CHAPTER 2 MATERIALS AND PROCESSES - THE EFFECTS OF VARIABILITY ON COMPOSITE PROPERTIES

2.1 INTRODUCTION

The properties of organic matrix composites are, in general, cure and process dependent. This may result in variations of glass transition (service temperature), corrosion stability, susceptibility to micro-cracking, general strength, or fatigue and service life. In addition, in most cases these materials or structural elements constructed from them are the products of complex multi-step materials processes. Figures 2.1(a) and (b) illustrate the nature of the processing pipeline from raw materials to composite end item. Each rectangle in Figure 2.1(b) represents a process during which additional variability may be introduced into the material. Utilization of a standard composite material property database necessitates an understanding of the dependency of the measured material properties on the characteristics and variability associated with the constituent materials and the sequence of processes used to combine these materials into end products. As a result, development and application of processing controls are essential to achieve the desired mechanical and physical properties for composite structures.

2.2 PURPOSE

The purpose of this chapter is to provide an understanding of the origins and nature of process-induced variability in these materials in the context of an overview of types of composite materials and the associated material processing methodologies. It also seeks to addresses various approaches to minimizing variability, including implementation of process control, and the use of materials and processing specifications.

2.3 SCOPE

This chapter includes descriptions of composite materials from the perspective of their introduction into the material pipeline as the constituent raw material, subsequent conversion of raw materials into intermediate product forms such as prepregs, and finally the utilization of these intermediate product forms by fabricators to process the materials further to form completed composite structures. Emphasis is placed on the cumulative effects that each processing phase in the pipeline contributes to the final products general quality as well as physical, chemical, and mechanical properties. Finally it includes an overview of common process control schemes and discusses preparation of materials and processing specifications.

2.4 CONSTITUENT MATERIALS

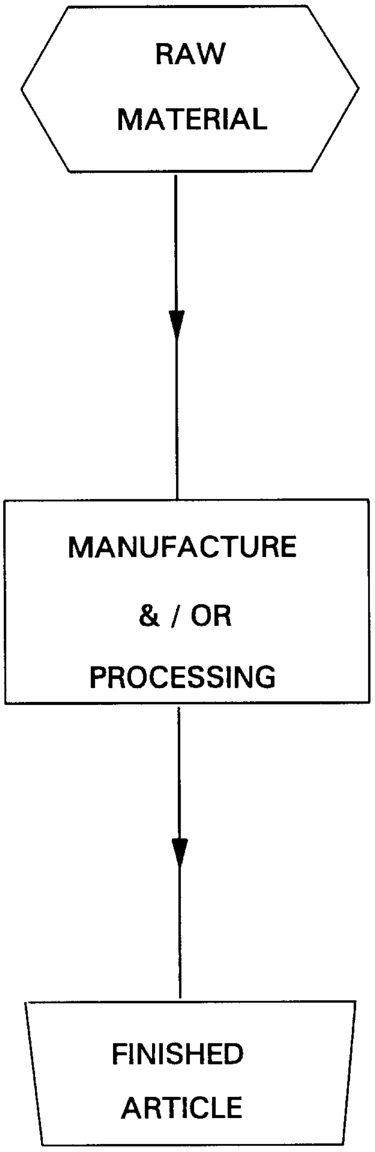
2.4.1 Fibers

2.4.1.1 Carbon and graphite fibers

Carbon and graphite have substantial capability as reinforcing fibers, with great flexibility in the properties that can be provided. Primary characteristics for reinforcing fibers in polymer matrix composites are high stiffness and strength. The fibers must maintain these characteristics in hostile environments such as elevated temperatures, exposure to common solvents and fluids, and environmental moisture. To be used as part of a primary structure material it should also be available as continuous fiber (Reference 2.4.1.1). These characteristics and requirements have substantial implications for the physical, chemical and mechanical properties of the fiber, which in turn implies processing and acceptance parameters.

2.4.1.1.1 Carbon vs. graphite

Interest in carbon fibers for structural materials was initiated in the late 1950s when synthesized rayons in textile form were carbonized to produce carbon fibers for high temperature missile applications (Reference 2.4.1.1.1). One of the first distinctions to be made is the difference between carbon and graphite fibers, although the terms are frequently used interchangeably. Background information for these differences is contained in the following sections. The primary purpose of making this distinction here is to alert the reader that users may mean different things when referring to graphite versus carbon fibers.



ALL PRODUCTS, REGARDLESS TO STAGE OF WORK, ARE CONSIDERED AS RAW MATERIALS. THESE MAY BE CHEMICALS FOR RESINS, OR SAND TO PROCESS INTO GLASS PRODUCTS, OR PRECURSORS FOR FILAMENTS, OR WOVEN GOODS, OR FLAT PROCESSED SHEETS AND/OR MANY OTHER ARTICLES WHICH HAVE YET TO BE PROCESSED TO AN END ITEM.

EACH RAW PRODUCT THEN IS PROCESSED, OR MIXED WITH OTHER RAW PRODUCTS, OR ALTERED TO BECOME STILL ANOTHER RAW ARTICLE TO EXPERIENCE YET ADDITIONAL PROCESS STEPS THROUGH THE PIPELINE. EACH AS RECEIVED RAW ARTICLE MUST BE PROCESSED IN SUCH A MANNER DURING ITS PROCESSING STEP(S) THAT VARIABILITY IS MINIMIZED AT THE NEXT PIPELINE FUNCTION. PROCESSING FUNCTIONS MAY BE COMPLEX; SUCH AS MATRIX IMPREGNATION, OR THEY MAY BE RELATIVELY SIMPLE; SUCH AS SHIPPING. REGARDLESS, EACH STEP MUST BE EFFECTIVE IN THAT IT DOES NOT INTRODUCE UNCONTROLLED CHANGES THAT ALTER THE PRODUCT FOR SUBSEQUENT USE OR END ITEM PERFORMANCE.

FINISHED ARTICLES LEAVING ONE PROCESSING FUNCTION IS USUALLY STILL CONSIDERED A RAW PRODUCT WHEN DELIVERED TO THE NEXT. THE ONUS FOR CONSISTENCY OF THIS PRODUCT MUST BE RECOGNIZED AND ATTENDED TO DURING THE JUST COMPLETED PROCESSING STEP(S). THE MATERIALS PIPELINE IS NOT COMPLETE UNTIL THE END ARTICLE IS FULLY FUNCTIONAL AS IS.

FIGURE 2.1(a) *Composite materials and processing, basic pipeline common to all materials and processes.*

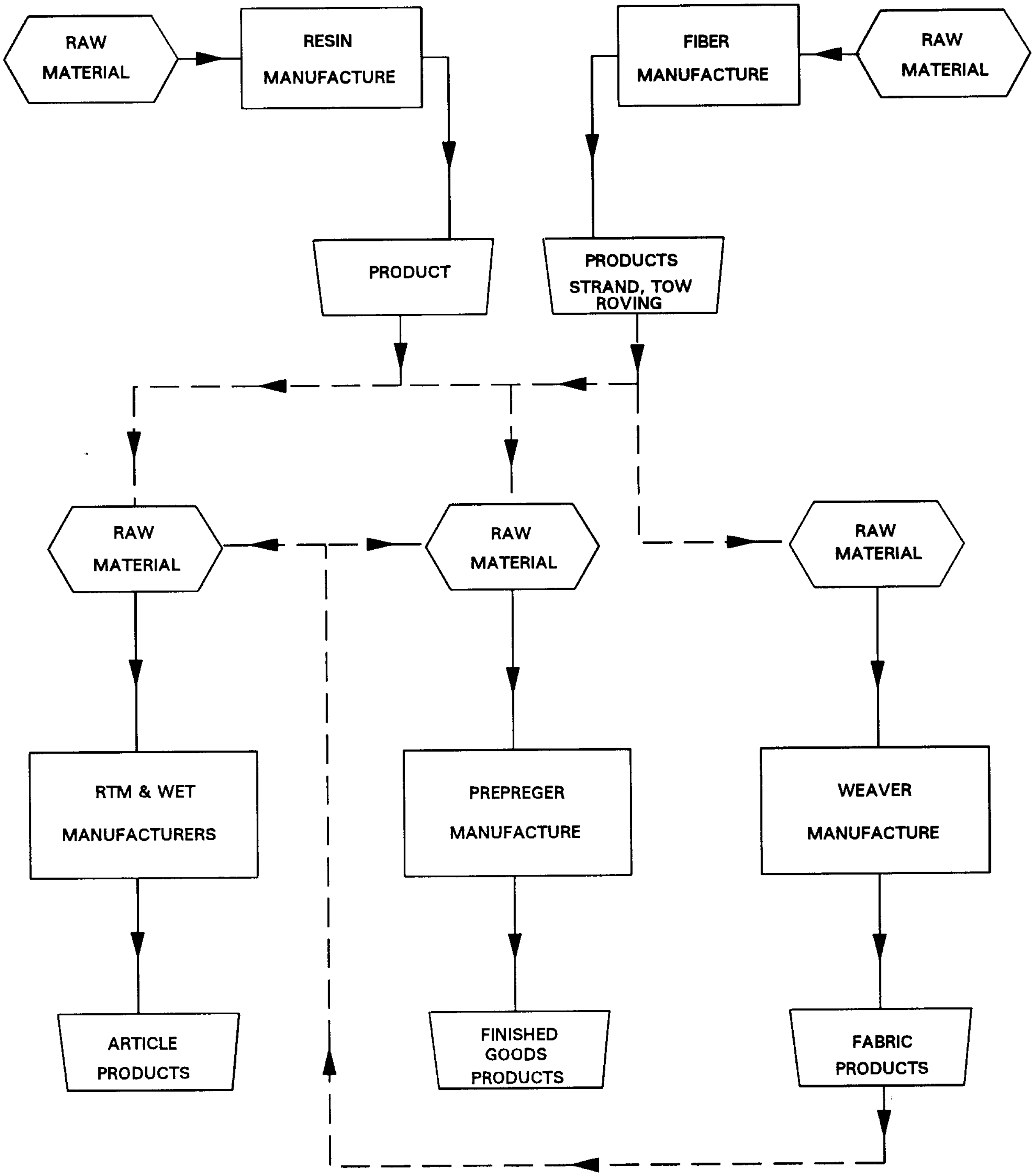


FIGURE 2.1(b) *Raw materials pipeline (example).*

Carbon and graphite fibers are both based on graphene (hexagonal) layer networks present in carbon. If the graphene layers or planes stack with three dimensional order the material is defined as graphite (Reference 2.4.1.1.1). Usually extended time and temperature processing is required to form this order, making graphite fibers more expensive. Because the bonding between planes is weak, disorder frequently occurs such that only the two dimensional ordering within the layers is present. This material is defined as carbon (Reference 2.4.1.1.1). With this distinction made, it should be understood that while some differences are implied, there is not a single condition which strictly separates carbon from graphite fibers, and even graphite fibers retain some disorder in their structure.

2.4.1.1.2 General material description

Three different precursor materials are commonly used at present to produce carbon fibers: rayon, polyacrylonitrile (PAN), and isotropic and liquid crystalline pitches (Reference 2.4.1.1.1). Carbon fibers are made predominately from carbonization of PAN. The fibers consist of intermingled fibrils of turbostratic graphite with basal planes tending to align along the fiber axis. This forms an internal structure reminiscent of an onion skin. Pitch fibers may have a different internal structure, more like sheafs or spokes (Reference 2.4.1.1).

The highly anisotropic morphology gives rise to moduli in the range of 200-750 GPa parallel to the fiber long axis, and around 20 GPa in the normal direction. For comparison, single crystal (whisker) of graphite is about 1060 and 3 GPa, respectively, but these properties are not attainable in fiber form. Ultra high modulus fibers can be prepared from liquid-crystalline mesophase pitch; the higher degree of orientation in the precursor translates through to the final carbonized fiber leading to larger and more oriented graphite crystallites.

2.4.1.1.3 Processing

High stiffness and strength implies strong interatomic and intermolecular bonds and few strength limiting flaws (Reference 2.4.1.1). Carbon fiber properties are dependent on the fiber microstructure, which is extremely process dependent, such that properties of fibers with the same precursor but different processing can be dramatically different. The precursor itself can also change these properties. The processing may be optimized for high modulus or strength, or traded off with economics.

2.4.1.1.3.1 Manufacture

The manufacturing process for carbon fiber described below is for the PAN variant, which is one of the most common. Some differences between PAN processing and the pitch and rayon precursors are then described afterwards. The manufacture of PAN based carbon fiber can be broken down into the white fiber and black fiber stages. Most manufacturers consider the details of these processes proprietary.

2.4.1.1.3.1.1 White fiber

Production of PAN precursor, or white fiber, is a technology in itself. Fairly conventional fiber processes are performed: polymerization, spinning, drawing, and washing. Additional drawing stages may be added in the process. Characteristics of the white fiber influence the processing and results for the black fiber processing.

2.4.1.1.3.1.2 Black fiber

The black fiber process consists of several steps: oxidation (or thermosetting), pyrolysis (or carbonizing), surface treatment, and sizing. In the oxidation process the PAN fiber is converted to a thermoset from a thermoplastic. For this oxidation process the fiber diameter is limited by waste gas diffusion. In the pyrolysis process, which is performed under an inert atmosphere, most of the non-carbon material is expelled, forming ribbons of carbon aligned with the fiber axis.

In the surface treatment step the fiber may be etched in either gas or liquid phase by oxidizing agents such as chlorine, bromine, nitric acid or chlorates. This improves the wettability for the resin and encourages formation of a strong, durable bond. Some additional improvement through removal of surface flaws may also be realized. This process can be electrolytic. The carbon fibers are often treated with solution of unmodified epoxy resin and/or other products as a size. The sizing prevents fiber abrasion, improves handling, and can provide an epoxy matrix compatible surface.

2.4.1.1.3.1.3 Carbon fiber differences due to pitch/PAN/rayon precursors

As a rule PAN precursor can provide higher strength carbon fibers, while pitch can provide higher moduli. Rayon based fibers tend to be less expensive but lower performance. Pitch fiber composites have been prepared with elastic moduli superior to steel, and electrical conductivity higher than copper conductor. The shear strengths and impact resistance are degraded, however (Reference 2.4.1.1.3.1.3). Yield for PAN is approximately 50%, but for pitch can be as high as 90%.

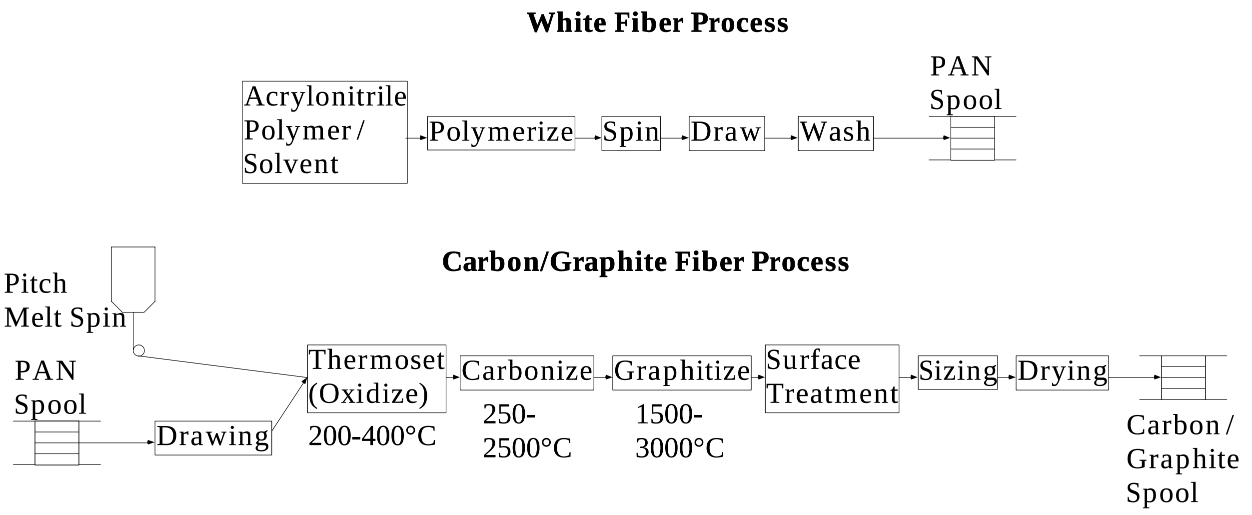


FIGURE 2.4.1.1.3.1.3 *Carbon fiber typical process flow diagram.*

2.4.1.1.3.2 Processing to microstructure

Carbon fiber properties are driven by the type and extent of defects, orientation of the fiber, and the degree of crystallinity. The precursor makeup and heat treatment can affect the crystallinity and orientation. The defect content can be driven by contaminants and processing. Orientation is also greatly affected by the drawing process which may be repeated many times in the processing of the fibers.

2.4.1.1.3.3 Microstructure to properties

The strength of a brittle material is frequently controlled by presence of flaws, their number and magnitude. The probability of finding a flaw is volume dependent, thus a fiber with a lower volume per unit length appears stronger. Elimination of defects drives tensile strength up, and also improves thermal and electrical conductivity, and oxidation resistance. However, increasing crystallinity too far can degrade fiber strength and modulus.

