18 The equal power reflection curve of lossless sandwich plate (vertical polarization, $\varepsilon = 2.70\,\varepsilon_0$).

Table 10.13 The effect of thickness of lossless sandwich facesheet on the maximum power reflection coefficient of minimum limit (a_s = 3.7,a_c = 1.4)

$\dfrac{d_s}{\lambda_0}$	Best $\dfrac{d_c}{\lambda_0}$	Best $\dfrac{h^{(1)}}{\lambda_0}$	0 reflection incident angle(°)	Maximum power reflection coefficient (approximation)
0.010	0.500	0.520	61.0	6
0.024	0.373	0.421	60.5	10
0.040	0.278	0.358	57.5	15

Note: (1) $h = 2d_s + d_c$.

In designing radome, we must consider that the dielectric property data come from the specific process. So we should be cautious when using the known high frequency dielectric properties of composites. When designing radome it can only be assumed that the dielectric coefficient ε and dielectric loss tanδ remains constant. In practice, many things can cause changes of ε and tanδ. Then the electric property deviates from designed data. Especially for radome using in broadband, the thickness tolerance is strict. So small change of ε may cause electric thickness of radome to change, worsening its electric property.

In radome production, there may be some process variables: ① unstable quality of raw material supplied by factory; ② imprecise formulations of resin system components or impurity mixed in resin compounds; ③ expiration of glue solution before curing; ④ deviating from cure specifications; ⑤ pressure at inappropriate time or too big or small pressure; ⑥ inappropriate layer stacking and manufacturing method or process program; ⑦ wrong post treatment condition; ⑧ not good size control.

Once badly controlled, these factors above can cause the change in resin content, porosity, low molecular or impurity content, curing degree, wall thickness dimension and degree of evenness of radome wall. Therefore selecting appropriate manufacturing method and controlling operation rule and strict quality inspection are necessary to build a radome with good properties.

Exercises

1. Why do we choose FRP to make airborne radome? What advantages does it have?

2. Reason the main influencing factors on dielectric properties of FRP.

3. What are power reflection coefficient $|R|^2$ and power permeation coefficient $|T|^2$? What are their influencing factors?

4. Why must thickness of radome wall be integral multiple of half wavelength of electromagnetic wave in dielectric material?

5. What is electrical thickness of radome? And what is its physical meaning?

6. Why do we choose centimeter wave in plane radar?

7. What is the main factors affecting the cover wall thickness tolerance?

8. How to consider the effect of dielectric loss in designing normal incident radome?

9. What is the aim of using sandwich structure for radome? How to increase its dielectric property?

10. What are the characters of streamline radome compared with normal incident radome?

11. How to calculate the dielectric property of lossless plate at any incident angle? What is the character?

12. What are the characters of dielectric property of loss plate at any incident angle under the vertical polarization?

13. Under the vertical polarization, why must the thickness be controlled strictly using low dielectric coefficient material to make radome?

14. What are technology factors to affect the electric property of radome? How to understand?

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11

Other properties of polymer composites

11.1 Thermal physical properties

11.1.1 Thermal conduction

The environmental temperature of material application is usually not constant. Variation of environmental temperature will change the structure and properties of materials to some extent in a certain way.

In aerospace technology, environmental temperature could vary from nearly zero degree centigrade to tens thousands of degree centigrade. Consequently, heat resistance becomes the deterministic factor whether a type of composite material can be used in such an environment as structure material. Its heat exchange with environment and temperature change depend on the thermal conductivity and heat capacity of composites. And thermal expansion properties determine dimensional stability of composites, which has a direct impact on composite's stress distribution and thermal shock resistance. The upper limit temperature as load-bearing material is determined by thermal decomposition and transition with the increase of temperature. In order to meet the application requirement, we should also design its thermal properties besides other properties (mechanical, electrical, etc.), while basis of heat design is the thermal properties of composites.

Composite's basic thermal properties are mainly related to raw materials' corresponding properties. However, it isn't a simple overlay of them. It also depends on other properties (such as stiffness, density) and the manner of composition. The interface also has some influences on thermal properties (such as thermal expansion, glass transition temperature, etc.). Besides, compared with traditional materials, composite's thermal properties show anisotropy.

1) Basic concepts of thermal conduction

The process that heat transmits from one part of object to another or from one object to another object contacting with it is called heat conduction. Polymer materials refer to heat conduction in many applications. In some cases, heat conduction is an accompanied effect, for instance, thermal conduction is an accompanied effect in the viscoelastic loss of tyre, as it produces heat.

For polymer, its internal heat flow is much more complex than metal, glass and ceramics because of its large number of motion units (side group, branched-chain, chain unit, chain segment, macromolecular chain). However, the basic analysis of heat flow is the same, mainly depending on thermal conductivity λ and specific heat capacity C_p.

At any point of internal solid, heat flow q and temperature gradient $\mathrm{d}T/\mathrm{d}x$ is in proportion:

$$q = -\lambda \frac{\mathrm{d}T}{\mathrm{d}x} \tag{11.1}$$

In the formula the negative sign indicates that the heat flow's direction is opposite to the temperature gradient's direction. Thus, if surface temperature of a plate is maintained at $T_1$and T_2 and the plate thickness is d and area is A, so its steady-state heat flow is as follows:

$$q = \lambda A \left(T_1 - T_2\right) / d \tag{11.2}$$

For a series of similar plates of different materials, heat conduction rate is directly proportional to thermal conductivity.

If heat flow is transient, the temperature changing rate in solid is calculated by the following formula:

$$A = \lambda / \rho C_p \tag{11.3}$$

In this formula, A refers to thermal diffusivity or temperature conducting coefficient. It indicates that when heat flows into materials in a specific rate, the internal temperature increasing rate of materials is directly proportional to thermal conductivity and inversely proportional to the heat capacity per unit volume ρC_p.

For different materials, thermal conductivity varies greatly and is usually the function of temperature. And even though for the same materials, it also has different thermal properties due to different density. Just because of these thermal conducting properties, it becomes possible to design the thermal properties. Table 11.1, Table 11.2 and Table 11.3 list some examples of the above cases respectively for reference.

Table 11.1 Thermal conductivity of some materials [W / (m·K)]

Material	λ(300K)	λ(900K)	Material	λ(300K)	λ(900K)
Diamond	600		Al	$\sim$ 220	$\sim$ 180
Graphite (parallel to c axis)	355		Al-8Si-3Cu	$\sim$ 175	
Graphite (perpendicular to c axis)	89		Low-carbon steel	$\sim$ 60	$\sim$ 35
Ag	425	325	Ti	$\sim$ 20	$\sim$ 14
Cu	400	340	Ti-6Al-4V	$\sim$ 6	$\sim$ 6
Cu-2%Ag	$\sim$ 390	$\sim$ 340	SiC(single crystal)	$\sim$ 100	
Cu-2%Be	$\sim$ 130		SiC(polycrystalline)	4$\sim$20	1$\sim$5
Cu-35%Zn	$\sim$ 100	$\sim$ 180	Al_2O_3(single crystal)	$\sim$ 100	$\sim$ 20
Cu-40%Ni	$\sim$ 20	$\sim$ 40	Al_2O_3(polycrystalline)	5$\sim$30	2$\sim$8

Thermal conductivity indicates its heat transferring capacity. It is defined as the quantity of heat flow per unit time for the unit area and unit thickness material when its temperature difference is 1 °C, its unit is usually W / (m·K).

Table 11.1, Table 11.2, and Table 11.3 list some materials' thermal conductivity. We see that thermal conductivity of polymers is small. The thermal conductivity of solid polymer is close to that of air and wood, the thermal conductivity of porous polymer is much smaller. Therefore, polymer is an excellent heat insulating material.

Table 11.2 Thermal conductivity of typical thermosetting resins at 35 °C

Material	Density (g/cm^3)	Thermal conductivity [W/(m·K)]
Phenolic resin	1.36	0.27
	1.25	0.29
Epoxy resin	1.22	0.20
	1.18	0.29
Polyester resin	1.22	0.26
	1.21	0.18

Table 11.3 Some commercial carbon fibers' thermal conductivity [W/(m·K)]

Fiber categories	Longitudinal thermal conductivity λ_L	Horizontal thermal conductivity λ_T
HMS	102	/
HTS	22	/
CY2-5	25	12.6
TL16	42	12.6
TL25	88	12.6
TL50	122	12.6

From atomic-scale view, when one side of a cold plate is heated, thermal vibration amplitude of the heated side increases, and then the heat will diffuses into all directions of the plate. For non-metallic materials, thermal diffusion rate depends on the adjacent atom's or group's vibration degree. For the materials binding with covalent bond a strong coupling vibration will be produced. Thermal conductivity is more obvious in orientation lattice. Therefore, quartz and diamond materials, which have crystal structure formed by the internal atom's strong covalent bond, are good conductor, especially at low temperature. At this time, their thermal conductivity is almost equal to that of metal. With the temperature increasing, the lattice's thermal movement resists the heat flowing, so λ decreases. The crystal structure's flaw will also resists the flow of heat. In amorphous solids, the structure is in extremely disordered state, so it shows a very low thermal conductivity. Some crystal materials are formed by secondary bond, such material has a poor thermal conductivity because its molecular binding force is very weak. Basic solid theory shows that:

$$\lambda = c_p \left(\rho k\right)^{\frac{1}{2}} l \tag{11.4}$$

In this formula, k is bulk elastic modulus; l is mean free path of thermal vibration.

For polymers, $k \approx 10^3$MN/m^2, $l \approx 200$pm, here l is the interchain distance of the adjacent macromolecules, then $\lambda = 0.3$W/(m·K).

For metals, in normal operating temperature, thermal conductivity is much more effective due to the free electron's movement from one point to another, so it covers up the lattice movement's contribution to thermal conductivity. Well-known Wiedemann-Franz law identified that the metal's thermal conductivity is directly proportional to its electrical conductivity. Except for extremely low temperature, it is usually much higher than dielectric material's and will decrease when the temperature rises. This is because the electrons disperse due to the crystal lattice's vibration with the temperature rising, and internal defects will also reduce λ. For example, when some alloy elements are introduced to materials, there will be some internal defects, so the λ will decrease.

The polymer's thermal physical properties are shown in follows. ① In solid polymer, λ has a narrow range, all values are within the range of λ. ② The crystal polymer's λ (such as PE, PP, PTFE) is slightly higher than the amorphous polymer's (such as PMMA, PVC, PS, EP). ③ Most polymers' λ will rise with the increase of its density and crystallinity (for example, compared HDPE with LDPE). ④ The amorphous polymer's λ will rise with the increase of molecular weight (i.e., chain length), because the heat flowing along the molecular chain is easier than across the molecules. For example, λ will decrease when plasticizer is added to PVC. ⑤ Some polymers' λ will rise with the increase of its temperature, but others are adverse. However, the changing value of λ is less than 10% when the temperature is in the range of $0° \sim 100$ °C. ⑥ When polymer's chain is stretched and oriented,λ will become anisotropic. λ rises along the axial direction (oriented direction), but decreases along the direction perpendicular to axial direction. When HDPE deforms to 1000%, λ increases by 10 times along the axial direction. The similar effect is also observed in some certain rubber materials.

Porous polymer's thermal conductivity is extremely low.

High and medium density foam's thermal conductivity decreases with the decrease of density. Its λ is the weighted average of corresponding solid polymer's and the foam gas's thermal conductivity. When the foam gas is halohydrocarbon gas[λ=0.09W/(m·K)] instead of air[λ=0.24W/(m·K)], λ can be reduced greatly. But a few weeks or months later, air will diffuse into pores gradually making the material age, causing a rise of thermal conductivity. For low-density foam, the heat conduction caused by heat convection and radiation is more significant. When its density reaches to the lowest ($\rho <$30kg/m^3), thermal conductivity increases again.

Thermal convection has great significance only when pore diameter is larger than 5mm. It was found that for porous PS 20% of total heat flow is caused by radiant heat conduction at 30 °C. And there are diffusion and absorption of infrared radiation in foam plastics. It is very complicated to study the rate of radiant heat conduction's dependence on the pore size and polymer composition. When the temperature rises, the radiant heat conduction is very important because it rises at the rate of T^2 approximately.

The polymer's thermal conductivity depends not only on its own structure and temperature, but also on the materials' moisture content, ambient temperature of testing, sample size and so on. If the moisture content of material increases, λ will generally rise. This is because when two surfaces of material have different temperature, there is temperature gradient in material and the internal water tends to migrate thus bringing about a degree of thermal conductivity.

Thermal physical properties of some polymers are shown in Table 11.4, and Table 11.5 refers to some porous polymer's thermal conductivity.

Table 11.4 Thermal physical properties of some polymers

Polymer	Thermal conductivity $\lambda[\mathrm{W/(m \cdot K)}]$	Specific heat capacity $C_p(\mathrm{kJ/(kg \cdot K)})$	Linear expansion coefficient$(10^{-5}/\mathrm{K})$
PMMA	0.19	1.39	4.5
PS	0.16	1.20	6~8
PUR	0.31	1.76	10~20
PVC(no plasticizer)	0.16	1.05	5~18.5
PVC(35% plasticizer)	0.15	/	7~25
LDPE	0.35	1.90	13~20
HDPE	0.44	2.31	11~13
PP	0.24	1.93	6~10
Copolymerized POM	0.23	1.47	10
PA6	0.31	1.60	6
PA66	0.25	1.70	9
PETP	0.14	1.01	/
PTFE	0.27	1.05	10
PCTFE	0.14	0.92	5
EP	0.17	1.05	6
CR	0.21	1.70	24
NR	0.18	1.92	/
Fluorocarbon Rubber	0.23	1.66	16
Polyester Rubber	/	/	17~21
PIB	/	1.95	/
Polyethersulfone	0.18	1.12	5.5

Table 11.5 Thermal conductivity of porous polymers

Polymer	Density (kg/m)	λ[W/(m·K)]
PS	16	0.039
	25	0.035
	32	0.032
PVC	35	0.028
	45	0.035
PU	16	0.040
	32	0.023
	64	0.025
	96	0.043
UF	8	0.030
PE	38	0.046

2) Influencing factors of thermal conduction of composites

The main factors that have effect on composite's thermal properties include the corresponding properties and content of component materials, composite state and its operation environment.

(1) Component materials.

① Category of component materials.

From above discussion, we can see that the components' own thermal property is the most important factor that affects composite's thermal conductivity. From the Table 11.1, Table 11.2, and Table 11.3, we see that thermal property of component materials is greatly different due to different category and grade. So, we should choose reasonable component materials firstly when designing composite materials. Table 11.6 lists several composites' thermal conductivity, from it we can see that the composite's thermal conductivity can change by several orders of magnitude when component materials change.

Table 11.6 Thermal conductivity of some composites [W/(m·K)]

Composites	Thermal conductivity	Composites	Thermal conductivity
Glass cloth/Novolac epoxy	0.36	Continuous carbon fiber/Epoxy	11.4
Unidirectional asbestos/Epoxy	0.5	Squeezing SiC/Ti	19

② Content of component materials.

The content of component materials has a direct impact on composite's thermal conductivity due to its great difference. In general, if the fiber of unidirectional composite has a better thermal conductivity than its matrix, the composite's thermal conductivity will rise linearly along the fiber direction with the fiber content's increasing, and its transverse thermal conductivity also increases. In fact, regardless of composite state, as the content of component material with good thermal conductivity increases, it always contributes to composite's thermal conductivity. And if void content is high in composites, thermal conductivity will decline greatly.

(2) Composite state.

① Continuity of dispersed phase.

If dispersed phase is granular, thermal conductivity of composites is basically isotropic, otherwise, common materials are generally anisotropic, and the more continuous the dispersed phase is, the more anisotropic composite's thermal conductivity is. For example, for a unidirectional continuous carbon fiber reinforced composite the thermal conductivity in the fiber direction is 10 times of that in the direction perpendicular to the fiber, and with fiber content increasing, the difference is growing. In addition, thermal conductivity in the fiber direction when fiber is continuous is 1.5 times of that when it is not continuous (see Table 11.7).

Table 11.7 Thermal conductivity of continuous and non-continuous unidirectional fiber reinforced composites

V_f (%)	λ_{cL} [W/(m·K)]		λ_{cT} [W/(m·K)]	
	Continuous fiber	Non-continuous fiber	Continuous fiber	Non-continuous fiber
20	4.5	3.0	0.42	0.40
30	6.8	4.5	0.48	0.51
40	9.0	6.0	0.58	0.64
50	11.4	7.5	0.68	0.81
60	13.5	9.0	0.81	1.01

② Orientation of dispersed phase.

The same as the continuity of dispersed phase, the orientation of dispersed phase also has a great impact on the thermal conductivity of composites. First, the greater the orientation of dispersed phase is, the more obvious the anisotropy of its conductivity is. Second, the more different the dispersed phase's and matrix's thermal conductivity are, the more obvious the thermal conductivity's anisotropy of composite due to the orientation of the dispersed phase is. Finally, no matter whether the thermal conductivity of dispersed phase is good or not, composite's thermal conductivity is always better in longitudinal direction than in transverse direction.

(3) Operation environment.

The thermal conductivity of composite has something to do with temperature, and its impact extent varies with fiber content (see Table 11.8).

Table 11.8 The relationship between thermal conductivity [W/(m·k)] and temperature for E-glass fiber reinforced epoxy composites with different fiber content

Fiber volume fraction V_f Temperature (°C)	0.195	0.375	0.478
32～46	0.30	0.32	0.49
57～63	0.30	0.39	0.49
88	0.35	0.43	0.56
109～113	0.38	0.52	0.62
135～137	0.43	0.60	0.69

When fiber volume fraction is 0.375 and temperature's change is about 100°C, composite's thermal conductivity has almost doubled.

11.1.2 Specific heat capacity

1) Basic concepts

Specific heat capacity as a basic thermal property is one of the main parameters for evaluation, calculation and design of thermal system. It is defined as the required heat per unit mass of material when raising 1°C. Composite has an extremely broad usage range, and there are different requirements on specific heat capacity according to different cases. For example, for high-temperature heat shielding composites used in a short term, high specific heat is required in order to absorb more heat in use; however, for thermal sensitive function composites, small specific heat is required in order to have a higher thermal sensitivity.

Specific heat capacity of polymer is higher than that of metal and other non-metallic materials. It depends mainly on its chemical structure but little on its microstructure. When the temperature reaches to a particular value, the required heat depends on the internal unit's rotation and vibration of solid polymer. When H atom is substituted by heavy F or Cl atom, it will decline, and re-crystallization may occur between T_g and T_m. At this time heat release occurs within polymer so that the temperature's rising rate may not be regular.