2.4.1.1.3.4 Testing

As with most composite material properties, the values obtained are greatly dependent on the testing performed. Determination of fiber modulus can be especially controversial. The stress/strain response can be nonlinear, so where and how measurements are taken can greatly influence the results. As a result, fibers which may appear to be substantially different in the literature may have little or no difference in modulus. Reported differences may be entirely the result of test and calculation differences. Chapter 3 in Volume I can be referenced for more information of fiber test methods.

2.4.1.1.4 Typical properties

Typically limitations on the end use for carbon fibers in composite structure depend more on the resin matrix than the fiber. Some exceptions to this are present, however, in which case the oxidative stability, thermal conductivity, coefficient of thermal expansion, or other properties of the fiber must be taken into account. Some key properties for carbon fiber, including cost, are listed in Table 2.4.1.1.4. Typical values for glass, aramid, and boron are shown for comparison. While some carbon fiber properties are fairly universal, different products from different manufacturers can have substantially different properties. Three of the major manufacturers for the US are Amoco, Hercules and Toray. It should be noted that translation of fiber properties to composite properties is dependent on many factors in addition to rule of mixtures.

TABLE 2.4.1.1.4 *Comparison of carbon and other fiber properties.*

	Tensile Modulus, Msi	Tensile Strength, ksi	Density, g/cm^3	Fiber Diameter, micron	Cost, $/#
Carbon (PAN)	30-50	350-1000	1.75-1.90	4-8	20-100
Carbon (Pitch)	25-110	200-450	1.90-2.15	8-11	40-200
Carbon (Rayon)	6	150	1.6	8-9	5-25
Glass	10-12.5	440-670	2.48-2.62	30	5-40
Aramid	20	410	1.44	--	25-75
Boron	58	730-1000	2.3-2.6	100-200	100-250

2.4.1.2 Aramid

In the early 1970's, Du Pont Company introduced Kevlar™ aramid, an organic fiber with high specific tensile modulus and strength. This was the first organic fiber to be used as a reinforcement in advanced composites. Today this fiber is used in various structural parts including reinforced plastics, ballistics, tires, ropes, cables, asbestos replacement, coated fabrics, and protective apparel. Aramid fiber is manufactured by extruding a polymer solution through a spinneret. Major forms available from Du Pont are continuous filament yarns, rovings, chopped fiber, pulp, spun-laced sheet, wet-laid papers, thermoplastic-impregnated tows, and thermoformable composite sheets.

Important generic properties of aramid fibers are: low density, high tensile strength, high tensile stiffness, low compressive properties (nonlinear), and exceptional toughness characteristics. The density of aramid is 0.052 lb/in^3 (1.44 gm/cm^3). This is about 40% lower than glass and about 20% lower than commonly used carbon. Aramids do not melt and they decompose at about 900°F (500°C). Tensile strength of yarn, measured in twisted configuration, can be varied from 500 - 600 ksi (3.4 - 4.1 GPa) by choosing different types of aramids. The nominal coefficient of thermal expansion is 3x10^{-6} in/in/F° (-5x10^{-6} m/m/C°) in the axial direction. Aramid fibers, being aromatic polyamide polymers, have high thermal stability and dielectric and chemical properties. Excellent ballistic performance and general damage tolerance is derived from fiber toughness. Aramid is used, in fabric or composite form, to achieve ballistic protection for humans, armored tanks, military aircraft, and so on.

Composite systems, reinforced with aramid, have excellent vibration-damping characteristics. They resist shattering upon impact. Temperature of use, in composite form with polymer matrix, range from -33 to 390°F (-36 - 200°C), The nominal tensile properties of composites reinforced with aramid are listed in Table 2.4.1.2(a) - in thermoset (Reference 2.4.1.2(a)) and thermoplastic (Reference 2.4.1.2(b)) resin matrix. At 60% fiber volume fraction, composites of epoxy reinforced with aramid fibers have nominal tensile strength (room temperature) of 200 ksi (1.4 GPa) and nominal tensile modulus of 11 Msi (76 GPa). These composites are ductile under compression and flexure. Ultimate strength, under compression or flexure, is lower than glass or carbon composites. Composite systems, reinforced with aramid, are resistant to fatigue and stress rupture. In the system of epoxy reinforced with aramid, under tension/tension fatigue, unidirectional specimens (V_f ~ 60%) survive 3,000,000 cycles at 50% of their ultimate stress (Reference 2.4.1.2(a)). Recently, thermoplastic resin composites reinforced with aramid have been developed. These thermoplastic composite systems have exhibited equivalent mechanical properties compared to similar thermoset systems (Reference 2.4.1.2(b)). In addition, thermoplastic systems provide potential advantages in economical processing (Reference 2.4.1.2(c)), bonding, and repair. A unique thermoformable sheet product, in thermoplastic matrix reinforced with aramid fibers, is available (Reference 2.4.1.2(d)). These composite systems are also used to achieve low coefficient of thermal expansion or high wear resistance. They are non-conductive and exhibit no galvanic reaction with metals. Aramid fibers are available in several forms with different fiber modulus (Table 2.4.1.2(b)). Kevlar™29 has the lowest modulus and highest toughness (strain to failure ~ 4%). These fibers are used mostly in ballistics and other soft composite systems such as cut- and slash- resistance protective apparel, ropes, coated fabric, asbestos replacement, pneumatic tires, etc. These are also used for composites where maximum impact and damage tolerance is critical and stiffness is less important. Kevlar™49 is predominantly used in reinforced plastics - both in thermoplastic and thermoset resin systems. It is also used in soft composites like core of fiber optic cable and mechanical rubber good systems (e.g., high pressure flexible hose, radiator hose, power transmission belts, conveyor belts, etc.). An ultra-high modulus Type 149 has been made available recently. It has 40% higher modulus than Kevlar™49. Kevlar™29 is available in fiber yarn sizes and two rovings sizes. Kevlar™49 is available in six yarn and two rovings sizes. Kevlar™149 is available in three yarn sizes. Yarn sizes range from the very fine 55 denier (30 filaments) to 3000 denier (1300 filaments). Rovings are 4560 denier (3072 filaments) and 7100 denier (5000 filaments). Composite thermoplastic tows, several types of melt-impregnated thermoplastic reinforced with different Kevlar™ yarns and deniers, are also available.

TABLE 2.4.1.2(a) *Nominal composite properties reinforced with aramid fiber (V_f ~ 60%).*

		Thermoset (epoxy)		Thermoplastic (J2)	
Tensile Property	Units	unidirectional	fabric[1]	unidirectional	fabric[1]
Modulus	Msi (GPa)	11 (68.5)	6 (41)	10.5-11.5 (73-79)	5.1-5.8 (35-40)
Strength	ksi (GPa)	200 (1.4)	82 (0.56)	180-200 (1.2-1.4)	77-83 (0.53-0.57)

[1] Normalized from V_f = 40%; fabric style S285

Aramid composites were first adopted in applications where weight savings were critical - for example, aircraft components, helicopters, space vehicles, and missiles. Armor applications resulted from the superior ballistic and structural performance. In marine recreational industries, light weight, stiffness, vibration damping, and damage tolerance are valued. Composites reinforced with aramids are used in the hulls of canoes, kayaks, and sail and power boats. These same composite attributes have led to use in sports equipment. Composite applications of aramid continue to grow as systems are developed to capitalize on other properties. The stability and frictional properties of aramids at high temperatures have led to brake, clutch, and gasket uses; low coefficient of thermal expansion is being used in printed wiring boards; and exceptional wear resistance is being engineered into injection-molded thermoplastic industrial parts. Melt-impregnated thermoplastic composites, reinforced with aramids, offer unique processing advantages - e.g., in-situ consolidation of filament-wound parts. These can be used for manufacturing thick parts where processing is otherwise very difficult (Reference 2.4.1.2(e)).

TABLE 2.4.1.2(b) *Nominal properties of aramid fiber.*

Tensile Property	Units	Type of Kevlar™ 29	49	149
Modulus	Msi (GPa)	12 (83)	18 (124)	25 (173)
Strength	ksi (GPa)	525 (3.6)	525-600 (3.6-4.1)	500 (3.4)

Aramid fiber is relatively flexible and tough. Thus it can be combined with resins and processed into composites by most of the methods established for glass. Yarns and rovings are used in filament winding, prepreg tape, and in pultrusion. Woven fabric prepreg is the major form used in thermoset composites. Aramid fiber is available in various weights, weave patterns, and constructions; from very thin (0.0002 in., 0.005mm) lightweight (275 gm/m^2) to thick (0.026 in., 0.66 mm) heavy (2.8 gm/m^2) woven roving. Thermoplastic-impregnated tows can be woven into various types of fabrics to form prepregs. These composites demonstrate good property retention under hot and humid conditions (Reference 2.4.1.2(f)). Chopped aramid fiber is available in lengths from 6 mm to 100 mm. The shorter lengths are used to reinforce thermoset, thermoplastic, and elastomeric resins in automotive brake and clutch linings, gaskets, and electrical parts. Needle-punched felts and spun yarns for asbestos replacement applications are made from longer fiber staple. A unique very short fiber (0.08 - 0.16 in., 2 - 4 mm) with many attached fibrils is available (aramid pulp). It can provide efficient reinforcement in asbestos replacement uses. Aramid short fibers can be processed into spun-laced and wet-laid papers. These are useful for surfacing veil, thin-printed wiring boards, and gasket material. Uniform dispersion of aramid short fiber in resin formulations is achieved through special mixing methods and equipment. Inherent fiber toughness necessitates special types of tools for cutting fabrics and machining aramid composites.

2.4.1.3 Glass

Glass in the forms used in commerce has been produced by many cultures since the early Etruscan civilization. Glass as a structural material was introduced early in the seventeenth century and became widely used during the twentieth century as the technology for flat pane was perfected. Glass fibrous usage for reinforcement was pioneered in replacement of metals and used for both commercial and military uses with the advent of formulation control and molten material which is die or bushing pulled into continuous filaments. These events lead to a wide range of aerospace and commercial high performance structural applications still in use today.

2.4.1.3.1 Chemical description

Glass is derived from one of our most abundant natural resources--sand. Other than for, possibly, transport and the melting process, it is not petro-chemical dependent. For purposes of this handbook the typical glass compositions are for electrical/Grade "E" glass, a calcium aluminoborosilica composition with an alkali content of less than 2%, chemical resistant "C" glass composed of soda-lime-borsilicates and high strength S-2 glass which is a low-alkali magnesi-alumina-silicate composition (See Table 2.4.1.3.1). Surface treatments (binders/sizing) can be applied directly to the filaments during the pulling step. Organic binders, such as starch oil, are applied to provide optimum weaving and strand protection during weaving of fabrics or "greige goods". These type binders are then washed and heat cleaned off the fabrics for finishing or sizing at the weaver with coupling agents to improve compatibility with resins. (See

Figure 2.4.1.3.1) The exception to this process for fabrics is when they are heat treated or "caramelized", which converts the starch to carbon (0.2 - 0.5%). Glass roving products (untwisted) type yarns are most often directly finished with the final coupling agents during the filament manufacturing step. Therefore, the products will be identified with the glass manufacturer's product codes and the desizing step is not necessary as common with fabric "greige goods" forms. Heat cleaned products are also available where the product is essentially pure glass. These products, which are subject to damage, are commonly utilized for silicone laminates. Another finish designation is applicable to the heat cleaned product when it is followed with a demineralized water wash (neutral pH). More common for structural applications are the coupling agents which are applied for use with standard organic polymers. During the 1940's Volan[1] finishes were introduced. Since then, many variations/improvements identified with various company designations have appeared. Perhaps the most recognized is Volan A. This finish provides good wet and dry strength properties in use with polyester, epoxy, and phenolic resins. Prior to the application of this finish the clean(ed) glass is saturated with methacrylate chromic chloride so that the chrome content of the finish is between 0.03% and 0.06%. This addition enhances wet-out of the resin during cure. Perhaps more typically called out for use, but not limited to, with epoxy are the silane finishes. Most all are formulated to enhance laminate wet-out. Some also produce high laminate clarity or good composite properties in aqueous environments. Others improve high-pressure laminating, or resist adverse environment or chemical exposures. Although other finishes are used in combination with matrix materials other than epoxy, finishes may have proprietary formulations or varied designations relative to the particular glass manufacturer or weaver, it is believed the compositions are readily available to the resin compounders (prepreggers) to determine compatibility and end use purposes. Note that, non-compatible finishes are purposely applied for ornament applications.

2.4.1.3.2 Physical forms available

Due to the high quantity of commercial applications for glass products, there are many product forms available. For purposes of this publication glass forms will be limited to continuous filament product forms. These forms fall into four major categories. They are continuous rovings, yarn for fabrics or braiding, mats, and chopped strand. (See Figure 2.4.1.3.2 and ASTM Specification D 579, Reference 2.4.1.3.2(a) for information on glass fabrics. Further discussion of fabrics may be found in Section 2.5.1 on fabrics and preforms.) They are available with a variety of physical surface treatments and finishes. Most structural applications utilize fabric, roving, or rovings converted to unidirectional tapes. Perhaps the most versatile fiber type to produce glass product forms is "E" glass. "E" glass is identified as such for electrical applications. This type or grade of glass has eight or more standardized filament diameters available. These range from 1.4 to 5.1 mils (3.5 to 13 micrometers). (See Table I, ASTM Specification D 578, Reference 2.4.1.3.2(b).) This facilitates very thin product forms. The "S" glasses are identified as such to signify high strength. The S-2 type glasses are available with but one filament diameter. This does not limit the availability of basic structural fabric styles for S-2 glass however. Although there are more "E" roving products, as to yields, available, this has not noticeably restricted the use of S-2 type roving products or roving for unidirectional tape. S-2 type rovings are available in yields of 250, 750, and 1250 yards per lb (500, 1500, and 2500 m/kg). Although woven rovings may be considered a fabric product form it should be noted for its importance for military applications. Also, there are glass product forms which could be considered as complimentary products for advanced structures. These would include milled fibers and chopped strand.

---

[1] E. I. Du Pont de Nemours

TABLE 2.4.1.3.1 *Typical chemical compositions of glass fiber.*

	%(wt)	E-Glass	S-2 Glass (Nominals)	H_R Glass (B)
Silicon Dioxide (SiO_2)		52-56 (A)	65	63.5 - 65.0
Aluminum Oxide (Al_2O_3)		12-16 (A)	25	24.0 - 25.5
Boron Oxide (B_2O_3)		5-10 (A)		
Calcium Oxide (CaO)		16-25 (A)		<0.5
Magnesium Oxide (MgO)		0-5 (A)	10	9.5 - 10.5
Lithium Oxide (Li_2O)				
Potassium Oxide (K_2O)	O.C.	0.0-0.2		
Sodium Oxide (Na_2O)	O.C.	0-2		
Titanium Oxide (TiO_2)	O.C.	0-1.5		
Cerium Oxide (CeO_2)				
Zirconium Oxide (Zr_2O_2)				
Beryllium Oxide (BeO)				
Iron Oxide (Fe_2O_3)	O.C.	0.0-0.8		
Fluorine (F_2)	O.C.	0.0-0.1		
Sulfate (SO_2)				
Alkaline Oxides	PPG	0.5-1.5		
Calcium Fluoride (CAF)	PPG	0.0-0.8		
Finishes/Binders		0.5/3.0		