Specific heat capacity usually has two concepts, real specific heat capacity C and average specific heat capacity $\overline{C}$. Real specific heat capacity C is defined as the required quantity of heat when material per unit mass is raised by 1 °C at a given temperature, that is

$$C = (1/m)\partial Q/\partial T \tag{11.5}$$

In this equation, m and Q are the mass of material and heat absorption quantity respectively.

The average specific heat capacity $\overline{C}$ is defined as the required average heat when material per unit mass is raised by 1 °C in the range of temperature T_1 and T_2, it is:

$$\overline{C} = (1/m) \cdot \Delta Q / \left(T_1 - T_2\right) \tag{11.6}$$

In addition, the heating conditions have some impacts on specific heat capacity, so it can be divided into constant pressure specific heat C_p and constant volume specific heat $C_{V.}$ They are defined respectively as:

$$C_p = (1/m) \cdot (\partial Q/\partial T)_p \tag{11.7}$$

$$C_V = (1/m) \cdot (\partial Q/\partial T)_V \tag{11.8}$$

Composite material belongs to solid substance, so they vary little with the volume and the temperature. Therefore, there is little difference between above two specific heat capacity, while constant pressure specific heat C_p is generally used. Resin matrix composites are usually used in the temperature between room temperature and 300 °C, and its relationship between specific heat capacity and temperature is:

$$C_p = aB^2E^B / \left(E^B - 1\right)^2 \tag{11.9}$$

In this equation, $B = b/T$; a and b are constants depending on material itself.

Composites' specific heat capacity has addition property, that is, the relationship between composites' and component's accords with the rule of mixture and has average composite effect. The formula is as follows:

$$C_p = \sum M_i C_{pi} \tag{11.10}$$

In this equation,C_p is composite's specific heat capacity, and M_i and C_{pi} are component's mass fraction and specific heat capacity respectively.

2) Impacting factors of composite's specific heat capacity

Table 11.9 lists some composites' specific heat capacity at room temperature, from which we can see the specific heat capacity's general distribution of polymer composites. Temperature's impact on composites takes effects by the corresponding parameters of components.

Table 11.9 Specific heat capacity of some composites at room temperature

Composites	Specific heat capacity [kJ/ (kg·K)]
Epoxy / Phenolic resin composite	1.92
Glass microsphere / Silicone rubber	1.96
Glass fiber / Silicone rubber / Phenolic	1.34
Nylon / Phenolic	1.46
Glass fiber / Phenolic	1.67
High silica fiber / Phenolic	$\sim$ 1.0
Graphite fiber / Epoxy	1.5

11.1.3 Thermal expansion coefficient

1) Basic concepts

The size and volume of materials will vary with temperature, and the thermal expansion coefficient usually expresses the expansion extent of materials. Thermal expansion coefficient is not only an important application requirement of materials but also a key structural designing parameter. Meanwhile, it is also closely related to thermal shock resistance, stress distribution and size after being heated.

Thermal expansion coefficient is divided into linear expansion coefficient and volume expansion coefficient, and linear expansion coefficient is defined as:

$$\alpha = (\partial L/\partial T)_p/L \tag{11.11}$$

In this equation, L is material's length; T is material's temperature.

Volume expansion coefficient is defined as:

$$\beta = (\partial V/\partial T)_p/V \tag{11.12}$$

In this equation, V is material's volume.

For fiber-reinforced composite laminate, linear expansion coefficient is obviously different between plate surface and its thickness direction. Even in plate surface, there exists difference in different direction.

When composites exhibit isotropy, the relationship between linear expansion coefficient and volume expansion coefficient is given by:

$$\beta = 3\alpha \tag{11.13}$$

If linear expansion coefficient is different in three directions, which are α_1, α_2, α_3 respectively, then the formula is as follows:

$$\beta = \alpha_1 + \alpha_2 + \alpha_3 \tag{11.14}$$

Table 11.10, Table 11.11, and Table 11.12 list thermal expansion coefficients of some materials, which are mostly positive, they are usually called "hot expansion and cold shrinkage". However, some is negative, that is "hot shrinkage and cold expansion". This is mainly because the interacting particle's amplitude varies asymmetrically with the change of temperature. If this asymmetric change tends to the interacting particle's outer side, then response of material to temperature shows "hot expansion and cold shrinkage". But if the asymmetric change tends to the internal side, then response of to temperature shows "hot shrinkage and cold expansion".

Table 11.10 Two common fibers' thermal expansion coefficient $\alpha(10^{-6}$ / K)

	Carbon fiber	Kevlar fiber
Axial	−1	−2
Radial	28	59

Table 11.11 Some component materials' thermal expansion coefficient(10^{-6} / K)

Material	α	Material	α	Material	α
Quartz glass	0.5	Polyester Resin	100	Nylon 6	80∼100
A-glass	10	Phenolic	55	Nylon 66	80∼100
Iron	12	Polyethylene	120	Nylon 1010	15
Aluminum	25	Polypropylene	100	Rubber	250
Copper	15	Polystyrene	80	Polycarbonate	70
Epoxy resin	50∼100	PTFE	140	ABS	90
SiC	3.5	Alumina	7.5	Ni	13.5

Table 11.12 Some composites' thermal expansion coefficient(10^{-6} / K)

Composites	α	Composites	α
30% Glass fiber / PP	40	Chopped GF / Polyester	18∼35
40% Glass fiber / PE	50	30% Carbon fiber / Polyester	9
35% Glass fiber / Nylon 66	24	Asbestos fiber / PP	25∼40
35% Glass fiber / Nylon 66	14	30% Glass Fiber / PTFE	25
Unidirectional GF / Polyester	5∼15	Glass fiber / ABS	29∼36
Glass fiber / Polyester	11∼16	25%SiC/Al	18

2) Impacting factors of composites' thermal expansion coefficient

Composite's thermal expansion coefficient depends mainly on its component materials, composite state and operation environment.

Thermal expansion coefficient of component materials is the most important factor. If it changes, composite's thermal expansion coefficient will change. The content and modulus of components affect thermal expansion coefficient of composites, the component with high thermal expansion coefficient has more impacts on corresponding parameters of composites.

Thermal expansion coefficient of composites is also influenced greatly by reinforced (filled) materials' arrangement and whether it is continuous in the matrix. If filler is not continuous and is distributed randomly, the thermal expansion coefficient is isotropic. If filler is continuous or arranged in certain direction, then it is anisotropic. For unidirectional continuous fiber composites, transverse thermal expansion coefficient is larger than the longitudinal. In addition, pre-stress of fiber also has some influence on it.

In operation environment, temperature has some impacts on thermal expansion coefficient too. In a certain temperature range, relative elongation is proportional linearly to temperature. In addition, thermal cycling will lead to micro-cracks in the interface of composites, and the matrix may further cure, so linear expansion coefficient and modulus will change, thus affecting thermal expansion coefficient.

11.2 Heat resistance of composites and its applications

11.2.1 Definition

Heating will lead to a series of physical and chemical changes of polymers. The physical changes include softening and melting, and the chemical changes include oxidation, crosslinking, hydrolysis and thermal decomposition, etc. As a result, physical mechanical properties will become bad, even lead to loss of practicality.

According to the two changes mentioned above, its heat resistance can be divided into physical and chemical heat resistance. See Table 11.13, physical heat resistance focuses on its practicality and chemical heat resistance focuses on the chemical reaction.

11.2.2 Evaluation standards of heat resistance

From the apparent view, polymer will lost its practicality once it softens, melts or decomposes after being heated. Therefore, T_m and T_g are often regarded as the upper limit temperature for crystalline polymers and amorphous polymers with constant size respectively. For thermosetting polymers, due to formed non-melting, insoluble cross-linked network structure, they are only damaged at above decomposition temperature, so T_d is often regarded as the upper limit temperature of thermosetting polymers. However in industry, the Martin heat-resistant temperature, Vicat softening temperature and heat distortion temperature, which are often called softening point, are usually used as evaluation standards of plastics heat resistance. Unlike T_g and T_m, softening point do not have clear physical meaning, but they are very practical standards of heat resistance. Polymer composites will be influenced by many factors in actual use. In general, the type, content and distribution of filler all have great impacts on composite's heat resistance.

Table 11.13 Definition of heat resistance

Category	Definition
Physical heat resistance	The temperature limit at which polymer's mechanical strength decreases under certain load ① heat distortion temperature, glass transition temperature ② flow temperature (such as melting point)
Chemical heat resistance	(1) Thermal stability (the permitted temperature in which there is no chemical reaction to change the properties of polymer) ① thermal decomposition temperature (at the inert atmosphere and vacuum) ② thermal decomposition residues (2)Thermal oxidation stability (the thermal stability particularly in air or O_2) ① thermal oxidation decomposition temperature ② thermal oxidation decomposition residues

11.2.3 Impacting factors of composites' heat resistance

1) Filler category

In general, the adding of filler improves composites' heat resistance. However, as its own heat resistance and its interaction with polymer matrix may have a great difference, the choice of filler has a great impact on the heat resistance. Fig. 11.1 gives the modulus-temperature curve of epoxy resin and three kinds of fiber-reinforced epoxy resin. There is an apparent turning in epoxy resin's modulus-temperature curve at 160°C, but for the others except Kevlar/epoxy composites, the curve exhibits slow and smooth decline. It can be concluded that for the three types of fiber, Kevlar fiber has the minimum impact on the epoxy matrix. And from the knowledge of materials science, we can see that the interface interaction between Kevlar fibers and epoxy is the weakest. So the two conclusions mentioned above are in coincidence.

2) Filler content

Fig. 11.2 shows Vicat softening point-asbestos content curve of asbestos/polystyrene composite, from that we can see that filler content can significantly affect composites' heat resistance.

3) Other factors

In addition to filler category and content, filler (fiber) arrangement in polymer matrix also affects the composite's heat resistance. The more evenly filler (fiber) arranges, the smaller polymer matrix is; the better filler disperses, the more interface is; the more dimensional fiber (if the filler is fiber) arrangement is, the more dimensional fiber's impact on polymer is. All the factors mentioned above are helpful to improve the composite's heat resistance. Even the way hybrid fibers are integrated can have impact on heat resistance of hybrid fiber-reinforced composites.

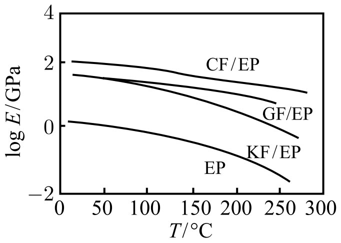


Fig. 11.1 Relationship curve of tensile modulus and temperature for four materials.

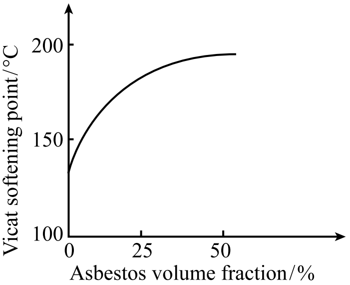


Fig. 11.2 Vicat softening point-asbestos content curve of asbestos/polystyrene composites.

11.2.4 Application of heat resistance of composite materials

People often face the issue of thermal control in aerospace, energy and other high-tech fields, and insulating materials are often used to resolve it, which is one of the important means people commonly used. Insulating materials can not only effectively keep certain equipment off thermal erosion and work normally in harsh heat environment, but also can effectively prevent materials with low ignition point adjacent to high thermal material from burning in some cases, which otherwise cannot be avoided technically. With the rapid development of science and technology, it is particularly urgent to use insulating materials to solve the issue of thermal control in super-high or super-low temperature, as well under high heat flow. Therefore, various types of insulating materials and high-performance insulating systems have been invented. These materials and systems are all composite materials, including porous insulating materials, fiber insulating materials, high efficient and high-strength insulating materials, multi-layer reflective insulating materials, and composite insulating systems.

The insulating properties of materials often require them to have low density. While in space technology, the structure is too loose to ensure its structural strength, especially high temperature strength, so the materials with heat resistance and load-bearing structure i.e., heat-resistant structure materials, are both needed. Heat-resistant structure materials must have not only smallest possible thermal conductivity, but also high specific strength, high specific modulus, high

T_g or T_m, as well as good oxidation resistance that common high-temperature structural composite materials own. In addition, the temperature may change a lot and frequency is high in its use, so the materials should have good thermal shock resistance (mainly small expansion coefficient). The component materials of composites should not only possess the properties mentioned above, but also have physical and chemical compatibility. High temperature heat-resistant structural composite materials include fiber/resin, fiber or whisker/ceramics, carbon/carbon and carbon/ceramic and so on.

When satellites, spacecraft and missiles enter the atmosphere, the ambient temperature is very high (up to 8000K) and the pressure and heat flow value are very high too, as well as the over loading (more than 100g). In such a bad thermal environment, ablation or thermal protective materials are needed. Generally, spacecraft is usually re-used and enters the atmosphere many times, so it is difficult to solve this problem with single measure of heat insulating or thermal protective. At this time, heat-resistant composite structure is available, which include the composition of ablation layer and heat insulating layer, or the composition of ablation layer and high temperature heat resistant layer and heat insulating layer.

11.3 Chemical corrosion resistance

11.3.1 Basic concept of corrosion

There are different appellation and characterization methods in different environment for corrosion resistance of materials: when material is in natural environment on earth, corrosion resistance is called weatherability (or resistance to natural aging, anti-oxidation for short, oceanic corrosion is one of the serious natural environment corrosion), which is characterized by performance retention through a certain period in the atmospheric environment; when material is in chemical medium (such as acid, alkali, salt, organic solvents, etc.), it is called resistance to chemical medium or sometimes resistance to medium corrosion, which is characterized by the corroded mass per unit time per unit area, or the corroded thickness per unit time; when material is in high humidity environment (including fresh water and sea water), it is called water resistance or sea water resistance, which is mainly characterized by the performance retention after a certain period of soaking; when in high temperature oxygen environment, it is called anti-oxidation, and which is mainly characterized by the nature of atmosphere (concentration of oxygen, flow state, temperature and pressure) and the corroded thickness per unit time or corroded mass per unit area. All in all, corrosion is the degradation caused by environmental factors.

For polymer composite materials, the properties of matrix play a decisive role in corrosion resistance. The extent of corrosion depends on: ① the properties of materials; ② the environmental conditions (temperature, pressure, the nature and state of medium); ③ the time under certain circumstances.

The corrosion of polymer materials is different to that of metal essentially. Most of corrosion behavior of metals can be illustrated with electrochemical process, because metal are conductors, at the same time dissolved in the form of metal ions. Generally, polymer materials are not conductive, not dissolved in the form of ions, so it is difficult to illustrate the corrosion process with chemical regularity. In addition, the corrosion of metals mostly takes place on the surface, while plastic is different. The infiltration of surrounding reagents (gas, steam, liquid, etc.) into material is the main reason of corrosion.

11.3.2 Main corrosion forms of polymer materials

The main corrosion forms of polymer materials are shown:

(1) Chemical cleavage. Under the effect of active medium, the medium molecules infiltrating into polymer materials may react with the macromolecules, such as oxidation, hydrolysis, and so on, so the macromolecular chains will break or crack.

(2) Swelling and dissolving. The solvent molecules infiltrating into the materials will destruct the secondary bond between macromolecules, and solvate with macromolecule. Three-dimensional polymer will swell, and get softening, so that the strength will reduce significantly; linear polymer will swell and dissolve further.

(3) Stress cracking. Under the effect of stress (extrinsic or residual internal stress) and some medium (such as surfactant), a lot of polymer materials will crack, even brittle fracture will occur.

(4) Infiltrating damage. For lining equipments, even if the infiltrating medium will have no effects on the lining layer above, the medium's going through the lining layer and contacting with the matrix will leads to corrosion, and the equipments will be damaged.

In addition, some ingredients in polymer materials, such as plasticizers, stabilizers and other additive agents or low molecular weight components, will also diffuse from the solid and migrate into environmental medium, making polymer materials to suffer metamorphism. The effect of medium on polymer materials is shown in Fig. 11.3.

11.3.3 Water resistance

Water infiltration and diffusion into polymer composites will make them swell, hydrolyze and start other physical or chemical actions, which will lead to reversible and irreversible changes of their properties. Both the speed and quantity of water infiltrating and diffusing into polymer composites and the interaction of the components with water decide the extent and speed of these effects.

Water resistance of composite materials primarily depends on water resistance of matrix. Generally speaking, the water resistance of epoxy resin is better than that of polyester; on one hand, epoxy is not easy to hydrolyze, on the other hand, it has high bonding strength. Therefore the water resistance of glass fiber reinforced epoxy is better than that of glass fiber reinforced polyester. And because thermal-curing glass fiber reinforced polyester is cured completely, so its water resistance is superior to glass fiber reinforced polyester in room temperature-curing.

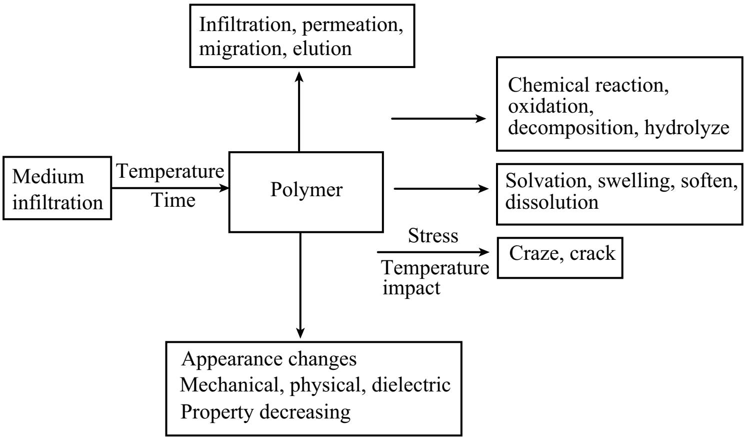


Fig. 11.3 The impact of medium on polymer materials.

The fiber is also an important factor on water resistance. The attack of water to the fiber will start from the surface of fiber, which will reduce the performance of fiber.

The effects of water on composite materials include: ① the density increases; ② the volume expands because of moisture absorption, so the distribution of internal stress will change; ③ the mechanical properties of composite materials will change (the Young’s modulus and strength will decrease, the toughness will increase); ④ the resistivity and transparency will reduce, thermal conductivity will increase, dielectric properties will reduce, too; ⑤ chemical degradation will take place further with time extending; ⑥ the biological activity will be accelerated.