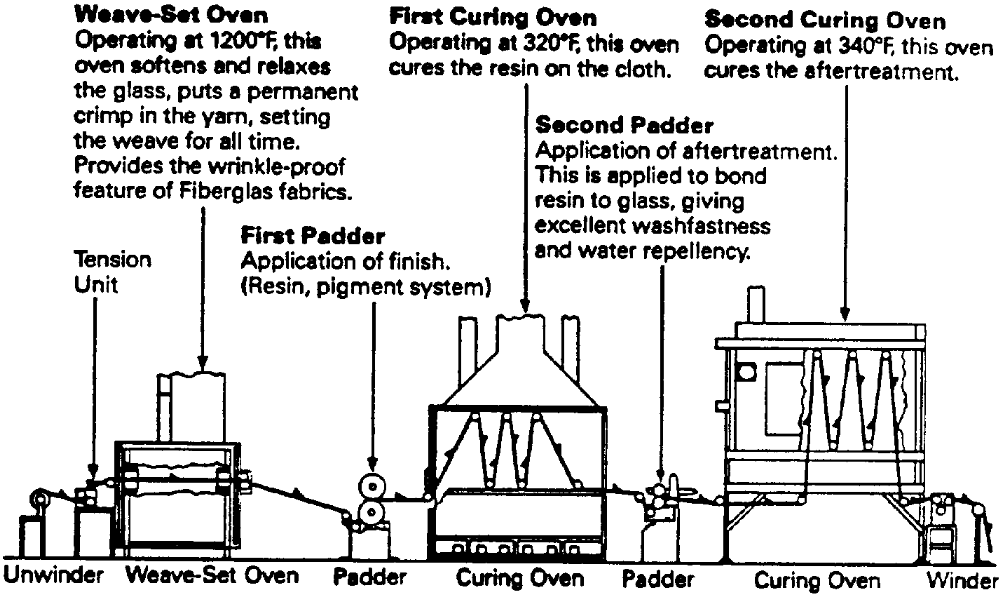


FIGURE 2.4.1.3.1 *Fabric finishing (Reference 2.4.1.3.1(c)).*

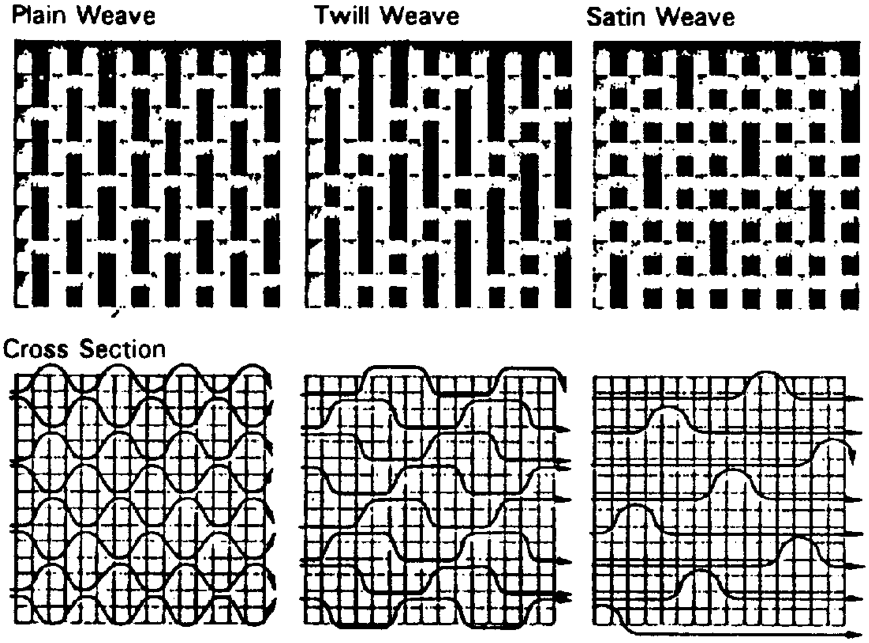


FIGURE 2.4.1.3.2 *Common types of weaves for glass fabrics (Reference 2.4.1.3.1(c)).*

2.4.1.3.3 Advantages and disadvantages

For many years glass composites have had a distinct strength to weight advantage. Although the rapid evolution of carbon and aramid fibers have gained advantages, glass composite products have still prevailed in certain applications. Cost per weight or volume, certain armament applications, chemical or galvanic corrosion resistance, electrical properties, and availability of many product forms remain as examples of advantage. Coefficient of thermal expansion and modulus properties compared to carbon composites may be considered as typical disadvantages. When compared to aramid composites, glass has a disadvantage as to tensile properties but an advantage as to ultimate compression, shear properties, and moisture pick-up.

Commercial uses for glass products are many-fold. These include filtration devices, thermal and electrical insulation, pressure and fluid vessels, and structural products for automotive and recreation vehicles. Many uses are applicable to military and aerospace products as well. A partial listing would include: asbestos replacement, circuitry, optical devices, radomes, helicopter rotor blades, and ballistic applications. Because of the many product forms, structural applications are limitless to fabricate. If there are limitations, compared to other fibers, they may include low thermal and electrical conductivity or perhaps melting temperatures when compared to carbon fibers.

Typical properties for glass fibers and composite materials reinforced with continuous glass fibers are shown in Tables 2.4.1.3.3(a)-(d).

TABLE 2.4.1.3.3(a) *Typical glass fiber electrical properties.*

	E	S-2	H_R
Density			
lb/in^3	0.094	0.089	0.090
g/cm^3	2.59	2.46	2.49
Tensile Strength			
ksi	500	665	665
MPa	34,450	45,818	45,818
Modulus of Elasticity			
Msi	10.5	12.6	12.6
GPa	72.35	86.81	86.81
% Ult. Elongation	4.8	5.4	5.4
Dielectric Constant 73°F (23°C) @ 1 MHZ	6.3-6.7	4.9-5.3	NA

Unburdened costs vary pending product forms and glass types. Typical yield certified "E" glass rovings cost $1.40 per lb., whereas certified S-2 type 750 yield rovings average $6.30 per lb. Lower costing for rovings are experienced with rail car purchases. Typical unburdened fabric costs also vary by weave and fiber type. "E" glass 120 style averages $13.10 per lb., 7781 averages $4.35 per lb., S-2 type 6781 style is $8.40 per lb.

TABLE 2.4.1.3.3(b) *Typical glass fiber thermal properties.*

	E	S-2	S_R
Coeff. Thermal Expan. 10^6			
in/in/F°	2.8	1.3	
m/m/C°	5.1	2.6	
Softening Point °F (°C)	1530 (832)	1810 (988)	1778 (970.)
Annealing Point °F (°C)	1210 (654)	1510 (821)	1490 (810.)

TABLE 2.4.1.3.3(c) *Typical corrosion resistance of glass fibers (Wt. Loss %).*

Fluid	E	S-2	S_R
10% H_2SO_4	42	6.8	NA
10% HCL	43	4.4	NA
10% HNO_3	43	3.8	NA
H_2O (Distilled)	0.7	0.7	NA
10% Na OH	29	66	NA
10% KOH	23	66	NA

Conditions: 200°F (96°C) - one week immersion

TABLE 2.4.1.3.3(d) *Typical cured epoxy/glass mechanical properties.*

E Glass, Woven 7781 Style	Standard Structural	Dual Purpose Structural/Adhesive
Tensile Strength, ksi (MPa)	63 (430)	48 (330)
Tensile Modulus, Msi (GPa)	3.8 (36)	2.8 (19)
Compressive Strength, ksi (MPa)	60. (410)	50. (340)
Compressive Modulus, Msi (GPa)	3.6 (25)	3.2 (22)
Flexural Strength ksi, (MPa)	80. (550)	65 (450)
Flexural Modulus Msi, (GPa)	3.7 (26)	3.3 (23)
Interlaminar Shear ksi, (MPa)	2.6 (18)	3.8 (26)
Sandwich Peel, lb/in width (N/m width)	N.A.	30. (3.4)
Metal-to-Metal Peel, lb/lin. in. (N/lin. m)	N.A.	55 (6.3)
Specific Gravity gm/cm^3 (lb/in^3)	1.8 (0.065)	1.6 (0.058)
Cured Resin Content % Wt.	33	48

Reference:	Fabric	MIL-C-9084, VIII B	
	Resin	MIL-R-9300, Ty I	MIL-A-25463, Ty I, C1 2

2.4.1.3.4 Common manufacture methods and variable

Most often raw products (and/additives) are mixed and are premelted into marbles. This form facilitates sampling for analysis but, more important, presents a raw product form for automated feeding to the individual melt furnaces. Another method is to feed, via hoppers, dried raw products directly to batch cans. Regardless of the raw form, the material is fed into furnaces to become molten at approximately 2800°F (1500°C). The molten mass flows onto plates which contain many bushings with small orifices from which the individual filaments are drawn. In some cases the individual bushings are heat controlled within <1F° (0.6C°). The diameter of the filaments is controlled by the viscosity of the glass melt and the rate of extrusion. Cooling or solidification occurs rapidly as the glass leaves the bushings in filament form under ambient conditions. Cooling is often added by water spray and/or application of the binders. The individual untwisted filaments are gathered and high speed wound on tubes or "cakes". Sometimes finishes are applied after the strands are wound on the tubes then conditioned (dried). For products common to this document the strands are "C" (continuous) filaments--not "S" (staple) filament. To produce rovings the strands are then creeled, unwound and gathered again to form ends or multiple untwisted strands. (See Table 2.4.1.3.4(a).) This process of gathering or combining is again repeated to form rovings of desired yields (yards per pound). For weaving of fabrics and braiding, the strands are twisted to form yarns. (See Table 2.4.1.3.4(b).) Single yarns are composed of single strands twisted by itself. Two (etc.) strand construction is two strands twisted to produce a single yarn. Plied yarns are made from twisting two or more yarns together. Twisting and plying is often referred to as "throwing". A variable in processing "C" filament products is the repeated tensioning required during the numerous product forms fabrication. Tensioning devices are used--such as: disc-type or "whirls", gate-type, tension bars or "S" bars, and compensating rolls in the delivery from the creels. Humidity is another controlled variable in the twisting, plying, braiding, warping, slashing, gulling and weaving areas. These operations are facilitated to maintain a relative humidity of 60 to 70 percent range. During the glass processing operations surface abrasion is a factor which must be monitored. The many devices such as: guide eyes, spacer bars, rollers and such are subject to wear and must be maintained. Wear could also affect tensioning. These contact devices are manufactured from materials including: stainless steel, chromium plating, and ceramics.

Additional information can be found in References 2.4.1.3.4(a) - (c).

TABLE 2.4.1.3.4(a) *Basic strand fiber designations and strand counts (Reference 2.4.1.3.1(c)).*

Filament Diameter Designation		Strand Count (Number)		
		TEX	U.S. Customary	
SI (µm)	U.S. Customary (Letter)	g/km	100 Yd. Cuts/Lb.	Yds./Lb.
5	D	11	450	45,000
7	E	22	225	22,500
9	G	733	150	15,000
10	H	45	110	11,000
13	K	66	75	7,500

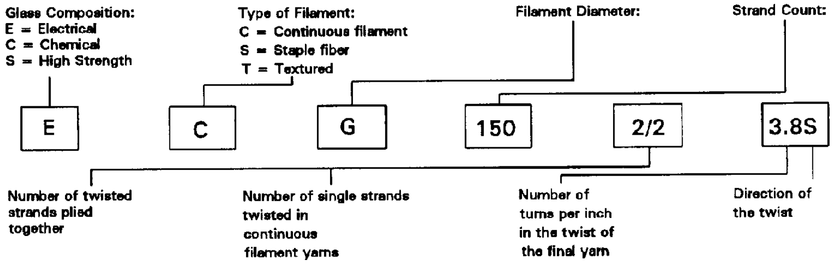
2.4.1.4 Boron

Elemental boron fiber is formed as a deposition reaction on a hot tungsten wire which is continuously drawn through a reactor containing BCl_3 and H_3. The tungsten wire substrate also reacts to form tungsten boride in the core. The crystalline structure of the deposited boron is considered amorphous due to its small size (20Å). Boron is available as a cylindrical fiber in two nominal diameters, 4- and 5.6-mil (0.10 and 0.14 mm), which have a density of 2.57 and 2.49 g/cm^3 (0.0929 and 0.0900 lb/in^3), respectively. Chemical etching of the fiber surface produces a higher strength, but the process is not used commercially.

Boron fiber is unmatched for its combination of strength, stiffness, and density. The tensile modulus and strength of boron fiber are 60 x 10^6 psi and 0.52 x 10 ^{6} psi (40 GPa and 3600 MPa). Thermal conductivity and thermal expansion are both low, with a coefficient of thermal expansion of 2.5-3.0 x 10^{-6}/F° (4.5-5.4 x 10^{-6}/C°). Typical end-use properties are shown in Table 2.4.1.4. Currently, the cost of boron fiber is approximately an order of magnitude higher than standard carbon fiber.

TABLE 2.4.1.3.4(b) *Typical yarn nomenclature (Reference 2.4.1.3.1(c)).*

Filament Designation	Nominal Filament Diameter, inches (mm)	Strand Count (x100 = yds/lb) (g/km)	Approximate Number of Filaments
D	0.00021 (0.053)	1800 (2.8)	51
D	0.00021 (0.053)	900 (5.5)	102
B	0.00015 (0.0038)	450 (11)	408
D	0.00021 (0.053)	450 (11)	204
D	0.00021 (0.053)	225 (22)	408
E	0.00029 (0.0074)	225 (22)	204
B	0.00015 (0.0038)	150 (33)	1224
C	0.00019 (0.0048)	150 (33)	750
DE	0.00025 (0.0064)	150 (33)	408
G	0.00036(0.0091)	150 (33)	204
H	0.00043 (0.011)	110 (45)	204
C	0.00019 (0.0048)	75 (66)	1500
DE	0.00025 (0.0064)	75 (66)	816
G	0.00036 (0.0091)	75 (66)	408
K	0.00053 (0.014)	75 (66)	204
H	0.00043 (0.011)	55 (90)	408
DE	0.00025 (0.0064)	37 (130)	1632
G	0.00036 (0.0091)	37 (130)	816
K	0.00053 (0.014)	37 (130)	408
H	0.00043 (0.011)	25 (200)	816
K	0.00053 (0.014)	18 (275)	816
G	0.00036 (0.0091)	15 (330)	2052



Available almost exclusively in filament or epoxy matrix prepreg form, boron fiber has been used for aerospace applications requiring high strength and/or stiffness, and for selective reinforcement in sporting goods. The most notable use of this fiber is the stabilizer sections of the F-14 and F-15 military aircraft, dorsal longeron of the B-1B bomber, and the repair of metallic airframe structures. High modulus (HM) or high strength (HS) carbon/epoxy composites can match either the tensile modulus or strength of boron composites at a more economical price, but boron/epoxy composites offer twice the composite strength. Additional information can be found in References 2.4.1.4(a) through (g).

TABLE 2.4.1.4 *Typical end-use properties of a unidirectional boron/epoxy laminate (V_f = 0.5).*

	Value, ksi (MPa)
Moduli	
Tensile, longitudinal	30 (207)
Tensile, transverse	2.7 (19)
Strength	
Tensile, longitudinal	192 (1323)
Tensile, transverse	10.4 (72)
Compressive, longitudinal	353 (2432)

2.4.1.5 Alumina

Continuous polycrystalline alumina fiber is ideally suited for the reinforcement of a variety of materials including plastics, metals, and ceramics. Alumina is prepared in the form of continuous yarn containing a nominal 200 filaments. It is supplied in bobbins containing continuous filament yarn, and alumina/aluminum and alumina/magnesium plates. Alumina staple is also available for short fiber reinforcement.

Fibers that are more than 99% purity α alumina have excellent chemical resistance, and have higher modulus and temperature capabilities than ceramic fibers containing silica. The high modulus of 55 Msi (380 GPa) is comparable to that of boron and carbon. The average filament tensile strength is 200 ksi (1.4 GPa) minimum. Since alumina is a good insulator, it can be used in applications where conducting fibers cannot. Nominal properties of alumina are listed in Table 2.4.1.5(a). Cost projections for alumina are competitive with carbon.

Alumina, in continuous form, offers many advantages for composite fabrication including ease of handling, the ability to align fibers in desired directions, and filament winding capability. The fact that alumina is an electrical insulator combined with its high modulus and compressive strength make it of interest for polymer matrix composite applications. For example, alumina/epoxy and aramid/epoxy hybrid composites reinforced with alumina and aramid fibers have been fabricated and are of potential interest for radar transparent structures, circuit boards, and antenna supports. Typical properties of unidirectional composites are listed in Table 2.4.1.5(b).

TABLE 2.4.1.5(a) *Nominal properties of alumina.*

Composition	> 99% α-Al_2O_3	Filaments/yarn	200, nominal
Melting Point	3713°F (2045°C)	Tensile Modulus	55 Msi (385 GPa)
Filament Diameter	$0.8x10^{-3}$ in. (20μm)	Tensile Strength	200 ksi (1.4 GPa) minimum
Length/Weight	(~4.7 m/gm)	Density	0.14 lb/in^3 (3.9 gm/cc)

TABLE 2.4.1.5(b) *Nominal properties of alumina composite (V_f ~ 50-55%).*

Moduli		
Tensile, axial		30-32 Msi (210-220 GPa)
Tensile, transverse		20-22 Msi (140-150 GPa)
Shear		7 Msi (50 GPa)
Strength		
Tensile, axial		80 ksi (600 MPa)
Tensile, transverse		26-30 ksi (130-210 MPa)
Shear		12-17 ksi (85-120 GPa)
Fatigue - Axial Endurance Limit		10^7 cycles at 75% of static ultimate (tension-tension, R=0.1, and rotating-bending)
Average Thermal Expansion		68-750° (20-400°C)
Axial		4.0 μin/in/F° (7.2 μm/m/C°)
Transverse		11 μin/in/F° (20 μm/m/C°)
Thermal Conductivity	68-750° (20-400°C)	22-29 Btu/hr-ft-°F (38-50 J/m-s-°C)
Specific Heat	68-750° (20-400°C)	0.19-0.12 Btu/lbm-°F (0.8-0.5 J/gm-°C)
Density		0.12 lbm/in^3 (3.3 gm/cm^3)

2.4.1.6 Silicon carbide

Various super-refractory fibers were first produced in the early 1950's based upon work by the Arthur D. Little Co. by various production methods. The primary of these based upon:

1. Evaporation for polycrystalline fiber process.

2. HITCO continuous process for polycrystalline fibers.

3. Vapor deposition of aluminum oxide single crystals (Reference 2.4.1.6(a)).

The most recent advances in the CVD type process in use by AVCO consist of substrate wires drawn through glass reaction tubes at high temperature.

Silicon carbide fibers are produced with a nominal 0.0055 in. (140 µm) filament diameter and are characteristically found to have high strength, modulus and density. Fiber forms are oriented toward the strengthening of aluminum or titanium alloys for both longitudinal and transverse properties. Additional forms are also produced as polycrystalline fiber whiskers of varying length and diameters (Reference 2.4.1.6(b)).