The following measures can be used to improve the water resistance of composite materials: ① select those fibers that have small water absorption and water has little effect on as reinforcement; modify the matrix resin such that it is hydrophobic, such as incorporating hydrophobic group into the main chain of resin macromolecule (benzene ring, long carbon chain etc.); ② select appropriate coupling agent to deal with the fiber surface, improving the fiber surface and increase its bonding with the matrix; ③ improve the process, such as curing at high temperature so that the matrix will cure completely and pressure-curing that will reduce the defects (micro-cracks and porosity) in composite materials; ④ avoid the end of fiber being exposed on the surface of composite materials, such as increasing the content of resin, or coating one waterproof layer on the surface of composite materials.

11.3.4 Weatherability

Weatherability of composite materials is mainly that composite materials can maintain their original performance with time extension outdoor. The natural factors causing the aging of composite materials include: sunlight, high-energy radiation, industrial waste gas, salt spray, micro-organisms and so on. Physical, chemical, biological and mechanical action will take place between composites and these factors, thus changing the properties of composites.

1) Sunlight

The chemical reaction under light is given by:

$$\mathrm{RH} \xrightarrow{h\nu} \mathrm{R} \cdot + \mathrm{H} \cdot$$

In the formula, RH stands for polymer; R·, H· stand for free radicals.

The polymer absorbing high-energy ultraviolet (UV) will cause aging. In addition, the ultraviolet will trigger and promote the effect of oxygen on the resin, which will also cause the aging of composite materials. The aging caused by UV mainly focuses on the surface and gradually develops into materials. UV occupies only a small proportion in sunlight and is absorbed fast. Most of the energy will be transformed into heat and longer wavelength light after the polymer absorbs photons, so the photooxidative aging is the main effect.

The visible light and infra-red can be easily absorbed by polymer, which will be transformed into heat to raise the temperature. It can promote oxidation so that thermal-oxidative aging of composite materials will take place.

2) Heat and oxygen

Heat and oxygen are often combined to have effect on composites. The matrix is sensitive to oxygen, and heat can promote the effect of oxygen. This oxidation is an autocatalytic process. The initial oxidation products are peroxides of hydrogen, which decomposes and causes chain reaction of free radical, and will finally lead to the aging of polymer.

The chemical activity of ozone is higher than that of oxygen. Ozone will be destructed and changed into oxygen by atmospheric dust, smoke, water vapor and other impurities when it close to the earth surface. It will generate higher activity oxygen of atomic state, which is more destructive than oxygen. So the ozone aging of polymer in light is stronger than that of pure ozone.

3) Rain and wet

Rain can wash out the dust on the surface to make it more acceptable to sunlight, thus facilitates the aging of light and the aging of light-oxygen. Wet provides the conditions for attachment and propagation of micro-organisms (mildew, bacteria), insects and small organisms, thus promotes the biological aging.

4) Space environment and its effects

The main factors of space environment are vacuum, high-energy charged particles, plasma and micro-meteoroids, etc.

The main effect of space vacuum on composite materials is: the metal components in composite materials, when impacted by electron with certain energy, will motivate more secondary electrons to escape and form a discharge, which leads to corrosion; for polymer components, it will cause evaporation, sublimation and decomposition, leading to changes in composition, mass loss and performance degradation. In addition, the low molecular weight gases released will condensate in the vicinity and cause contamination; deflation effect: the gas adsorbed or absorbed by the surface and the gas adsorbed or dissolved in the internal diffuse to the surface, both them can separate from the surface of composite materials, which may cause pollution to the neighboring parts.

High-energy charged particles and plasma are of high energy and penetrating power, which mainly affect the electrical properties of composite materials, change the resistance and lead to the discharge.

The diameter of micro-meteoroids is less than 1cm, and its mass is less than 1g. The movement speed is 10~30km/s under the sun gravity, even up to 72km/s. The most threatening meteoroid for the spacecraft is sporadic micro-meteoroid whose mass is less than 10^{-7}g. They will cause roughness and damage loss of the surface, damage of heat-control layer, reduction in the efficiency of the optical surface and solar cell, and even a disaster accident.

The measures to improve the weatherability of composite materials are shown in follows: ① coat a paint film on the surface; ② make a gel coat on the surface (resin-rich layer); ③ paste a transparent UV-absorbing film on the surface; ④ increase the resin content in the surface, such as using surface felt to reduce the channel that oxygen and moisture intrude; ⑤ improve the weatherability of the matrix, such as modifying the matrix, choosing the additive that can improve the weatherability, adding UV-absorbers into the matrix.

11.3.5 Medium corrosion resistance

Medium corrosion resistance of composite materials mainly refers to their ability to resist performance decline to acids, alkalis, salts, organic solvents and other chemical medium.

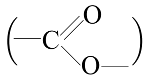
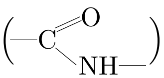
The effect of chemical medium on polymer include: after penetrating into polymer they will swell and react with the polymer, such as generating salts, hydrolysis, saponification, oxidation, nitration and sulfonation. That will lead to the damage of primary bond, its splitting decomposition, and so on. Thus corrosion and performance decline of the polymer will be caused by these chemical reactions.

The type of groups in molecular structure is the key factor of polymer resistant to corrosion. The groups that are good or bad for resistance to chemical medium are shown in Table 3.5.

In the effects of chemical medium on polymer, hydrolysis by acid or alkali-catalyzed is a common corrosion reaction. Table 3.4 gives the hydrolysis activation energy of some groups. We see from the data, the molecular structure including amide bond or imide bond is less liable to hydrolyze in acidic medium and alkaline medium.

Table 11.14 lists the active groups of various types of polymers and the possible reaction, we should take special care when they contact with the medium that can react with these groups.

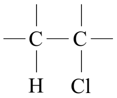
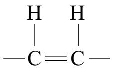
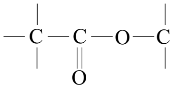
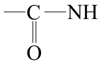
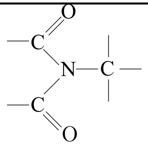
Generally, there exist some laws in corrosion damage of plastics.

(1) In polymer, if there are ester bond  $\left(-\mathrm{C}\begin{array}{l}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{O}-\end{array}\right)$, amide bond  $\left(-\mathrm{C}\begin{array}{l}\diagup\!\!\diagup\mathrm{O}\\ \diagdown\mathrm{NH}-\end{array}\right)$, ether bond (—O—) and silicon-oxygen bond (—O—Si—) and other bond without space obstacles, they will easily hydrolyze in acid or alkaline solution. For example, polyester resin (with ester bond) is liable to hydrolyze in acid or alkaline, or hydrolyze under high temperature; nylon (with amide bond) is easily soluble in strong acid; organic silicon (with Si—O bond) can pyrolyze in high-temperature acidic water vapor; polyoxymethylene and polyethylene oxide (containing ether bond) will degrade at an accelerated rate under the effect of acid; phenolic resin (including ether bond) is not resistant to alkali.

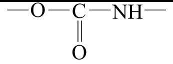
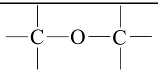
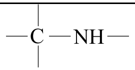
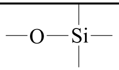
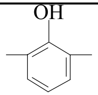
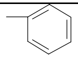
(2) Erosion is prone to occur when the polarity of polymer materials is close to that of the medium, and vice versa. For example, non-polar polymers, such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polybutylene, whose primary chain or side chain contain —H, $—CH_3$, $—C_6H_5$ or other groups, are resistant to acids, alkalis, salts, water, alcohol, and so on, but not resistant to oil, benzene and carbon tetrachloride and other non-polar solvents. The polymers containing —OH, —COOH, $—OCH_3$, $—NH_2$, such as polyvinyl alcohol, polyamide, phenolic, amino-plastic and cellulose plastics, which are not resistant to acid, alkali ,water and other polar medium and will damage in various degree, while stable in non-polar organic solvents.

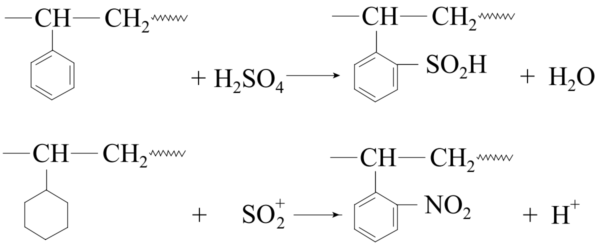
(3) In addition to the erosion of acid, alkali, salt and water and other electrolytes, the nitration of nitric acid, the sulfonation of concentrated sulfuric acid and their oxidation are other corrosion damage. Nitrification and sulfonation always occur easily in the benzene ring of the molecules, take polystyrene as an example:

Table 11.14 The active groups in polymer materials and the possible reaction

Reaction type	Atom or group	Polymer	Medium	Erosion way
Elimination reaction	C—F	Fluorine plastics	Fused alkali metals	Fluorine atom off and generate double bond
	 $-\underset{\mathrm{H}}{\mathrm{C}}-\underset{\mathrm{Cl}}{\mathrm{C}}-$	PVC	Heat, light, oxygen can accelerate	Hydrochloride off, generate double bond or cross-linked bond
Addition reaction	 $-\overset{\mathrm{H}}{\mathrm{C}}=\overset{\mathrm{H}}{\mathrm{C}}-$	Natural rubber	Hydrochloride	Generate hydrochloride rubber on the surface and prevent further infiltration of HCl, which can be used for lining
Oxidation reaction	Carbon chain or heterogeneous chain polymer, particularly with double bonds or tertiary carbon atom	The rubber and resin with double bond, plastics with tertiary carbon atom	Oxidation medium	Oxidation
Hydrolysis	 $-\mathrm{C}-\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}-\mathrm{O}-\mathrm{C}$ Ester bond	Unsaturated polyester, acid-curing epoxy resin	Alkali	Ester saponification
	 $-\underset{\mathrm{O}}{\underset{\Vert}{\mathrm{C}}}-\mathrm{NH}$	Polyamide	Acidic medium	Amine (imine)
		Polyimide	Strong acid medium	Bond hydrolysis

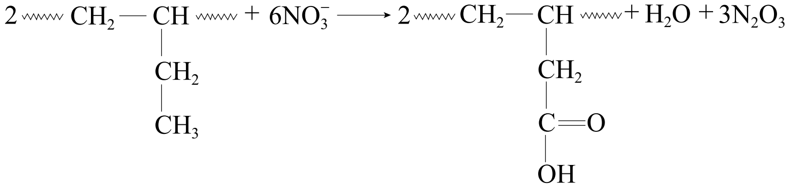
(Continued)

Reaction type	Atom or group	Polymer	Medium	Erosion way
Hydrdysis	 $-O-\underset{\underset{O}{\|}}{C}-NH-$	Polyurethane	Alkali medium	Carbamate bond hydrolysis
	 $-\overset{\|}{\underset{\|}{C}}-O-\overset{\|}{\underset{\|}{C}}-$ Ether bond	Epoxy resin, chlorinated polyether	Strong acid medium	Ether bond hydrolysis
	$-C\equiv N$ Cyano group	ABS resin, nitrile rubber	Alkali medium	Hydrolysis
	 $-\overset{\|}{\underset{\|}{C}}-NH-$	Amine-curing epoxy resin	Strong acid	hydrolysis
	 $-O-\overset{\|}{\underset{\|}{Si}}-$ Silicon-oxygen bond	Silicone Resin	High-temperature steam containing acid	Hydrolysis of silicon-oxygen bond
Salt-forming reaction	 Phenolic hydroxyl	Phenolic resin	Alkali	Phenolic hydroxyl group into salt
	$-NH_2$ amino-group	Amino resin	Acid	Amino salt formation
Chlorination	 Benzene ring, etc.	Phenolic resin Polyphenylene sulfide	Chlorine	Benzene chlorination
	C—H bond	General polymer materials	Chlorine	Hydrogen was replaced by chlorine



(11.15)

In addition, both nitric acid and fuming sulfuric acid are strong oxidants, which cause macromolecules' oxidation. Oxidation easily occurs in the hydrocarbon chain of the macromolecule, take polybutylene as an example:



$$2\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{CH_3}}}{\mathrm{CH}}\sim + 6\mathrm{NO_3^-} \longrightarrow 2\sim\mathrm{CH_2}-\underset{\substack{|\\ \mathrm{CH_2}\\ |\\ \mathrm{C{=}O}\\ |\\ \mathrm{OH}}}{\mathrm{CH}}\sim + \mathrm{H_2O} + 3\mathrm{N_2O_3} \tag{11.16}$$

This shows that vast majority of plastics are not resistant to concentrated nitric acid, fuming sulfuric acid and other strong oxidants.

For some of polycondensation thermosetting resins, chemical corrosion resistance has been improved because of cross-linked macromolecular structure, but they are also highly selective. Common unsaturated polyesters and their FRP are resistant to acid, whereas not resistant to alkali, benzene and ketone. Common epoxy resins and their FRP have good alkali-resistance and good acid-resistance, which have relation with curing agent. The amine-curing are poor acid-resistant and acid-curing are poor alkali-resistant. Phenolic resins and their FRP have good acid-resistance and poor alkali-resistance. Furan resins and their FRP have good acid-resistance and good alkali-resistance except for nitric acid and other strong oxidizing acid. In addition, diallyl phthalate resin and its FRP, diphenylether formaldehyde resin and its FRP, xylene formaldehyde resin and its FRP, all have good alkali-resistance, acid-resistance and organic solvent-resistance.

Usually, adding a variety of additives to the resin also has impact on the corrosion resistance of the resin. The corrosion resistance of composite materials depends not only on the nature of resin, but also on fiber, other additives and their combination with resin.

Table 11.15 gives the corrosion resistance of some common FRP. Table 11.16 gives applications of some corrosion-resistant FRP.

Table 11.15 The main characteristics of FRP with epoxy, phenolic, furan, polyester as matrix respectively

Property	Epoxy FRP	Phenolic FRP	Furan FRP	Polyester FRP
Acid resistance	Better	Good	Good	General
Alkali resistance	Better	Poor	Good	Poor

(Continued)

Property	Epoxy FRP	Phenolic FRP	Furan FRP	Polyester FRP
Solvent resistance	General	Good	Good	Poor
Water resistance	The best	Very good	Good	Very good
Heat resistance	Lower	Higher	High	Low
Mechanical properties	Good	Better	Better	Good
Electrical performance	The best	Good	Good	Good
Curing volatiles	No	Have	Have	No
Shrinkage rate after curing	Small	Large	Large	Larger
Forming pressure	Low∼Middle	Low ∼ High	Low∼High	Low∼Middle
The biggest advantage	Good mechanical properties	Excellent acid-resistance	Resistant to strong alkali and acid	Superior process
The biggest disadvantage	Demolding is not easy	Brittle	Poor process	Large shrinkage
The cost	Higher	Lower	Lower	Low

Table 11.16 Applications of corrosion-resistant FRP

Medium	Concentration (%)	Temperature (K)	Pressure (10^5N/m^2)	Device name and specifications	Methods of construction and the material	Service time (a)
Sulfuric acid	8∼12	Normal temperature	Normal pressure	Car tank	Paste 2-layer epoxy FRP lining	1
Sodium hydrate, fuming sulfuric acid	20	343∼353	—	Mist collector (ϕ1200× 1500)	Paste 2-layer epoxy FRP lining	2
Hydrochloric acid	32	Normal temperature	Normal pressure	Tank of all plastic (30m^3)	Paste 10-layer epoxy FRP lining	6
Sulfuric acid	140g/L	303	—	Zinc smelting tank (concrete)	Paste 5-layer epoxy FRP lining	4
Waste sulfuric acid	40∼60	Normal temperature	Normal pressure	Acid regeneration pot	Paste 5-layer epoxy FRP lining	12
Mother liquor of ammonium sulfate	4∼16	333	1.8	Central gas pipeline	Paste 5-layer epoxy FRP lining	8 small patch
Mixture of Nitric acid and sulfuric acid	—	Normal temperature	—	Nitrocellulose pickling tank	Paste 4-layer epoxy FRP lining	9

11.4 Wearability

11.4.1 Character of polymer materials wearability

Many polymer materials have relatively low friction coefficient, especially PTFE, which is good lubricants. Polymer materials are used to replace metal as friction parts. They can work well in the absence of oil, less oil, or in corrosive medium, which are particularly advantageous to sophisticated technology, chemical machine, textile machine, as well as other anti-oil or machine parts inconvenient to refuel. Polymer materials have strong corrosion resistance, so they are not easily corroded by chemicals. Therefore they are suitable for friction parts working in a corrosive medium. And polymer materials can absorb metal particles, dust and other impurities. When these impurities go into the friction surface, they can be embedded into polymer materials to reduce the wear of polymer or the metal surface. In addition, the anechoic and antiseismic properties of polymer materials are much better than that of metal, which is favorable to improve the operating speed of the friction parts in high-speed machine. Generally speaking, polymer materials can meet the major performance requirements as friction material basically, but there are also some disadvantages. They have relatively low compressive strength, large compressive deformation and obvious cold flow creep when compressed, leading to poor dimensional stability. Although the friction coefficient is small, its wearability is poor. So they are easy to be worn out generally. As a result of poor heat resistance, they are far from enough to meet the needs of certain engineering fields. The temperature of the friction interface will increase because the heat is not easily to dissipate as a result of low thermal conductivity. In addition, they are easily affected by temperature in size due to high thermal expansion coefficient, which can affect its normal operation and precision.

11.4.2 Friction characteristics of polymer materials

Friction between objects can be classified to static friction and kinetic friction (rolling friction and sliding friction). What impedes the sliding trend of objects is static friction force, which is often characterized by the static friction force when the sliding begins. Kinetic friction is the force when two objects are in relative motion.

1) Friction force

During friction process, two mutual friction parts comprise a friction pair. Applying force in the friction pair is equal, and the direction is opposite, which is called as friction force. Generally the friction force between friction pairs is composed of three parts: deformation resistance F_d of convex peaks of friction surface, plough force F_p produced by wear particles and rigid convex peak ploughing into friction surface and the adhesion shear force F_a of flat part on the surface. If F

stands for the friction between friction pairs, then:

$$F = F_a + F_p + F_d \tag{11.17}$$

For polymer, F_a is mainly caused by the van der Waals' force or hydrogen bonds, it has weak adhesion with metal; the adhesion force will be the key component of friction force when the friction surface of polymer materials has been rub down (parts of peak and rough have been removed). At this time, deformation force F_d and plough force F_p can be ignored, then:

$$F = F_a \tag{11.18}$$

Assumed that the actual contact area of the friction surface is A_r, and τ stands for the shear force per unit area (shear stress) between the materials of friction pair, then:

$$F = A_r \cdot \tau \tag{11.19}$$

The friction force between the friction pairs is mainly decided by the actual contact area between them and the shear stress on contact surface. But the actual contact area depends on the deformation mode when materials contact and the compressive strength or modulus of materials.