Several systems for describing the material morphology exist, the alpha and beta forms designated by Thibault and Lindquist being the most common (Reference 2.4.1.6(c)).

Practically all silicon carbide monofilament fibers are currently produced for metal composite reinforcement. Alloys employing aluminum, titanium, and molybdenum have been produced (Reference 2.4.1.6(b)).

General processing for epoxy, bisimide, and polyimide resin can be either via a solvated or solventless film impregnation process, with cure cycles equivalent to those provided for carbon or glass reinforced products. Organic matrix silicon carbide impregnated products may be press, autoclave, or vacuum bag oven cured. Lay-up on tooling proceeds as with carbon or glass composite products with all bleeding, damming, and venting as required for part fabrication. General temperature and pressure ranges for the cure of the selected matrix resins used in silicon carbide products will not adversely affect the fiber morphology.

Silicon carbide ceramic composites engineered to provide high service temperatures (in excess of 2640°F or 1450°C) are unique in several thermal properties. The overall thermal resistance is determined by the through conductivity, thermal expansion, thermal shock and creep resistance. Thermal conductivities of silicon carbide ceramics have a range in Btu-in/s-ft^2-°F of 0.12 at room temperature to 0.09 at 1470°F (W/m·K of 60 at room temperature to 48 at 800°C). Expansion values range, in percentage of original dimension, from 0.05 at 390°F (200°C) to 1470°F (0.30% at 800°C). The creep resistance of the silicon carbide ceramic will vary as the percentage of intra-granular silicon phase increases. In general, the creep rate is very low when compared to aluminum oxide or zirconium oxide materials.

Mechanical properties of silicon carbide materials are shown in Table 2.4.1.6(a). Fracture toughness as measured by double torsion analysis has reported literature values for K_{Ic} ranging from 0.55 ksi Jm (0.6 MPa $\sqrt{m}$) for monocrystalline SiC/Si to 5.5 ksi Jm (6.0 MPa Jm) for hot pressed SiC ceramics (Reference 2.4.1.6(g)). Corrosion resistance, of consideration in advanced structural material design, has been evaluated with a variety of mineral acids on the basis of corrosive weight loss as shown in Table 2.4.1.6(b).

General cost ranges for the CVD processed fibers are currently in the $100.00 per lb., with the control in crystalline form requiring additional expense (Reference 2.4.1.6(e)).

TABLE 2.4.1.6(a) *Material properties of silicon carbide materials.*

Property	Reported Values (ksi)	Reported Values (MPa)	Reference Information
FLEXURAL STRENGTH	100-1000	700-7000	single crystal, 99+% purity (1)
	10-60	70-400	polycrystalline materials, 78-99% purity, with < 12+% free silicon, sintered (1)
	5-8	30-60	sintered SiC - graphite composites - epoxy, imide, polyimide matrix. (2)
COMPRESSIVE STRENGTH	500-1000	3000-7000	single crystal, 99+% purity (1)
	10-25	70-170	polycrystalline materials, 78-99% purity, with < 12+% free silicon, sintered.(2)
	14-60	97-400	Sintered SiC - graphite composites - epoxy, imide, polyimide matrix. (2)
TENSILE STRENGTH	~20	~140	single crystal, 99+% purity (1)
	5-20	30-140	polycrystalline materials, 78-99% purity, with < 12+% free silicon, sintered.(2)
	2.5-25	17-170	sintered SiC - graphite composites - epoxy, imide, polyimide matrix. (2)
MODULUS OF ELASTICITY	~9.5	~66	single crystal, 99+% purity (1)
	~7.0	~48	Polycrystalline materials, 78-99% purity, with < 12+% free silicon, sintered.(2)

(1) Reference 2.4.1.6(b)
(2) Reference 2.4.1.6(d)

TABLE 2.4.1.6(b) *Corrosive weight loss at 212°F (100°C) (Reference 2.4.1.6(e)).*

TEST REAGENT	Si/SiC COMPOSITES 12% Si *mg/cm^2·yr*	SiC - NO FREE Si *mg/cm^2·yr*
98% Sulfuric Acid	55	1.8
50% Sodium Hydroxide	complete within days	2.5
53% Hydrofluoric Acid	7.9	< 0.2
70% Nitric Acid	0.5	< 0.2
25% Hydrochloric Acid	0.9	< 0.2

2.4.1.7 Quartz

Quartz fiber is very pure (99.95%) fused silica glass fiber. Typical fiber properties are shown in Table 2.4.1.7(a). Quartz is produced as continuous strands consisting of 120 or 240 individual filaments of 9 micron nominal diameter. These single strands are twisted and plied into heavier yarns. Quartz fibers are generally coated with an organic binder containing a silane coupling agent which is compatible with many resin systems. Strands for rovings are combined into multiple ends without applied twist. These strands are coated with a "direct size" which is compatible with many resins. Woven fabrics may be used as woven or may be "scoured" (washed) to remove the nonfunctional components of the binder and some, but not all, of the silane coupling agent. Following scouring, the fabric may be finished with a variety of silane coupling agent finishes having specific resin compatibility.

Quartz fiber nomenclature is the same as that for E or S glass fibers except that the glass composition is designated by the letter Q as shown in Table 2.4.1.7(b). Commonly used quartz fabrics are listed in Table 2.4.1.7(c). Quartz rovings are continuous reinforcements formed by combining a number of 300 2/0 zero twist strands. End counts of 8, 12, and 20 are available having yields from 750 to 1875 yards per pound (660 to 264 g/km). Quartz fibers are also available in the form of chopped fiber in cut lengths from 1/8 inch to 2 inches (3 to 50 mm).

Quartz fibers with a filament tensile strength of 850 ksi (5,900 MPa) have the highest strength-to-weight ratio, virtually exceeding all other high temperature materials. The quartz fibers can be used at temperatures much higher than "E" glass or "S" glass fiber with service temperatures up to 1920°F (1050°C) possible. Quartz fibers do not melt or vaporize until the temperature exceeds 3000°F (1650°C), providing potential in ablative applications. Additionally, these fibers retain virtually all of the characteristics and properties of solid quartz.

The quartz fibers are chemically stable. They are not affected by halogens or common acids in the liquid or gaseous state with the exception of hydrofluoric and hot phosphoric acids. Quartz fibers should not be used in environments where strong concentrations of alkalies are present.

Quartz fibers, when combined with certain matrix systems, offer potential advantages in stealth application due to their high electrical resistivity properties. Quartz does not form paramagnetic centers, nor does it capture neutrons in high energy applications. These fibers offer a low dielectric constant and loss tangent providing excellent properties as electrical insulators. Typical properties for quartz fibers combined with three different polymer matrix systems are shown in Tables 2.4.1.7(d) - (f). Quartz products are relatively expensive compared to "E" or "S-2" glass products, with prices ranging from $45 to $150 per pound. Additional information can be found in Reference 2.4.1.7

Table 2.4.1.7(a) *Properties of quartz fiber*.

Specific gravity	2.20
Density, lb/in^3	0.0795
g/cm^3	2.20
Tensile strength	
Monofilament, ksi	870
GPa	6.0
Roving, ASTM D2343 Impregnated	
Strand Test -	
Astroquartz II 9779, ksi	530.5
GPa	3.6
Modulus, Msi	10.0
GPa	72.0
Elongation, percent	
$\frac{\text{Monofilament Tensile Strength x 100}}{\text{Modulus}}$	8.7
Thermal	
Coefficient of expansion	
10^{-6} in/in/°F	0.3
10^{-6} cm/cm/°C	0.54
Thermal conductivity	
Cal/sec/cm/°C	0.0033
Btu/hr/ft/°F	0.80
Btu/hr/sq ft/in/°F	9.5
Specific heat	
Joules/Kg/°C	7500
Btu/lb/°F	1.80
Electrical	
Dielectric constant, 10 GHz, 75°F (24°C)	3.78
Loss tangent, 10 GHz, 75°F (24°C)	0.0001

TABLE 2.4.1.7(b) *Quartz continuous strands.*

Strand Number	Number of filaments	Strand Count		Filament Diameter	
		yds/lb	g/km	10^{-5} in.	µm
QCG 300 1/0	119[a]	30,000	6.5	45	1.1
QCG 300 2/0	240[b]	15,000	33	35	0.89
QCG 300 1/2	240[a]	15,000	33	35	0.89
QCG 300 2/2	480[a]	7,500	66	35	0.89
QCG 300 2/8	1920[a]	1,875	264	35	0.89

[a] Used for fabric yarns.
[b] Used for roving and fabric yarns.

TABLE 2.4.1.7(c) *Construction of woven fabrics for aerospace applications.*

Style	Count	Warp Fill	Fill Yarn	Weave	Weight Oz/Sq.Yd.
503	50x50	300 1/2	300 1/2	plain	3.5
507	27x25	300 1/2	300 1/2	plain	2.0
525	50x 50	300 1/0	300 1/0	plain	2.0
527	42x32	300 2/2	300 2/2	plain	5.6
531	68x65	300 1/2	300 1/2	8HS	5.1
557	57x31	300 2/2	300 1/0	crowfoot	5.0
570	38x24	300 2/8	300 2/8	5HS	19.3
572	17x16	300 2/8	300 2/8	plain	9.9
581	57x54	300 2/2	300 2/2	8HS	8.4
593	49x46	300 2/2	300 2/2	5HS	7.5

TABLE 2.4.1.7(d) *Typical properties for quartz/epoxy.*

PROPERTY	Room Temperature U.S.	Room Temperature SI	1/2 hr at 350°F (180°C) U.S.	1/2 hr at 350°F (180°C) SI
Tensile Strength (ksi, MPa)	74.9 - 104	516 - 717	65.4 - 92.2	451 - 636
Tensile Modulus (Msi, GPa)	3.14 - 4.09	21.7 - 28.2	2.83 - 3.67	19.5 - 25.3
Flexural Strength (ksi, MPa)	95.5 - 98.9	658 - 682	53.9 - 75.9	372 - 523
Flexural Modulus (Msi, GPa)	3.27- 3.46	22.5 - 23.8	2.78 - 3.08	19.2 - 21.2
Compressive Strength (ksi, MPa)	66.4 - 72.4	458 - 499	42.6 - 49.9	294 - 344
Compressive Modulus (Msi, GPa)	3.43 - 3.75	23.6 - 25.9	3.10 - 3.40	21.4 - 23.4
Laminate Resin Content (wt%)	33.5 - 32.0			
Specific Gravity (g/cm^3)	1.73 - 1.77			

TABLE 2.4.1.7(e) *Typical properties for quartz/toughened epoxy.*

PROPERTY	Room Temperature U.S.	Room Temperature SI	180°F (82°C) U.S.	180°F (82°C) SI
Flexural Strength (ksi,MPa)	129.0	889	111.7	770
Flexural Modulus (Msi,GPa)	4.0	27.6	3.9	26.9
Compressive Strength (ksi,MPa)	88.2	608	77.5	534
Compressive Strength, Wet (ksi,MPa)	76.6	528	70.8	488
Compressive Modulus (Msi,GPa)	4.2	29.0	3.8	26.2
Compressive Modulus, Wet (Msi,GPa)	3.7	25.5	4.0	27.6
Short Beam Strength (ksi,MPa)	13.2	91.0	11.8	81.4
Short Beam Strength, Wet (ksi,MPa)	9.2	63.4	9.3	64.1
Resin Content (wt%)	32.0			
Ply Thickness (in,mm)	0.009	0.23		

TABLE 2.4.1.7(f) *Typical properties for quartz/polyimide.*

PROPERTY	Room Temperature U.S.	Room Temperature SI	1/2 Hour at 350°F (177°C) U.S.	1/2 Hour at 350°F (177°C) SI
Tensile Strength (ksi,MPa)	79.1 - 105	545 - 724		
Tensile Modulus (Msi,GPa)	3.9	27		
Flexural Strength (ksi,MPa)	93.7 - 102	646 - 703	62.4 - 68.3	430 - 471
Flexural Modulus (Msi,GPa)	3.2	22	2.6 - 2.8	18 - 19
Compressive Strength (ksi,MPa)	67.0 - 67.4	462 - 465	38.6 - 45.2	266 - 312
Compressive Modulus (Msi,GPa)	3.5 - 3.7	24 - 26	2.8	19
Laminate Resin Content (wt%)	36.2 - 36.2			

2.4.1.8 Ultrahigh molecular weight polyethylene.

Material Description

Ultrahigh molecular weight polyethylene fiber (UHMWPE) is the generic name for a high performance fiber which is more widely known today by the trade name Spectra®, assigned by the major marketer of UHMWPE fiber, Allied Signal Inc. Non-oriented UHMWPE was first synthesized in the mid 1950s. A number of academic and commercial institutions in the United States and Europe worked to develop oriented UHMWPE fiber. Allied developed Spectra® fiber in the 1970s and it was first offered as a commercial product in 1985.

The generally accepted definition of what constitutes "ultrahigh molecular weight" is a molecular weight greater than 3,000,000. The properties of polyethylene depend strongly on the molecular weight and the degree of branching. UHMWPE fiber is a linear polymer and its molecular weight typically varies between 3,000,000 and 6,000,000. This fiber is highly oriented axially and the chains form a highly crystalline structure, between 95-99%, but the crystallinity is not in the form of folded chains as is typically found in thermoplastics. Instead, the chains are fully extended (Figure 2.4.1.8(a)).

The fiber is formed by a gel-spinning process where the polymer is dissolved in order to disentangle the polymer chains. From solution the fibers are then drawn and the molecules become axially aligned to an extremely high degree. The resulting fiber diameter is rather large at 27 microns (for Spectra® 1000) compared to other high performance fibers (typical aramid fiber diameter is 12 microns; S-2 glass, 7; carbon fibers, 7).

The cost of UHMWPE relative to other high performance fibers is competitive, ranging from $16/lb. for lower performance, high denier Spectra® 900 products to as much as $80/lb. for high performance, low denier forms of Spectra® 1000.

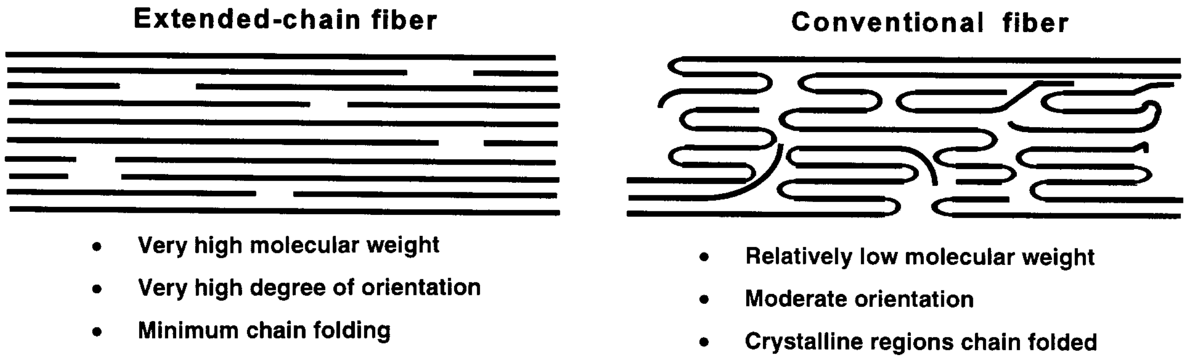


FIGURE 2.4.1.8(a) *Schematic representation of a UHMWPE fiber compared to ordinary polyethylene fiber (Reference 2.4.1.8(a)).*

Advantages and Limitations

The main drawback to UHMWPE is poor temperature performance. The fiber melting point is 300°F (149°C) and the typical maximum service temperature is 230°F (110°C). Temperature is always a consideration when combining UHMWPE with a thermosetting matrix to form a composite by curing, post curing and/or molding. The upper processing limit of UHMWPE (250°F, 121°C) coincides with the recommended cure temperature of many commercially popular structural resin system. 350°F (177°C) cures are not possible. For all practical purposes UHMWPE can not be used in a high performance thermoplastic matrix due to the required high processing temperatures.

Creep is also a problem, even at room temperature (Figure 2.4.1.8(b)). For this reason design for long-term constant-load-bearing applications should be carefully considered. Load bearing at elevated temperature will lead to serious creep problems.