2) Friction coefficient

Friction coefficient is one of the parameters that characterize friction properties of friction pair, which is defined by:

$$\mu = \frac{F}{P} \tag{11.20}$$

In the formula, μ is the friction coefficient; P is the load of friction pair vertical to the friction surface; F is friction force. Take formula (11.19) into formula (11.20), we can get:

$$\mu = \frac{A_r \cdot \tau}{P} \tag{11.21}$$

The friction coefficient of polymer materials has these following characteristics:

(1) Related to the load.

The friction coefficient of polymer materials will have a slight decrease with the load increasing, as shown in the Fig.11.4. The yield strength of rubber is low, the friction coefficient decreases fast with the load increasing. If the friction mechanism changes from typical shear deformation of contact point into friction of scraping a trench on the surface, then the friction coefficient may increase because of load increasing.

(2) Related to the sliding speed.

For steel and other materials, μ can decrease only when the material in a very high speed (100m/s or above), but high speed has great effect on polymer materials. Fig.11.5 shows that the friction coefficient of rubber, plastics depend on the sliding speed. The friction coefficient of rubber will increase with sliding speed increasing, and then remain unchanged or decline. However, the friction coefficient of hard plastics will often decrease with speed increasing, at the same time the temperature of surface contact point will become very high, sometimes forming an a lubricating layer of molten plastics on the surface, so its friction coefficient decreases. However, rolling friction has different dependence on speed due to internal friction (the increase in mechanical damping). And the friction coefficient of thermosetting resin is less affected by speed.

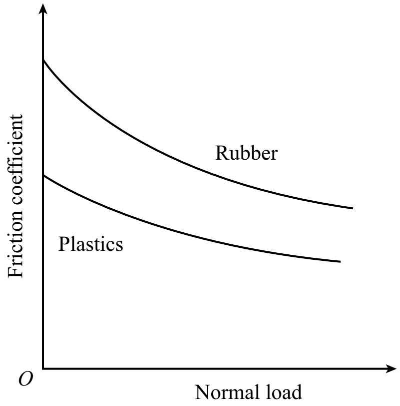


Fig. 11.4 The effect of load on friction coefficient.

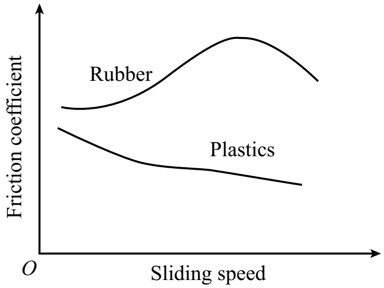


Fig. 11.5 The effect of sliding speed on friction coefficient.

(3) Related to the temperature.

The environment temperature increases or the temperature of materials rises due to a large amount of heat generated by high-speed sliding friction. That softens polymer material, and the shear strength and yield strength decrease, the total area of contact point increases. Friction force is the shear strength multiplied by the total area of contact point, so the effect of temperature is inconsistent and the curve often gives an extreme value, as shown in Fig. 11.6.

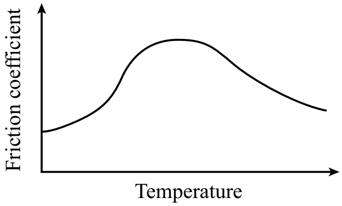


Fig. 11.6 The effect of temperature on friction coefficient.

(4) Related to the surface finish.

The rough surface can lead to μ decreasing in a certain range.

(5) Related to the wetting performance and surface tension of materials.

The smaller the surface tension is, the easier the shear of contact point. Generally, if the surface tension of polymer is small, its friction coefficient is small, too. μ of fluoroplastics is the smallest in polymers. The static friction coefficient of Nylon is the biggest, while its dynamic friction coefficient is very small, so it is often used for bearings, bushing and piston ring, and so on. The friction coefficient of crystalline polymer materials is affected by the size of spherulite and the microcrystalline morphology. The friction coefficient of polypropylene rises with spherulite becoming bigger. The surface tension of rubber is the smallest, but its mechanical damping is very large, so its friction coefficient is higher than most plastics.

Practice and theoretical analysis show that the friction pair consisting of plastics and metal usually has a small friction coefficient, because the majority of plastics have low shear strength and high yield stress, μ is in the range of 0.1~0.4; and except for fluoroplastics, μ when plastics rubbing with metal is smaller than themselves, some plastics (such as polytetrafluoroethylene, polyimide) are excellent self-lubricating materials.

11.4.3 Abrasion of polymer materials

Like other materials, the abrasion of polymer materials refers to the phenomenon that the particulates continuously isolate from the friction surface of materials during the friction process. Abrasion is also known as friction corrosion or wear, which leads to the change of material size. The amount of abrasion is usually used to express abrasion resistance, which is the assumption amount (weight, volume, etc.) that the sample was abrased after a certain period of time or a certain distance of friction under test conditions (load, speed, temperature, wet, etc.).

It is clear that abrasion is closely related to friction, especially with the scratch part of the friction. Therefore abrasion is greatly affected by the relative hardness of materials. In addition to the physical damage of the surface, abrasion is often accompanied by chemical erosion. The local temperature can be very high in the friction or abrasion process of polymer materials, which can cause oxidative pyrolysis.

The abrasion of different polymer will increase linearly with the increase of load and friction distance, but decrease slightly with friction speed increasing.

The harder the metal is, the smaller the abrasion will be, nor are polymer materials, the abrasion resistance of the hard is often poor. Moreover, there is a general tendency that the abrasion will increase with the friction coefficient rising. But both the impact of hardness and friction coefficient are not constant.

Abrasion is related to the nature of counter materials, and especially their hardness. Generally speaking, abrasion will decrease with the hardness increasing, as shown in Fig. 11.7.

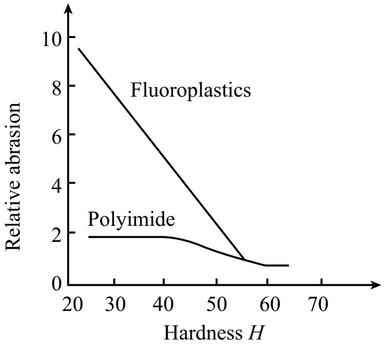


Fig. 11.7 The impact of counter material hardness on abrasion.

In addition, abrasion is also related to the surface finish. The abrasion of most polymer materials will reduce with the surface finish improving. Because the more rough the surface is, the more easily the polymer materials will be grinded. Some materials are not like that, for example, when fluorine plastics rubbing with the surface with good finish, the abrasion will increase, as shown in Fig. 11.8. This may be because part of PTFE transfers onto the friction surface when the surface with a certain degree of roughness and embeds in the recess of the surface, which will lead to fluoroplastics friction themselves. If the surface finish is perfect, this shift will not occur so the abrasion will increase.

For the friction of plastics to metal, abrasion includes planing abrasion, adhesion abrasion and particle abrasion. Therefore, generally speaking, the harder the material is, the more difficult for it to be planed, also mean the planing abrasion is small. The materials, such as MC nylon, POM and filled phenolic plastics, are all more resistant to abrasion than fluoroplastics. The higher the softening point is, the more resistant to adhesion abrasion the material is. For example, the PMMA and polystyrene with low softening point have poor abrasion resistance. Plastics usually have feature of burying foreign body, so particle abrasion is not the dominating abrasion, but the effect of hardness on particle abrasion is contrary to that to planing abrasion. In sum, plastics with moderate hardness and high softening point are often abrasion-resistant materials.

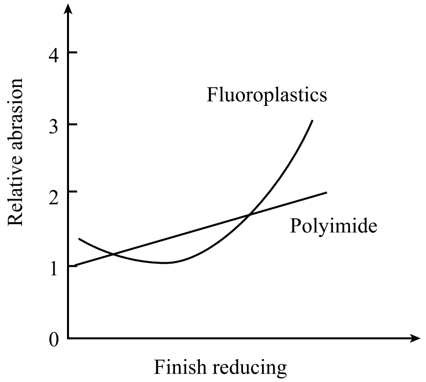


Fig. 11.8 The effect of surface finish on abrasion.

11.4.4 Improvement of friction and friction resistance of polymer materials

The method to improve the friction and friction resistance of polymer materials is mainly to add reinforced materials and lubricants to polymer materials, such as graphite and molybdenum disulfide, or other common solid lubricants. They not only greatly reduce the friction coefficient and improves the self-lubricating properties, but also can improve the thermal conductivity and reduce abrasion.

The materials with low friction coefficient are not necessarily resistant to abrasion. For example, the friction coefficient of PTFE is low, but its abrasion is large. It will increase μ of PTFE from 0.13 to 0.23 by adding 20% of glass fiber, but the relative abrasion reduces from 4450mg to 2.8mg because the strength increases significantly.

As high temperature friction-resistance materials, they should not only have high heat resistance, but also have high temperature friction resistance. Carbon fiber reinforced plastics have excellent high temperature friction resistance, so they are expected to be widely used.