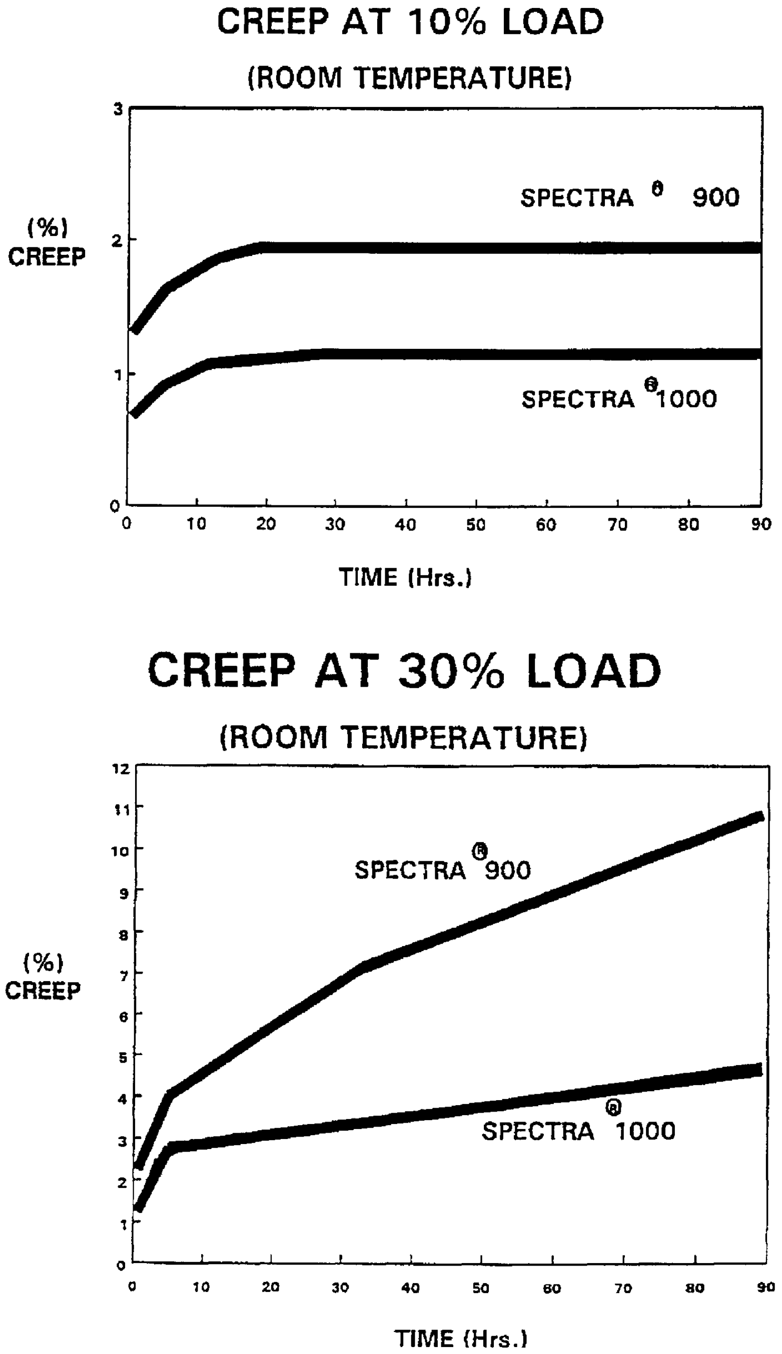
When used in a composite UHMWPE bonds poorly to most matrix resins. This is due to its chemical inertness and poor wettability (low surface energy). To improve bonding, gas plasma treatments are often used to modify the fiber surface to make it more compatible with the various resins.

Although its temperature and creep limitations are severe, UHMWPE still has many applications. Outstanding impact strength, even at cold temperatures, combined with a 33% weight reduction over aramid make it an appealing choice in applications where temperature is not an issue.

Ballistic protection is one of its major uses. The fiber is commercially successful in ballistic applications, particularly lightweight body armor and riot shield applications for military and law enforcement personnel. The U.S. Army is studying it as an alternative to aramid in the standard issue soldier helmet. Two other ballistic applications are ground vehicle mine blast shields and ultra-lightweight armor for aircraft. For example, the AC-130H Spectre Gunship, flown by the Air Force Special Operations Command, uses UHMWPE armor as its attack mode calls for low altitude (500 feet (150m)) flight.

UHMWPE is also used in radomes, which take advantage of a low dielectric constant (2.2) and loss tangent (0.0002). Other applications include cut-resistant fabrics, heavy lift cargo cables, snow and water skis and other sporting goods, and high-wear applications.

Mechanical properties of composites reinforced with UHMWPE fiber are generally quite good. Tensile strength and modulus, elongation, and toughness compare favorably with other fiber types, especially when normalized on a weight basis (although compression and shear properties do not compare as well).


CREEP AT 10% LOAD
(ROOM TEMPERATURE)

CREEP AT 30% LOAD
(ROOM TEMPERATURE)

FIGURE 2.4.1.8(b) *Room temperature creep properties of Spectra® fiber at 10% and 30% loading (Reference 2.4.1.8(a)).*

UHMWPE is a hydrophobic material and is extremely resistant to moisture effects. In fact, with the exception of its poor high temperature performance, UHMWPE stands up well to the environment, including prolonged exposure to sunlight. It has superior solvent resistance (chemical inertness) even to strong acids and bases. Its stability is outstanding in common solvents such as water, gasoline, hydraulic oil and cleaning solvents. The fiber also exhibits good abrasion resistance and self-lubricating properties.

One feature unique to UHMWPE among high performance fibers is that it floats on water. Of the four common high performance fibers, UHMWPE is by far the lightest with a density of 0.97 g/cm^3 (0.035 lb/in^3) (the density of aramid is 1.4 g/cm^3 (0.051 lb/in^3); carbon is 1.8 g/cm^3 (0.065 ls/in ^{3}); S-2 glass is 2.5 g/cm ^{3} (0.091 lb/in^3)). UHMWPE is most often compared to aramid fibers. The strength and modulus of this fiber are about the same as aramid, but due to a lower density its specific strength and modulus are higher, reaching nearly as high as today's high modulus carbon fibers on a weight basis.

Machining UHMWPE is difficult without special equipment. Generally, the machining requirements of UHMWPE are the same as those of aramid, except that, due to its low melting temperature, UHMWPE can also be cut with a hot knife. Table 2.4.1.8 lists some key properties of two grades of Spectra® fiber. Additional information can be found in References 2.4.1.8(b) - (e).

TABLE 2.4.1.8 *Properties of Spectra® 900 and Spectra® 1000 Fibers (Reference 2.4.1.8(a)).*

Property	Spectra® 900	Spectra® 1000
Filament Diameter, microns(mils)	38(1.5)	27(1.1)
Density, g/cm^3(lb/in^3)	0.97(0.035)	0.97(0.035)
Tensile Strength, ksi(MPa)	375(2.58)	435(3.00)
Tensile Modulus, Msi(MPa)	17.4(120)	24.8(171)
Spec. Tensile Strength, M-in(M-m)	10.7(0.272)	12.4(0.315)
Spec. Tensile Modulus, M-in(M-m)	486(12.3)	714(18.1)
Elongation, %	3.5	2.7
Dielectric Constant	2.2	2.2
Loss Tangent	0.0002	0.0002

2.4.2 Resins

2.4.2.1 Overview

Resin is a generic term used to designate the polymer, polymer precursor material, and/or mixture or formulation thereof with various additives or chemically reactive components. The resin, its chemical composition and physical properties, fundamentally affect the processing, fabrication and ultimate properties of composite materials. Variations in the composition, physical state, or morphology of a resin and the presence of impurities or contaminants in a resin may affect handleability and processability, lamina/laminate properties, and composite material performance and long-term durability. This section describes resin materials used in polymer matrix composites and adhesives, and considers possible sources and consequences of variations in resin chemistry and composition, as well as the effects of impurities and contaminants, on resin processing characteristics and on resin and composite properties.

2.4.2.2 Epoxy

The term epoxy is a general description of a family of polymers which are based on molecules that contain epoxide groups. An epoxide group is an oxirane structure, a three-member ring with one oxygen and two carbon atoms. Epoxies are polymerizable thermosetting resins containing one or more epoxide groups curable by reaction with amines, acids, amides, alcohols, phenols, acid anhydrides, or mercaptans. The polymers are available in a variety of viscosities from liquid to solid.

Epoxies are used widely in resins for prepregs and structural adhesives. The advantages of epoxies are high strength and modulus, low levels of volatiles, excellent adhesion, low shrinkage, good chemical resistance, and ease of processing. Their major disadvantages are brittleness and the reduction of properties in the presence of moisture. The processing or curing of epoxies is slower than polyester resins. The cost of the resin is also higher than the polyesters. Processing techniques include autoclave molding, filament winding, press molding, vacuum bag molding, resin transfer molding, and pultrusion. Curing temperatures vary from room temperature to approximately 350°F (180°C). The most common cure temperatures range between 250° and 350°F (120° and 180°C). The use temperatures of the cured structure will also vary with the cure temperature. Higher temperature cures generally yield greater temperature resistance. Cure pressures are generally considered as low pressure molding from vacuum to approximately 100 psi (700 kPA).

2.4.2.3 Polyester (thermosetting)

The term thermosetting polyester resin is a general term used for orthophthalic polyester resin or isophthalic polyester resin. Polyester resins are relatively inexpensive and fast processing resins used generally for low-cost applications. In combination with certain fillers, they can exhibit resistance to breakdown under electrical arc and tracking conditions. Isophthalic polyester resins exhibit higher thermal stability, dimensional stability, and creep resistance. In general, for a fiber-reinforced resin system, the advantage of a polyester is its low cost and its ability to be processed quickly.

Fiber-reinforced polyesters can be processed by many methods. Common processing methods include matched metal molding, wet lay-up, press (vacuum bag) molding, injection molding, filament winding, pultrusion, and autoclaving. Polyesters can be formulated to cure more rapidly than do phenolics during the thermoset molding process. While phenolic processing, for example, is dependent on a time/temperature relationship, polyester processing is primarily dependent on temperature. Depending on the formulation, polyesters can be processed from room temperature to 350°F (180°C). If the proper temperature is applied, a quick cure will occur. Without sufficient heat, the resin/catalyst system will remain plasticized. Compared to epoxies, polyesters process more easily and are much tougher, whereas phenolics are more difficult to process and brittle, but have higher service temperatures.

2.4.2.4 Phenolic

Phenol-formaldehyde resins and their direct precursors were first produced commercially in the early 1900's for use in the commercial market. Ureaformaldehyde and melamine-formaldehyde appeared in the 1920 - 1930's as a less expensive alternative for lower temperature use. Phenolics, in general, cure by a condensation route with the off-gassing of water. The resulting matrix is characterized by both chemical and thermal resistance as well as hardness, and low smoke and toxic degradation products.

The phenolic polymers, often called either phenolic resole or novolacs resins, are condensation polymers based upon either a reaction of excess formaldehyde with a base catalyst and phenol (resole), or a reaction of excess phenol with an acidic catalyst and formaldehyde (novolac). The basic difference between resoles and novolacs consist of no methylol groups in the novolacs and the resulting need for an extension agent of paraformaldehyde, hexamethylenetetraamine, or additional formaldehyde as a curative. These resins have higher molecular weights and viscosities than either parent material. Consequently, they are optimal for processing parts of unusual conformations and complex curvature. The resins allow either press or autoclave cure and allow relatively high temperature free-standing postcures.

2.4.2.4.1 Resoles

The reaction of phenol and excess formaldehyde in the presence of base is characterized by low-molecular-weight prepolymers that are soluble in base and contain a large degree of methylol groups ($-CH_2OH$). These prepolymers are processed to a workable viscosity (resites) and then cured to an intractable solid of high crosslink density. Water is lost as a volatile (as much as 10-12% of the resin by weight).

2.4.2.4.2 Novolacs

The second type of phenolic consists of excess phenol reacted in the presence of an acid catalyst with formaldehyde. These prepolymer resins are complex mixtures of low molecular weight materials slightly soluble in acids and exhibiting random methylene ($-CH_2$) at the ortho-, para-, and ortho-para-positions on the aromatic ring. Unless a large excess of phenol is present, the material will form an infusible resin. The excess phenol used to moderate the processing viscosity can be varied as the application requires. Both water and formaldehyde are volatile products.

2.4.2.5 Bismaleimide

Bismaleimides are a class of thermosetting resins only recently available commercially in prepreg tapes, fabrics, rovings, and sheet molding compound (SMC). Bismaleimide resins, as the term implies, are the maleimide formed from the reaction of a diamine and maleic anhydride. Typically the diamine is aromatic, with methylenedianiline (MDA), the most common by far.

Bismaleimides form useful polymers by homopolymerization or by polymerization with diamines, epoxies, or unsaturated compounds, singular or in mixtures. A wide range of materials like allyl-, vinyl-, acrylate-, epoxy-, and polyester-, and phenolic-type reactive diluents and resins can be used to tailor the properties of the bismaleimide system. However, attention to the specific components is required for useful polymers.

The physical form of the bismaleimide resin depends on the requirement of the final application. The form can vary from a solid to a pourable liquid at room temperature. For aerospace prepregs, sticky resins are required resulting in proprietary specific formulations.

The advantages of BMI resins are best discussed in the relation to epoxy resins. Emerging data suggests that BMI's are versatile resins with many applications in the electronic and aerospace industries. Their primary advantage over epoxy resins is their high glass transition temperature, in the 500-600°F range (260-320°C). Glass transition temperatures for high temperature epoxies are generally less than 500°F (260°C). The second advantage of BMI resins is high elongation with the corresponding high service temperature capabilities. While the high temperature epoxies have approximately one percent elongation when cured with diaminodiphenylsulfone (DDS), BMI's can have two-three percent elongation. Thus, bismaleimide resins deliver higher temperature capability and higher toughness providing excellent performance at ambient and elevated temperatures.

The processing of bismaleimide resins are essentially like that of epoxy resins. BMI's are suitable for standard autoclave processing, injection molding, resin transfer molding, and SMC, among others. The processing time of BMI's are similar to epoxies, except that for the additional higher service temperature, a free-standing post-cure is required. The only limitation is that room temperature curing BMI's have not yet been developed.

The cost of current BMI's is generally higher than the high temperature epoxies. The main disadvantage of bismaleimide resins is their recent commercial introduction. This results in few literature sources or authoritative reviews. Additionally, the suppliers are as limited as the types of BMI's. This latter disadvantage is partially offset by the wide variety of suitable co-monomers.

2.4.2.6 Polyimides

The polyimide resin family comprises a diverse number of polymers all of which contain an aromatic heterocyclic ring structure. The bismaleimides discussed in Section 2.4.2.5 are a subset of this family. Other polyimides are synthesized from a variety of cyclic anhydrides or their diacid derivatives through reaction with a diamine. This reaction forms a polyamic acid which then undergoes condensation by the removal of water and/or alcohol.

Polyimide matrix composites excel in high temperature environments where their thermal resistance, oxidative stability, low coefficient of thermal expansion and solvent resistance benefit the design. Their primary uses are circuit boards and hot engine and aerospace structures.

A polyimide may be either a thermoset resin or a thermoplastic. The thermoplastic varieties are discussed in Section 2.4.2.7.2. Thermosetting polyimides characteristically have crosslinkable end-caps and/or a rigid polymer backbone. A few thermoplastic polyimides can become thermoset polymers if a sufficiently high postcure temperature is employed during part processing. Alternately, partially cured thermoset polyimides containing residual plasticizing solvents can exhibit thermoplastic behavior. Thus, it is difficult to state with certainty that a particular polyimide is indeed a thermoset or thermoplastic. Polyimides, therefore, represent a transition between these two polymer classifications.

Polyimide properties, such as toughness and thermal resistance, are influenced by the degree of crosslinking and chain extension. Molecular weight and crosslink density are determined by the specific end cap group and by the stoichiometry of the anhydride:amine mixture which produces the polyamic acid by stepwise chain growth, after which the polyamic acid is recyclized by continued thermal cure to form the final polymer structure. The choice of solvent employed in the resin formulation has a significant impact on crosslinking and chain extension. Solvents such as N-methyl 2-pyrrolidone (NMP), promote chain extension by increasing resin flow, chain mobility and molecular weight prior to formation of a substantial crosslink network. From a practical standpoint, these solvents are beneficial to polymerization, but they are detrimental to part manufacture because of their tendency to cause ply delaminations.

Most polyimide resin monomers are powders. Some bismaleimides are an exception. As a result, solvents are also added to the resin to enable impregnation of unidirectional fiber and woven fabrics. Commonly, a 50:50 by weight mixture is used for fabrics, and a 90:10 by weight high solids mixture is used to produce a film for unidirectional fiber and low areal weight fabric prepregs. Solvents are further used to control prepreg handling qualities, such as tack and drape. Most of the solvents are removed in a drying process during impregnation, but total prepreg volatiles contents typically range between 2 and 8% by weight. This includes all volatiles, including those produced by the condensation cure reactions.

Polyimides require high cure temperatures, usually in excess of 550°F (~90°C). Consequently, normal epoxy composite consumable materials are not usable, and steel tooling becomes a necessity. Polyimide bagging and release films, such as Kapton and Upilex, replace the lower cost nylon bagging and polytetrafluoroethylene (PTFE) release films common to epoxy composite processing. Fiberglass fabrics must be used for bleeder and breather materials instead of polyester mat materials.

2.4.2.7 Thermoplastic materials

2.4.2.7.1 Semi-crystalline

Semi-crystalline thermoplastics are so named because a percentage of their volume consists of a crystalline morphology. The remaining volume has a random molecular orientation termed amorphous, the name given to thermoplastics containing no crystalline structure. The total percentage of volume which can become crystalline depends on the polymer. Low density polyethylene, for example, can be as high as 70% crystalline (Reference 2.4.2.7.1(a)). Semi-crystalline thermoplastics are characterized by the ability of their molecules to form three-dimensionally ordered arrays (Reference 2.4.2.7.1(b)). This is in contrast to amorphous polymers that contain molecules which are unable to pack in an ordered crystalline structure. A partial list of semi-crystalline thermoplastics includes polyethylene, polypropylene, polyamides, polyphenylene sulfide, polyetheretherketone, (polyetherketoneketone) and polyarylketone.