11.5 Flame resistance

Polymer materials are all organic compounds with high hydrogen and carbon content. Their mechanical properties will lose or reduce in some cases when the temperature increases. Some of them may melt, decompose or burn, resulting to accident and loss. At the same time, polymer materials are likely to produce much smoke when the temperature is in 300~700°C, which will cause suffocating and poisoning to people. It should be avoided as far as possible since this is not expected.

11.5.1 Characterizing and evaluating methods of flame retardance

For polymer composites, there are four indicators to characterize the flame retardance: the surface burning rate, burning percentage weight loss, fire burning index FI and oxygen index OI.

The surface burning rate v is the average burning rate that composites specimen begins burning in 1min or 3min.

$$v = \Delta L / \Delta t \tag{11.22}$$

In the formula, ΔL is surface burning length of the specimen; Δt is burning time.

The burning percentage weight loss ΔP is weight loss of specimen burning for 1min or 3min.

$$\Delta P = \frac{W_0 - W_{\Delta t}}{W_0} \times 100\% \tag{11.23}$$

In the formula is W_0 is the original weight of specimen; $W_{\Delta t}$ is the weight of specimen after burning for 1min or 3min.

Fire burning index FI refers to that the surface burning rate is multiplied by the burning percentage weight loss.

$$\mathrm{FI} = v \cdot \Delta P \tag{11.24}$$

Oxygen index OI refers to the minimum oxygen concentration that can maintain stable combustion in the mixed gas of oxygen and nitrogen under specified conditions, represented by the volume fraction of oxygen.

For rigid thermosetting resin composite materials especially glass fiber reinforced composite materials, we usually evaluate the flammability by testing the surface burning rate, percentage weight loss, as well the burning index.

11.5.2 Flame retardant mechanism of polymer composites

Combustion is a specific auto-catalytic reaction of free radicals, which have three necessary conditions, the so-called three elements: inflammable materials, oxidation and heat. Combustion will occur and maintain when the three elements can be reached at the same time. The measure which can eliminate one or more elements will be the flame retardant mechanism.

1) To reduce inflammable materials

Adding some substances into polymer composites can make it easy to produce a carbonized layer when burning, which will suppress the production of flammable gases. Try to generate noncombustible gases, which can dilute flammable gases and segregate oxygen to some extent, playing a role of inhibiting combustion. In addition, HO· radical plays an important role during combustion process. So we can add certain substances into materials, which can produce certain groups to receive and capture the HO· radical in combustion process. This may terminate the chain reaction in combustion process.

2) To cut off heat source

Both high density gases and carbonized layer can effectively delay the heat transfer from the surface to the inner. The endothermic decomposition of retardants or the endothermic reaction with the combustion products will be able to eliminate the heat source of internal materials and suppress the further spread of combustion, which is more efficient.

3) To dilute or isolate oxygen

Try to make polymer composites generate a carbonized layer when burning. On the one hand, this can separate the oxygen from the inner layer; on the other hand, it can effectively delay the transmission of heat to the internal layer, playing the role of retardants. The high density gases generated in combustion process can cover the major surface, which also plays the role of diluting or isolating oxygen.

11.5.3 The flame retardant mechanism of composite materials

The flame retardancy of composite materials is mainly from flame retardants. Flame retardants used in composite materials mainly include halogen, phosphorus, phosphorus halides and inorganic hydrates, and so on. Adding methods are surface coating, physical adding and chemical reactions, etc. The last two ways are more effective and commonly used.

1) The species of flame retardants and their corresponding mechanism

Halogen flame retardant will produce hydrogen halide in combustion process, which can react with active center HO· . Then the low active products X· and R· will replace HO·, inhibiting combustion reaction. Moreover, in combustion process hydrogen halide can halogenate polymer molecular and strip down hydrogen halide to produce unsaturated bond, which lead to the formation of carbonized layer on the surface and suppress combustion.

The mechanism of phosphorus flame retardants: phosphorus or phosphides will generate phosphoric acid when heated. It will further generate polyphosphoric acid. Polyphosphoric acid has strong effect of dehydration on polymer materials, which will generate carbides to inhibit combustion. Phosphorus halides flame retardants contain both the halogen and phosphorus elements, which will not only take effect respectively and also have synergistic effect, further increasing the effect of flame retardants.

Inorganic hydrates, such as $Al(OH)_3$, $Al_2(SO_4)_3{\cdot}18H_2O$, and so on, will decompose and absorb heat when the temperature rises. Decomposition products alumina can react with carbides produced in burning process to generate inactive materials, which will result in the insulation from the heat and oxygen. At the same time, the volatilization of decomposition products water can not only absorb heat, but also dilute the combustible gases and oxygen. All these play the role of flame retardants. Table 11.17 lists a number of flame retardants and application as reference.

Table 11.17 Some common flame retardants

	Flame retardant	Flame retardant element content(%)	Application
Halogen flame retardant	Tetrachloro phthalic anhydride	Cl 49.5	Epoxy, unsaturated polyester
	Tetrabromobisphenol A	Br 61	Epoxy, phenolic, ABS
	Chlorinated paraffin	Cl 70	PVC, polyester,
	Tetrabromo-butane	Br 85.5	PS, polyolefins, ABS
	Hexabromo-cylcodecane	Br 70	ABS
Phosphorus flame retardant	Phosphorus-containing polyols	P 10.3∼11.5	Polyurethane
	Trimethyl phosphate	P 22	
	Trioctyl phosphate	P 7.1	Synthetic rubber, PVC
	Butoxy ethyl phosphate	P 8.7	PVC, PMMA, NC, etc.
	Triphenyl phosphate	P 9.5	Cellulose triacetate
Phosphorus halogen flame retardant	Tris(chloropropyl bromide)phosphate	P 5.5, Cl 10, Br 42	PE, PVC, synthetic fibre
	Chlorinated polyphosphate	P 12, Cl 27	Polyurethane foam
	Chlorinated polyphosphate	P 13.3, Cl 128.5	Polyester, epoxy, acrylate
	Tri(chloroethyl) Phosphate	P 10.8, Cl 7	PU, PVC, PDAC, etc.
	Tri (2-chloropropyl) phosphate	P 9.45, Cl 32.5	PVC, PU, polyester

2) The flame retardant matrix of different adding methods

According to the different ways of adding flame retardants to the matrix of composites, the flame retardant matrix can be divided into three types which are coating type, reaction type and adding type. And the reaction type can be divided into polymerization type and curing type. The so-called polymerization type is that the monomer of synthesizing matrix resin contains flame-retardant elements, which can be introduced into the matrix resin through polymerization reaction. Table 11.18 lists a formulation of such matrix.

Table 11.18 A formulation of unsaturated polyester reaction type flame-retardant matrix

Raw materials	Weight fraction (%)	Mole fraction (%)
Tetrabromo phthalic anhydride	28.2	7.3
Phthalic anhydride	51.6	12.6
Maleic Anhydride	22.8	27.8
Propanediol	33.3	52.4

When the curing agent, initiator, additives and other small molecules contain flame-retardant elements in the curing matrix system, we can introduce the flame-retardant elements into curing network structure to form flame-retardant matrix through curing reaction, which is called curing type flame-retardant matrix. Table 11.19 gives a few formulas.

Table 11.19 The three formulae and the corresponding performance of curing type flame-retardant matrix

Raw materials	Formula and performance		
	Group A	Group B	Group C
Unsaturated polyester resins (share)	100	100	100
Tribromo-acrylic resin (share)	15	50	100
Dicumyl peroxide (share)	2	2	2
PTFE powder (share)	20	50	50
Content of bromine (%)	6.8	15.3	24.6
Test results of flammability(ASTM D-635)	Self-extinguishing	Non-flammable	Non-flammable

The species and amount of flame retardants in adding type flame-retardant matrix have relatively small restriction, thus can be used to adjust the flame retardancy of composite materials in large extent. However, the combination of flame retardants and the matrix is only physical mixing, and flame retardants have effect on the mechanical properties of matrix and even composite materials. In some cases, using adding type and reaction type jointly will make flame-retardant matrix to exhibit characteristics of both types. Table 11.20 gives an example of mixed-type flame-retardant matrix.

Table 11.20 The formulation of mixed flame-retardant unsaturated polyester matrix

Raw materials	Weight fraction (%)
Unsaturated polyester phthalate	44.5
Styrene	3.1
Dried aluminum hydroxide	47.6
Chlorinated styrene	4.8
Methyl ethyl ketone peroxide	0.45

Exercises

1. What are the characteristics of thermal physical properties of polymers? What are its influencing factors?

2. What is the relationship between the thermal expansion coefficient and the behavior in response to temperature?

3. What is the index to evaluate the heat resistance of composite materials? How to improve heat resistance of materials from the components? What's the difference of heat resistance and thermal insulation?

4. Why do we say that the property of heat and humidity resistance is an important performance of plastics and composite materials? How to improve it?

5. Which factors does the water resistance of composites depend on? How to improve it?

6. What are friction and abrasion? What are the characteristics of the friction and abrasion of polymer materials? How can we improve them?

7. What is the flame-retardant mechanism of polymer composite materials? How to improve the flame retardancy?

8. How to evaluate the flammability? How to improve it?

9. Which matrix resin is commonly used in corrosion-resistant composite materials?

10. What's the corrosion-resistant mechanism of polymer material?

11. What are the factors that impact the corrosion resistance of composite materials?

12. Compared with metals, what are the characteristics of corrosion resistance of polymer composites?

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