Semi-crystalline thermoplastics can be converted into several physical forms, including films, powders and filaments. Combined with reinforcing fibers, they are available in injection molding compounds, compression-moldable random sheets, unidirectional tapes, towpregs, and woven prepregs. Fibers impregnated include carbon, nickel-coated carbon, aramid, glass, quartz, and others.

Semi-crystalline thermoplastics reinforced with short fibers have been used for over two decades in the injection molding industry. The inherent speed of processing, ability to produce complicated, detailed parts, excellent thermal stability, and corrosion resistance have enabled them to become established in the automotive, electronic, and chemical processing industries (Reference 2.4.2.7.1(c)).

The combination of long and continuous fibers with higher performance semi-crystalline thermoplastics is a recent development, but these composites have already shown several advantages over existing materials. The chemical stability of the materials provides for unlimited shelf life. Pot life problems and the need for cold storage are eliminated. The semi-crystalline materials usually possess better corrosion and solvent resistance than amorphous polymers, exceeding that of thermosets in some cases (Reference 2.4.2.7.1(c)). This corrosion resistance is exploited in chemical processing industry equipment. Another benefit of the crystal structure is retention of properties above the glass transition temperature (T_g) of the material. These materials may be used in applications above their T_g depending on loading requirements. One example is down-hole oil field sucker rod guides (Reference 2.4.2.7.1(d)).

Some semi-crystalline thermoplastics possess properties of inherent flame resistance, superior toughness, good mechanical properties at elevated temperatures and after impact, and low moisture absorption which have led to their use in the aerospace industry in secondary and primary structures (References 2.4.2.7.1(e)-(f)). Inherent flame resistance has made these materials good candidates for aircraft interiors and for ship and submarine applications. The superior toughness makes them viable candidates for aircraft leading edges and doors where impact damage resistance is required (Reference 2.4.2.7.1(g)). Low moisture absorption and low outgassing has stimulated interest in space structures where moisture swelling is a problem (Reference 2.4.2.7.1(h)). Also nickel-coated carbon/thermoplastic systems are finding uses in EMI shielding applications.

The primary disadvantages of semi-crystalline thermoplastic composites are lack of a design data base, 0° compression properties that are lower than those of 350°F (180°C) epoxy systems, and creep resistance (Reference 2.4.2.7.1(c)). The creep resistance of semi-crystalline thermoplastics is superior to that of amorphous thermoplastics. Creep resistance in the fiber direction of a laminate is not expected to be a problem.

Processing speed is the primary advantage of thermoplastic materials. Chemical curing of the material does not take place during processing. Therefore, reduced cycle times compared to thermoset composites are experienced (References 2.4.2.7.1(i) and (j)). However, thermoplastic prepregs are typically boardy and do not exhibit the tack and drape of thermosets. Forms are available that consist of thermoplastic and reinforcing fibers interlaced together, known as commingled which are drapeable. The present costs of high performance engineering thermoplastic materials are slightly higher than equivalent performance epoxies, and tooling costs may be higher. However, final part cost may be reduced, due to the decreased processing time. The ability to postform or reprocess molded parts also offers cost saving advantages.

A wide variety of methods and techniques are available for processing semi-crystalline thermoplastics, including stamp molding, thermoforming, autoclave molding, diaphragm forming, roll forming, filament winding, and pultrusion. Semi-crystalline thermoplastics differ from amorphous ones in that the morphology can change based on the time/temperature history of the material during molding. Therefore, the degree of crystallinity can be controlled by controlling the cooling rate. The material must be processed above its melt temperature, which requires temperatures ranging from 500 to 700°F (260 -

370°C) for the higher performance materials. Thermal expansion differences between the tool and the thermoplastic material should be addressed, due to the high processing temperature. The actual pressure required varies with the process, but can be as high as 5000 psi (34 MPa) for stamp molding and as low as 100 psi (0.7 MPa) for thermoforming. Once formed, semi-crystalline thermoplastics can be joined by a variety of methods, including ultrasonic welding, infrared heating, vibration, hot air and gas, resistance heating, and conventional adhesives.

2.4.2.7.2 Amorphous

The majority of thermoplastic polymers are composed of a random molecular orientation and are termed amorphous. The molecules are unable to align themselves in an ordered manner, since they are non-uniform or composed of units which have large side groups. In contrast, semi-crystalline thermoplastics have molecules that form ordered three-dimensional arrays (Reference 2.4.2.7.1(b)). Some amorphous thermoplastics include polysulfone, polyamide-imide, polyphenylsulfone, polyphenylene sulfide sulfone, polyether sulfone, polystyrene, polyetherimide, and polyarylate.

Amorphous thermoplastics are available in several physical forms, including films, filaments, and powders. Combined with reinforcing fibers, they are also available in injection molding compounds, compressive moldable random sheets, unidirectional tapes, woven prepregs, etc. The fibers used are primarily carbon, aramid, and glass.

Amorphous thermoplastics are used in many applications; the specific use depends on the polymer of interest. Their applications are well established in the medical, communication, transportation, chemical processing, electronic, and aerospace industries. The majority of applications use the unfilled and short fiber form. Some uses for the unfilled polymers include cookware, power tools, business machines, corrosion resistant piping, medical instruments, and aircraft canopies. Uses for short-fiber-reinforced forms include printed circuit boards, transmission parts, under-the-hood automotive applications, electrical connections, and jet engine components (Reference 2.4.2.7.2(a)).

The use of amorphous thermoplastics as matrix materials for continuous fiber reinforced composites is a recent development. The properties of composites have led to their consideration for primary and secondary aircraft structures, including interior components, flooring, fairings, wing skins, and fuselage sections (References 2.4.2.7.2(b) and (c)).

The specific advantages of amorphous thermoplastics depend upon the polymer. Typically, the resins are noted for their processing ease and speed, high temperature capability, good mechanical properties, excellent toughness and impact strength, and chemical stability. The stability results in unlimited shelf life, eliminating the cold storage requirements of thermoset prepregs. Several amorphous thermoplastics also have good electrical properties, low flammability and smoke emission, long term thermal stability, and hydrolytic stability (Reference 2.4.2.7.2(a)).

Amorphous thermoplastics generally have higher temperature capabilities than semi-crystalline thermoplastics. Polymers with glass transition temperatures as high as 500°F (260°C) are available. Also, processing is simplified, because the formation of a crystalline structure is avoided, resulting in less shrinkage due to their lower melt viscosities. Amorphous polymers generally have lower solvent and creep resistances and less property retention above the glass transition temperature than semi-crystalline thermoplastics (Reference 2.4.2.7.1(f)).

The primary advantages of amorphous thermoplastics in continuous fiber reinforced composites are potential low cost process at high production rates, high temperature capability, good mechanical properties before and after impact, and chemical stability. High temperature capability and retention of mechanical properties after impact have made amorphous thermoplastics attractive to the aerospace industry. A service temperature of 350°F and toughness two to three times that of conventional thermoset polymers are typical (Reference 2.4.2.7.1(f)). The most significant advantage of thermoplastics is the speed of processing, resulting in lower costs. Typically, cycle times in production are less than for thermosets since no chemical reaction occurs during the forming process (References 2.4.2.7.1(i) and (j)).

Amorphous thermoplastics share many of the disadvantages of semi-crystalline thermoplastics, such as a lack of an extensive database and reduced 0° compression properties compared to 350°F (180°C) cure thermosets. Solvent resistance, which is good for semi-crystalline thermoplastics, is a concern for most amorphous ones. They can be attacked to varying degrees, depending on the polymers and solvents of interest. The creep resistance of the polymer is a concern, but should be good for composite forms loaded in the fiber direction. The materials do not have tack and drape as thermosets do; however, some amorphous thermoplastics are available in commingled forms, which are drapable.

The costs of amorphous thermoplastics prepreg used for advanced composites are higher than equivalent performance epoxies. Finished part costs may be lower due to the processing advantages discussed above. Reprocessibility of material results in reduced scrap rates, translating into additional cost savings. For example, the same sheet laminate can be thermoformed several times until the desired configuration is achieved. In addition, certain forms can be recycled.

The processes used with continuous reinforced composites include stamp molding, thermoforming, autoclave molding, diaphragm forming, roll forming, filament winding, and pultrusion. The high melting temperatures require process temperatures ranging from 500°F to 700°F (260 to 370°C). Thermal expansion differences between the tool and the thermoplastic material should be addressed due to the high processing temperatures. Forming pressures range from 100 psi (0.7 MPa) for thermoforming to 5000 psi (35 MPa) for stamp molding. Several amorphous thermoplastics that are hygroscopic must be dried before processing. Hot molds are also recommended to increase material flow. The materials can be joined by several methods, including common adhesives, or fusion bonding such as; ultrasonic welding, infrared heating, hot air and gas, and resistance heating. Surface preparation techniques for using adhesives can be different from those for thermosets. Solvent bonding techniques can be used for joining amorphous thermoplastics but not most semi-crystalline thermoplastics.

One important class of amorphous thermoplastic matrices is the condensation cure polyimides. Examples include polyamideimides, such as Torlon, and polyimides having more flexible backbones, such as AvimidR K3B, NR 150B2 and the LaRC polymers developed by NASA. As stated in Section 2.4.2.1.6, polyimides represent a transition between thermoset and thermoplastic polymers. Thus, these thermoplastics also have many characteristics typical of epoxy and phenolic thermoset polymers (e.g., excellent solvent resistance and high maximum operating temperature limits).

Due to negligible crosslink density, these polymers impart some toughness to composite laminates and permit limited flow during processing, although this flow is more like the high creep rates exhibited by superplastic metals. Unlike other thermoplastics, these polymers do not produce liquid flows, even under high consolidation pressures. Typical processing conditions for the condensation cure thermoplastics are 550°F (290°C) and greater temperatures with consolidation pressures starting at 200 psi (1.4 MPa).

Many of these thermoplastic polymers have been developed with the intent to rapidly stamp or compression mold structural composites parts at low cost. However, this potential has yet to be realized because of low production volumes, high capital equipment and tooling costs as well as excessive fiber distortion in the formed part. The most successful structural applications of these polymers have utilized autoclave processing to reduce tooling costs and fiber distortion. Other polymers in this class have been developed for use in circuit boards because of their low dielectric constant, low moisture absorption and low coefficient of thermal expansion. In these applications, compression molding had been found to be advantageous and cost effective.

Compared to other thermoplastic polymers, the condensation cure thermoplastics have not found a wide variety of applications. Their processability is very similar to the thermosetting polyimides, and this has been a limiting factor. Volatiles are produced by the condensation reaction, and they cause laminate porosity unless consolidation pressures are high enough to suppress void nucleation and growth. Costly high temperature tooling and consumable materials (e.g., vacuum bags and release films) are also required for part processing. While the toughness and processability of many of these condensation cured thermoplastic polyimides are slightly better than those of competing thermosetting polyimides, their maximum operation temperature limit is somewhat lower. For the present, these thermoplastic polymers are limited to special niche markets which take advantage of their unique performance capabilities.

2.4.2.8 Specialty and emerging resin systems

2.4.2.8.1 Silicone

The silicones are a synthetic resin, composed primarily of organosilicon. The term silicone resin is a general term used for high temperature poly methyl siloxane. Silicone resins are available from a low viscosity liquid to a solid friable resin.

The silicone resin is used where high temperature stability, weatherability, good electrical properties and moisture resistance are required. These excellent properties have allowed the silicone resin to be used in laminates, varnishes, mineral filled molding compounds, and long glass fiber molding compounds. The silicone resin has been used as an impregnant for mica paper, flexible glass tape, glass cloth, and mica products. The molding compounds may be processed by conventional methods: injection, compression, and transfer molding. The cure temperature varies from 250°F to 450°F (120°C to 230°C). The cure time varies from 30 minutes to 24 hours, depending upon cure temperature, wall thickness of molded part, and the desired cured properties. In some applications, additional post cure will be required.

2.5 PROCESSING OF PRODUCT FORMS

2.5.1 Fabrics and preforms

2.5.1.1 Woven fabrics

Woven or knitted fabric product forms, unlike tapes and rovings, are in most circumstances produced prior to the resin impregnation step. Therefore, these product forms, in most part, offer product continuity or retention of fiber placement prior to, during, and after the impregnation step. Most fabric constructions offer more flexibility for lay-up of complex shapes than straight unidirectional tapes offer. Fabrics offer the option for resin impregnation either by solution or the hot melt process. Generally, fabrics used for structural applications use like fibers or strands of the same weight or yield in both the warp (longitudinal) and fill (transverse) directions. However, this is not a set rule as the number of combinations of reinforcement fibers and weave styles are essentially unlimited for custom applications. Also some fabrics are produced which incorporate thermoplastic strands that then become the resin matrix when the fabric is processed to its final state.

Woven fabric selections for structural applications have several parameters which may be considered. These variables are strand weight, tow or strand count, weave pattern, and fabric finish. The variables for glass fabrics are considerably greater than carbon fabrics due to the availability of a greater range of yarn weights. The availability of carbon tow weights or filament count tows are few in comparison. Generally, the lighter or thinner the fabric, the greater the fabric cost. Also factored into the cost is the complexity of the weave pattern or machine output for heavy fabrics. For aerospace structures, tightly woven fabrics are usually the choice for areal weight considerations, minimizing resin void size, and maintaining fiber orientation during the fabrication process.

2.5.1.1.1 Conventional woven fabrics

Woven structural fabrics are usually constructed with reinforcement tows, strands, or yarns interlocking upon themselves with over/under placement during the weaving process. The more common fabrics are plain or satin weaves. The plain weave construction results from each fiber alternating over and then under each intersecting strand (tow, bundle, or yarn). With the common satin weaves, such as 5 harness or 8 harness, the fiber bundles traverse both in warp and fill directions changing over/under position less frequently. (See Figures 2.5.1.1.1(a) and (b).)

These satin weaves have less crimp and are easier to distort than a plain weave. With plain weave fabrics and most 5 or 8 harness woven fabrics the fiber strand count is equal in both warp and fill directions. Example: 3K plain weave often has an additional designation such as 12 x 12, meaning there are twelve tows per inch in each direction. This count designation can be varied to increase or decrease fabric areal weight or to accommodate different fibers of varying weight.

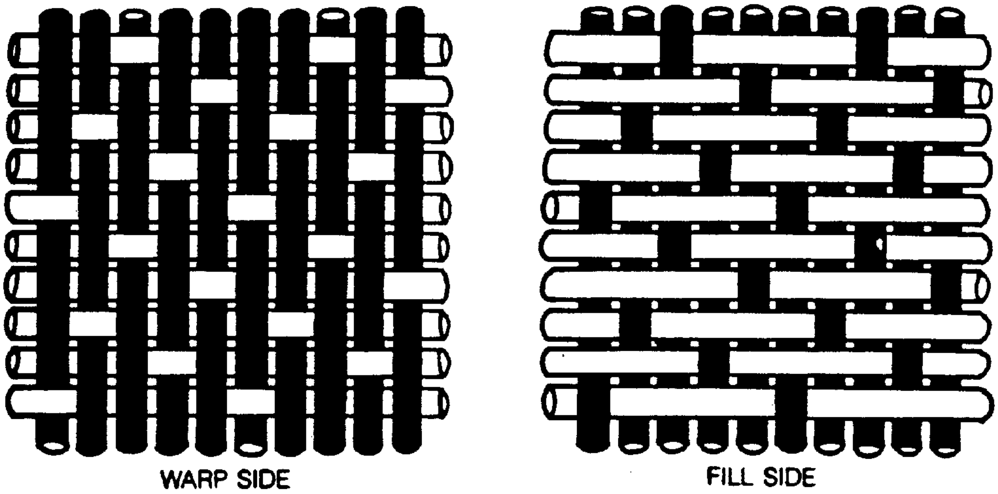


FIGURE 2.5.1.1.1(a) *5 Harness satin weave construction. In this weave construction each yarn goes over 4 and under 1 yarn in both directions.*

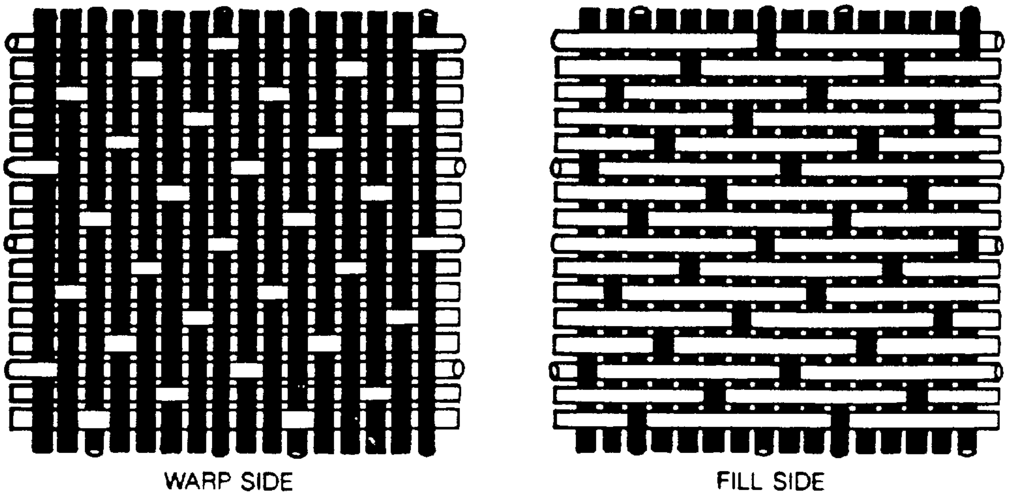


FIGURE 2.5.1.1.1(b) *8 Harness satin weave construction. In this weave construction each yarn goes over 7 and under 1 yarn in both directions.*

2.5.1.1.2 Stitched or knitted fabrics

These fabrics can offer many of the mechanical advantages of unidirectional tapes. Fiber placement can be straight or unidirectional without the over/under turns of woven fabrics. The fibers are held in place by stitching with fine yarns or threads, after preselected orientations or one or more layers of dry plies. This product form, much like preplied unidirectional tapes, offers a wide range of multi-ply orientations. Although there may be some added weight penalties or loss of some ultimate reinforcement fiber properties, some gain of interlaminar shear and toughness properties may be realized. Some common stitching yarns are polyester, aramid, or thermoplastics.

2.5.1.1.3 Specialty fabrics

To list all the possible woven or knitted fabric forms would require space beyond the scope of this document. As an example, there are in excess of one hundred glass fabrics listed in a standard weaver's handbook. These fabrics vary in weight from 0.55 oz./square yard (18.65 gm/m^2) to 53 oz./square yard (1796 gm/m^2) and vary in thickness from 0.0012 in (0.0305 mm) to 0.0450 in (1.143 mm). Such an industrial listing is limited to but a few basic patterns such as plain, basket, Leno, harness, and twill weaves. There are many other fabrics such as triaxial, orthogonal, knitted bidirectional, stitched multilayer, and angle interlock, to name a few. From these also arise combinations and three-dimensional weaves.

2.5.2 Preimpregnated forms

2.5.2.1 Prepreg roving

This impregnated product form generally applies to a single grouping of filament or fiber ends, such as 20 end or 60 end glass rovings. Carbon rovings are usually identified as 3K, 6K, or 12K rovings. Other counts are available. It is possible, preferably during the resin impregnation step, to combine two or more counts or filaments or ends to increase the rovings weight, width, etc. per linear length. For mechanical testing purposes individual rovings are usually wound, side by side, to form single ply tapes and processed as such. The roving product form, with its packaging on individual spools, offers the means for automated fiber placement during the manufacture of parts. The rovings can be placed in a unidirectional pattern, like tapes, or to generate a crossover interlocking effect. Most applications for roving products utilize mandrels for filament winding and then resin cure to final configuration. In addition, this product form is used for efficient build-up of oriented filaments to create preforms. The preforms are combined with other lay-ups or processed individually in closed tools rather than the conventional mandrel cure process. Most rovings are supplied untwisted, in nearly flat continuous bands. Band widths can be controlled to a degree during the impregnation step. Compared to tapes or fabrics, roving areal weights for individual plies or wraps are more dependent on the winding process than the impregnation step. However, resin control of the preimpregnated rovings shares a like degree of accuracy.

2.5.2.2 Prepreg tape

All product forms generally begin with spooled unidirectional raw fibers packaged as continuous strands. Normally, untwisted tows or ends are specified for unidirectional product forms to obtain ultimate fiber properties. This particular product form depends on the proper fiber wet-out and the tenacity of the uncured resin to maintain proper fiber placement until the tape reaches the curing procedure.

2.5.2.2.1 Conventional unidirectional tapes

This particular form has been the standard within the user industry for many years and is common with thermosetting resins. The most common method of manufacture is to draw collimated raw (dry) strands into the impregnation machine where hot melted resins are combined with the strands using heat and pressure. The combination of fibers and resin usually travels through the machine between coated carrier papers or films for ease of release. The tapes are usually trimmed to specified widths in line. One side of the carrier is usually removed prior to the roll-up position to facilitate continuous visual inspection. The remaining carrier is usually left in place with the tape to serve as a separator on the roll and as a processing aid for fabrication purposes. The tape manufacturing process is continuous within the linear limits of the raw strands creeled to the machine or specified lot size or availability of resin. Most impregnation machines are designed to permit in-line change over to new rolls (take-ups) without interruption. Raw strand collimation is adjusted to control specified areal weight (dry weight/area). Resin filming for tape machine operations is often done as a separate controlled operation. Some machines accommodate in-line filming that permit resin content adjustments during the impregnation process. Tapes as wide as 60 inches (1.5 m) are commercially available.

2.5.2.2.2 Two-step unidirectional tapes

Although not a general practice within the prepreg industry, there are unidirectional tapes manufactured from preimpregnated rovings. The collimation of these rovings to make tapes allow the use of solution impregnated resins, rather than hot melt systems. Although the product form may be similar to conventional tapes, thin uniform flat tapes may be difficult to produce.

2.5.2.2.3 Supported unidirectional tapes

To enhance specific mechanical properties or part manufacturing handling operations, it is sometimes advantageous to add product form during the manufacture of unidirectional tapes. Generally, these added fibrous forms are lightweight to be accommodated during the normal tape manufacture operation. The added form may be combined in the machine dry or preimpregnated prior to the tape production. More common added forms are lightweight mats or scrim fabrics of the same or unlike fiber type. The added product form will affect material properties compared to tapes without the supporting material.

2.5.2.2.4 Coated unidirectional tapes

Some tape suppliers offer the option of added tape surface coating. These resinous coatings of films are usually of different rheology or viscosities from the fiber impregnation resin to remain as distinct boundaries between plies of the cured tapes. As with supported unidirectional tapes, the added layer may be combined during the tape manufacturing operation.

2.5.2.2.5 Preplied unidirectional tapes

These tapes originate as any of the above-described tape forms in single-ply form. Then through a process of stacking, two or more layers of individual tapes are oriented at predetermined angles in relation to the centerline of the new progressively generated tape or broadgoods form. The original individual tapes are located side to side in each angled layer to form a continuous linear form. The original single-ply tapes are usually precut in segments at angles to correspond to the new product form's edges. The progressive stacking sequence usually takes place on a continuous carrier (paper or film) atop a flat surface much like the fabrication process. The carrier, with the preplied form in place, is utilized to take up the preplied tapes onto a shipping/handling core. The predetermined length of the individual precut segments will generally regulate the width of the preplied tapes. However, a final trim of both edges to control specified widths can be incorporated during the take-up step. For economic purposes the preplying operation usually is done in widths of approximately 24 inches (0.6 m) or greater. Should narrow widths be required, they can be accommodated with a secondary slitting operation. To some extent the retention of this product form's continuity is, like single ply tapes, dependent on the tack or tenacity of the uncured resin.

2.5.2.3 Prepreg fabric

This section is reserved for future use.

2.5.2.4 Preconsolidated thermoplastic sheet

This section is reserved for future use.

2.6 SHIPPING AND STORAGE PROCESSES

Composite precursor materials and adhesives can be very sensitive to how they are stored and shipped. Contamination must be avoided, as it will invariably reduce properties. Materials that have been preimpregnated (prepreg), film adhesives, and other resins are temperature variation sensitive. They can also be very sensitive to moisture and humidity before they are cured. As a result, these materials need special handling and storage in order to provide desired results.

2.6.1 Packaging

Prepreg and film adhesive should be supported on cardboard rolls, or in some other manner. They should be sealed in moisture-proof bags, with desiccant packages if possible. Once packaged, they should be stored in conditions as recommended by the manufacturer, usually at or below 0°F (-18°C) for a shelf life of six months or longer. Since the cure of thermoset materials continues to progress at room temperature, and even these lower storage temperatures, a record must be kept of the time exposed at room and storage temperatures. This record will be used to establish the useful life of the material and to determine when retesting is required. The time that material can be at room temperature and still usable, known as the out-time, can range from minutes to thirty days or longer. For some materials the processing characteristics can change dramatically depending on how much storage and out-time they have experienced.

2.6.2 Shipping

Since these materials require a carefully controlled environment, maintaining that environment while shipping the product can be challenging. Usually the material, still in its moisture-proof sealed bag, is placed in a shipping container approved for use with dry ice. Enough dry ice is placed in the container to allow some to be remaining upon the scheduled arrival, plus about 24 hours. Chemically based temperature sensitive materials, or electronic temperature recording devices can be placed in the container to assure material integrity upon delivery.

2.6.3 Unpackaging and storage

Upon receipt the material should be placed in a freezer to maintain the recommended storage temperature. Any time during shipping where the material temperature has exceeded this storage temperature is deducted from the out-time for the material. When the material is needed for use it needs to be allowed to reach room temperature before the moisture-proof bag is opened. If this is not done moisture will condense on the cool material, and may result in prebond moisture problems with the material.

2.7 CONSTRUCTION PROCESSES

Construction processes are those used to bring various forms of fiber and fabric reinforcement together to produce the reinforcement pattern desired for a given composite part or end item. The resin may or may not be in its final chemical or physical form during placement of the reinforcement. Construction processes include both manual and automated methods of fiber placement, as well as adhesive bonding and sandwich construction.

2.7.1 Hand lay-up

This section is reserved for future use.

2.7.2 Automated tape placement/automated tape lamination

2.7.2.1 Background

Composite tape lamination machines have been in use in industry for about 20 years. The early developmental machines were usually custom made for the aerospace industry in small machine shops under the guidance of developmental engineers. Once the technology was proven in the laboratory, commercial machine tool manufacturers began producing and further developing tape laying machines for industrial applications.

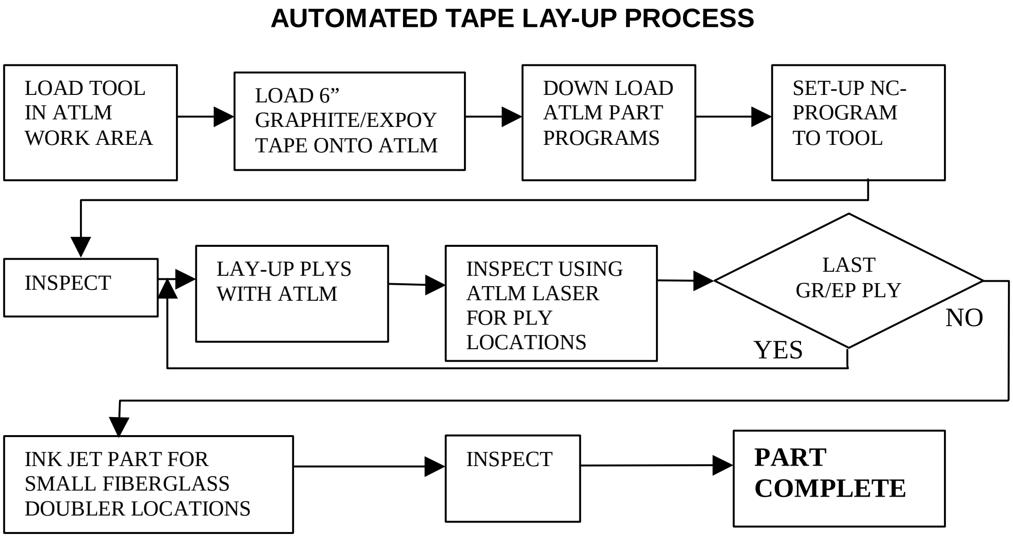


FIGURE 2.7.2.1 *Typical process sequence.*

2.7.2.2 Benefits/capabilities

The use of automated tape lamination machine allows lay-up of unidirectional composite tape in 3", 6" and 12" (7.62 cm, 15.24 cm, and 30.48 cm) widths. The machines are able to lay-up 10-20 lbs./hr, compared to 2-3 lbs./hr for typical hand lay-up operations. Automated tape laying enables fabrication of large composite components using a minimum of manual labor without the ergonomic problems associated with personnel climbing onto large tools to lay-up parts. Material utilization is increased by at least 50% when compared to historical manual lay-up data. The process can be used on flat or contoured parts, the current commercial heads have a contour limit of 30° out of a horizontal plane. Typical applications in the aerospace industry are for wing and empennage components as well as control surfaces with mild contours. If more contour is required, a custom machine would be required.

2.7.2.3 Sources of variability

Material Tack*:* The machine performance is dependent on the characteristics of the composite material that is being laid. The development of the material must include manufacturing trials on a tape laminating machine. The relationship between the tack of the prepreg to the backing paper and the adhesion of the prepreg to itself is critical for efficient lamination with a machine. The laminating machine has continuous paths for the backing paper, that is the supply roll will have prepreg and backing paper and the take up roll will only have backing paper. The machine relies on the backing paper/prepreg adherence to deliver the prepreg to the head and the prepreg/prepreg tack to laminate it to the part and release it from the backing paper. These relationships need to be consistent over the range of temperature and humidity variations that occur in the clean room environment. Tack is also affected by material outtime. In the manufacturing environment the material outtime needs to be closely monitored. For machine lay-up, the handling life of the prepreg is typically half that of hand lay-up materials.

Backing Paper*:* The backing paper used for the prepreg is coated with a release agent to ensure the level of adhesion to the prepreg is consistent. It also must be very consistent in thickness and not have a propensity to rip when scored with a knife. The reason the material thickness is critical is because of the use of stylus or ultrasonic cutters. The cutter cuts the prepreg against an anvil with the backing paper in between, the cutter depth must be set as to always cut through the prepreg but not cut the backing paper. The cutters are set at depths such that the backing paper gets scored during cutting and is in tension from the machine, therefore, a high notch sensitivity property is required in the release paper.

Impregnation Level: The impregnation level of the prepreg needs to be sufficient to allow removal of prepreg from the release paper with required stiffness to facilitate placement. Additionally, the impregnation level will allow prepreg cutting without tow separation and possess the required surface tack.

Width Tolerances: The prepreg width tolerances must be maintained to achieve required gap and overlap requirements established for the process/application.

Natural Path Part Programming*:* The tape lamination machines use natural path part programming to define tape paths. The tape paths are defined to minimize the laps and gaps associated with the part contour. On heavily contoured parts, the natural path may result in excessive laps and gaps that will require engineering coverage.

Automated tape lamination has proven to be a very efficient and cost effective manufacturing process for large contoured composite parts. For maximum efficiency of the machines, engineers tailor the part design to the machine capabilities. This tailoring results in reduced scrap lays, minimizes manual operations, and ensures an affordable manufacturing process.

2.7.3 Automated tow placement/fiber placement

2.7.3.1 Background

Fiber placement is an automated machine process utilizing narrow strips of composite material (preimpregnated tows or slit prepreg tape) taken from multiple spools. The machine collimates the material into a band up to 6 inches wide which is a function of the individual tow width, the number of tows a particular machine can process, and/or the width that the part geometry can accommodate and laminates the material onto a work surface (tool). As each band is placed, some machine heads are capable of adding or dropping individual tows to either widen or narrow the bandwidth accordingly. This capability, allowing a true fiber orientation to be maintained on a contoured surface, is unique to the fiber placement process. The process allows material to be placed only where needed thereby greatly reducing material scrap factors. The uniqueness of the machine process requires a unique manufacturing and design approach. In addition to machine operation and fiber placement specific knowledge, manufacturing personnel must pay close attention to off-machine preparation steps within the work cell and designers must incorporate the physical operating limits of the machine into the component design. These factors are critical to maintaining an efficient process, to maximizing machine capacity, and to ensuring that the component will meet the engineering requirements.

Automated tow placement or fiber placement was first conceived in the early 1980’s. Early machines were developed by Hercules Aerospace (now Alliant Techsystems) and Cincinnati Milacron (now Cincinnati Machine). Production programs, mainly military aircraft systems such as the V-22 Osprey, F/A-18E/F Super Hornet, and F-22 Raptor, began using fiber placement for the fabrication of composite parts in the early 1990’s. By the mid-nineties business jet manufacturers, most notably Raytheon, began using fiber placement for fuselage sections. Today fiber placement is an accepted production process and a preferred approach for the manufacture of many mild-complex contoured composite parts. With over twenty production capable machines available worldwide, fiber placement operations can be found on the factory floors of most major aerospace contractors and composite part suppliers.

2.7.3.2 Fiber placement process flow

The typical work flow for fiber placement is shown in Figure 2.7.3.2 and generally consists of: (1) preparation of the tool or mandrel surface that the material will be applied to; (2) loading and aligning the mandrel into the fiber placement machine; (3) preparation of the machine by loading material, threading the tows (tapes) through the delivery system, and loading the computer path programs for the part being built, which have been generated offline; (4) machine collation or automated fiber placement of the tows (tapes) included in a particular ply or layer; (5) inspecting/reworking defects after each ply is placed; (6) continuation of machine collation until all plies are placed; (7) Preparing the part for cure; and (8) bagging/curing the part. Some parts are cured right on the placement tool and other may require transferring the part to a cure tool.

After cure, the part is unbagged and removed from the tool. The bagging, cure, part removal and finishing steps are identical to those required for hand collated parts. This workflow may vary depending on the application. For example, some parts have other materials introduced during fabrication, such as core or alternate fibers, and interim compaction steps may occur.

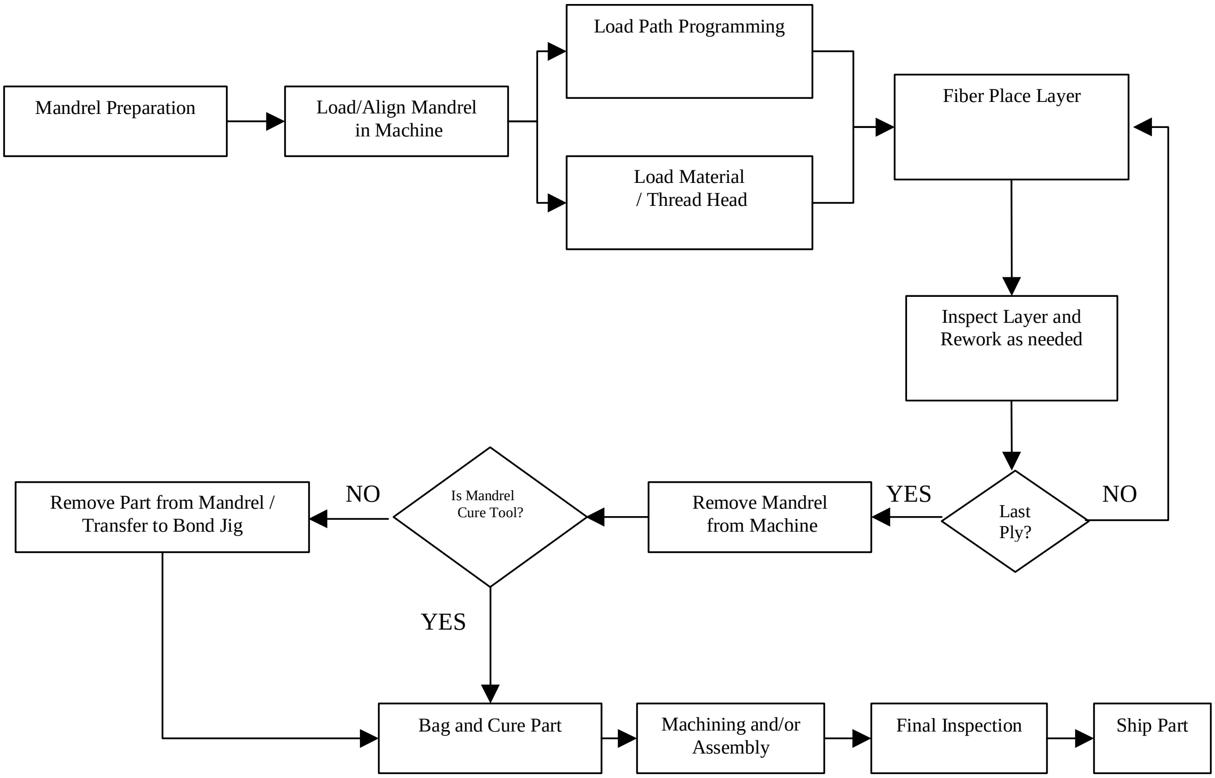


FIGURE 2.7.3.2 *Typical work flow for fiber placement.*

2.7.3.3 Benefits/capabilities

The use of a fiber placement machine allows the precise control of individual unidirectional composite tows. The ability to control the speed, feed, and tension in each individual tow allows the composite to be steered over complex contours as it's being laid into position. The fiber placement deposition head can accommodate anywhere between 1 to 32 individual tows. The width of the tow is typically 0.125” (.317 cm) (although other tow sizes such as 0.128", 0.157” and 0.182” (.325 cm, .398 cm .462 cm) are also used) which results in lay down widths ranging between 0.125” and 6” (.317 and 15.24 cm). The equipment is also capable of varying the width of the material band by dropping and adding tows as it goes along during the course of placing a layer. The use of fiber placement to collate and compact the material also minimizes the need for intermediate debulk operations, which are typically done every 3-5 plies for fabric hand lay-up, 5-10 plies for prepreg tape hand lay-up, but only every 10+ plies for fiber placement.

The lay down rates and cost savings achieved with automate fiber placement are very part dependent. On a complex contoured part, labor savings can be as high as 50% while for flat or mildly contoured surfaces as little as 10%. For most parts that are good candidates for fiber placement labor savings are in the neighborhood of 25%. Additional savings are possible through reduced material scrap factors. Fiber placement usually results in material utilization factors in the 1.05-1.20 range, far less than manual operations which can be as high as 2.25. The lower material utilization is somewhat offset by the higher price of the unidirectional tow/slit tape material required for fiber placement which can cost 10-15% more than conventional prepreg material. This price differential is reducing, however, as the use of tow/slit tape material increases. Typical applications in the aerospace industry are: inlet ducts, contoured fuselage panels, full fuselage barrel sections, contoured fairings, nacelle skins, payload shrouds/adapters, and structural shafts (straight and contoured).

2.7.3.4 Material product forms

Fiber placement material is available in two product forms, slit tape and prepreg tow (towpreg). Both product forms are wound onto a core, which is 11 inches (27.94 cm) long and can vary between 3 to 6 inches (7.62 cm to 15.24 cm) in diameter. The towpreg is generally wound in an open helical winding pattern without any separation films. The slit tape is generally spiraled on in a tight helix pattern with a separation film introduced to keep the tape from sticking to the underlying layer.

The prepreg tow or towpreg manufacturing process involves unspooling a dry fiber spool, impregnating it with the proper resin content, shaping it to the specified width and thickness and respooling it as a prepreg tow or towpreg spool. The impregnation can be either a hot melt process or a solvent process. The process often involves first making parent tape, generally 6 to 12 inches (15.24 to 30.48 cm) wide, impregnating it with resin using normal unidirectional tape technology, then separating it back into individual tows again with a predetermined width based on the tray size of the fiber placement machine. Because the width is set to a specific dimension, the thickness of the towpreg is dependent on the size of the fiber bundles used during prepregging. Towpreg typically is not respooled with any kind of backing film or separator sheet. The process is continuous from the point of unspooling the dry fiber to spooling the towpreg in its final condition. Precise width control is the biggest challenge for the prepreg tow suppliers. Prepreg tow has the potential to be less expensive because it does not use a separation film and does not require a secondary slitting process.

Slit tape is first manufactured in the form of 6-48 inch (15-122 cm) wide unidirectional tape (broadgoods) which are then cut into multi-sected rolls. These multi-sected rolls are then slit to the final width, which is specified for the individual fiber placement machine (most common is 0.125 inches (.317 cm)). Slit tape typically has a 0.002 inch thick polyethylene interleaf or backing sheet which is 0.5 inches (1.27 cm) wide and centered over the tow in order to facilitate spooling and unspooling of the slit tape without damaging the material. This backing sheet is removed during the fiber placement process using vacuum tubes, which are part of the fiber placement machine. Once the blades are set for slitting the multi-sected rolls, the process yields a tow with a very precise width along the tow length. One of the advantages of slit tape is the ability to deliver a tow width that matches existing fiber placement machines at a variety of thicknesses. The thickness of the slit tape is primarily dependent on the fiber areal weight and uncured resin content of the original un-slit tape on the master roll. In cases where fiber placement efficiency can be improved by using thicker material, the master roll may consist of multiple layers of pre-plied unidirectional tape.

Another difference between the product forms is the cross-sectional shape of the material. The towpreg operation, which generally involves peeling individual tows off the parent tape, will yield a tow with a tapered cross-sectional shape. Some prepreg tow suppliers are using dies to shape the tow before spooling, but there still will be some widening of the tow at the turnarounds. Slit tape will have a more rectangular shape. Figure 2.7.3.4 illustrates this difference. If the width of the towpreg tows is a little over nominal size, the tapered shape allows each individual tow to overlap within a course band. This individual overlapping reduces the occurrence and severity of band to band overlaps. The rectangular shape of slit tape and their more precise width allows them to stack nicely together, but does not facilitate individual tow overlapping within a band if the tows are oversize. If the tows are oversize each tow butts up against an adjacent tow within the band or stacks on the one next to it at full band thickness. If they butt side to side it can spread out the overall bandwidth, and will increase the occurrence of band to band overlaps within a part.

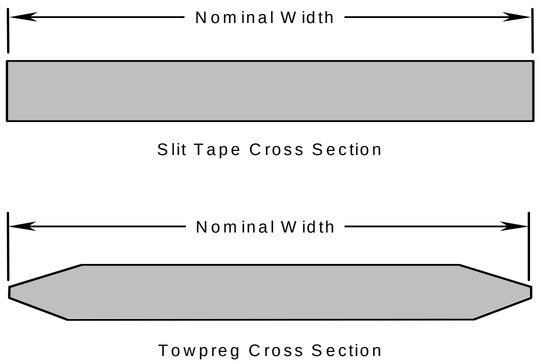


FIGURE 2.7.3.4 *Cross-sectional shape of fiber placement materials.*

2.7.3.5 Special considerations

The machine performance is dependent on the characteristics of the composite material that is being placed. The development of the material must include manufacturing trials on a fiber placement machine. When developing and qualifying a material for fiber placement several factors to be considered are:

Material Tack*:* The relationship between the tack of the prepreg to the backing paper (in the case of slit tape) and the adhesion of the prepreg to itself (in the case of prepreg tow and general adhesion) is critical for efficient lamination with a machine. These relationships need to be consistent over the range of temperature and humidity variations that occur in the clean room environment. Although “CTLM (Contoured Tape Lamination Machine) grade” material typically works best for fiber placement, the process is less sensitive to tack level than contoured tape laminating machines. However materials with too much tack will tend to gum up the machine and greatly reduce efficiency. Tack is also affected by material out time. While fiber placement machines have environmentally controlled creels for use during material collation, the out time is still important and needs to be monitored. It is important for the material to stiffen-up and have very low tack when it is cooled (the delivery head components are cooled to reduce resin build-up and let the material slide through with little friction, while at the same time making the tow stiff so it can be fed back out during adds) and have good tack to itself when gently heated at the lay-down point.

Impregnation Level: If tow materials are not completely impregnated with resin, dry fibers tend to fray and the edges of the tow will become fuzzy. This problem is mainly seen in slit tape. Early in the development of the slit tape product form, it was believed that prepreg manufactured for hand lay-up operations could simply be slit and used for fiber placement. However, broadgoods for hand lay-up are commonly fabricated with the center (through the thickness) fairly dry. This allows more resin on the surface of the prepreg, which will increase the tack and aid in debulking. It is after these hand lay-up broadgood rolls are slit that the dry center section is exposed. As the tow begins to fray the fuzziness will accumulate along the fiber path. Whenever tow material that is extremely fuzzy is used, it requires increased maintenance to keep the fiber paths clear. The fuzz will eventually build-up enough to prevent tows from freely moving through the head and the machine operators will have to stop and clean the machine head. This problem can be greatly reduced by ensuring that the parent tape fibers are fully impregnated through the thickness. Broadgoods fabricated for hand collation will have a higher degree of fuzziness than those specifically made to be slit. It is recommended that prepreg material be purchased specifically for slit tape use, and that standard hand collation material not be used for fiber placement.

Width Tolerances: Width control and tolerance of the material is one of the most important parameters to consider. Width tolerances must be maintained to achieve required gap and overlap requirements established for the process/application. Slit tape will have much less variation in the tow width than towpreg. When the tow width deviates from the nominal value, a part fabricated with this material will have either gaps or overlaps. Gaps and overlaps must be repaired on a ply-by-ply basis, which can be costly and labor intensive. Since the tow guide trays in the fiber placement machines are set to a constant width, material that is too wide (out of tolerance) will not smoothly move through the head. In some cases the tow will become stuck in the head and the part fabrication process has to be stopped while the tow is removed. For part quality and possible effects on mechanical performance, the width standard deviation is an important parameter to control. Slit tape will typically have a lower standard deviation than towpreg. To get good parts, typical expectations for slit tape and towpreg are as follows:

Tow Width	Slit Tape Tolerance	Towpreg Tolerance
0.125-0.128 (3.18-3.25 mm)	±.005” (0.127 mm)	±.007” (0.178 mm)
0.157 (3.98 mm)	±.005” (0.127 mm)	±.007” (0.178 mm)
0.182 (4.62 mm)	±.007” (0.178 mm)	±.009” (0.228 mm)

Materials outside these specs have been used successfully, but generally more downtime is involved, and/or part quality is reduced, and the potential implications on mechanical properties must be thoroughly evaluated. Depending on the application, using a lower standard material at a lower cost may still be acceptable.

Material Handling: When using slit tape, the spools of material can be stored and handled according to the same specifications used for broadgoods; however, some towpreg systems require special handling procedures. These special handling procedures are required at room temperature because if a towpreg spool is allowed to sit and come up to room temperature, the resin will creep and flow causing the tows to fuse together on the roll. During despooling, the tow being pulled from the spool will stick to the material still wrapped around the spool causing the tow to bend back on itself. The fibers then kink and break or snap free and cause undesirable tension spikes. This sticking action will occur even if the towpreg (that has already been exposed to room temperature for too long) is re-refrigerated or despooled in an environmentally controlled creel. Accumulated room temperature exposure should be minimized - limited to eight hours for most epoxy products. Towpreg spools should never be stored with their weight on the prepreg (don’t lay them on their side). The spools should be stored with the weight on the cardboard core whenever possible. This is not as critical if the material is at 0°F, but as it warms up, the added contact pressure will cause the tows to fuse even quicker and tighter.

In addition to tow sticking, stringers may develop when using towpreg. Stringers are caused when part of the tow frays off and remains wrapped around the spool during despooling. It will eventually create a ring and will cut the tow in half or fault out the tensioner on the machine. Tow sticking and stringers are not commonly seen in slit tape because the spools have a backing sheet.

Mechanical Properties: In many cases it is desirable to utilize existing material databases/allowables when designing fiber-placed parts. Typically these allowables were generated from hand lay-up coupons/elements. Laminates produced using the fiber placement process are capable of delivering mechanical properties equivalent ot hand lay-up. However, the ability to do so depends upon carefully setting and controlling several parameters, the most important of which are lap/gap criteria. The frequency, location, and size of the laps/gaps is influenced by several factors including raw material width variability, path programming settings (when to drop/add tows, convergence settings), and part geometry. It is recommended that a limited test series be conducted to demonstrate the equivalency of fiber-placed laminates to hand lay-up.

Mandrel Tool Design: Tooling coordination is essential to the successful fabrication of a fiber placed part. As in all tooling programs, proper coordination must exist between the “as designed” part, the “as fabricated” part, NC programming, hard tooling, soft tooling, and inspection aids. The tool-to-machine interface is critical to fiber placement accuracy. The introduction of misalignment, play, or non-repeatability, especially at the headstock end, can translate to positioning errors on the tool surface. Fiber placement collation tools must meet minimum strength and stiffness requirements. Tool size, tool weight, part weight, and head compaction force all affect the tool design. Fiber placement tooling structure should be designed to be as light and rigid as possible. It must not sustain any permanent deformations due to part weight and compaction forces. These deformations can be in bending and in torsion. Torsional rigidity is an important design consideration that is often overlooked. It must be remembered that the point of application of these forces can be dimensionally far from the axis of rotation and that the tailstock is free to rotate.

***Part Path Programming**:* Fiber placement machines are capable of several path programming schemes including fixed fiber angle, band offset, and limited parallel (a combination of the other two). The best method selected depends on the geometry of the part, the desired tolerance control of the fiber orientation, and the allowable laps/gaps. Many features exist in the offline programming software that controls both on-part and off-part motions of the machine. Time well spent in offline programming will pay dividends during fiber placement.

2.7.4 Braiding

The braiding process fabricates a preform or final shape at the same time that it generates the woven form. This product form is a unique fiber reinforcement which can use preimpregnated yarn as well as dry fibers. The main advantage of the braiding process is its ability to conform to odd shapes and maintain fiber continuity while developing high damage tolerance compared to unidirectional and laminated products. This allows formation of square, oval, and other constant cross-section shapes. The three-dimensional form of braiding has evolved to the point of allowing the non-uniform cross-sections to be fabricated while maintaining weaving in all three planes.

The uses of braiding have varied during its development. The best known example of braided structure is the fiberglass and carbon fishing rods that became popular in the 1980's. Braiding has also found uses in pressurized piping and complex ducting. A demonstration of its versatility is the open-wheel race car body which was fabricated by braiding. The process has also been used in rocket applications for motorcases and launchers.

In biaxial and triaxial braiding, a mandrel is usually used to form the braid. The mandrel also acts as the mold for the final product. The braiding machine controls the rate of feed of the mandrel and the rotational speed of the carriers. The combination of these parameters and the size of the mandrel controls the braid angle. The braid angle, along with the effective yarn, tape, or tow width (width of the specific size yarn, tape, or tow on the mandrel as placed by the braiding process), ultimately controls the coverage of the braid on the surface of the fabricated form. As the braid angle increases, the maximum size of the mandrel which can be covered with a specific yarn, tape, or tow size decreases. For complicated forms, expendable mandrels may be used. These include mandrels made from low melting temperature metal alloys and water-dissolvable casting materials, and collapsible mandrels.

In three-dimensional (3D) braiding, the weaving process itself is used to control the shape of the fabricated product. The typical 3D braiding process involves a bed of cops, or weaving loops, which are moved in a systematic manner. This systematic movement creates an interwoven product in the x-y plane. As the yarns, tapes, or tows are pulled into the weaving process, the z-direction is also intertwined. The resulting product is essentially self-supporting due to interweaving in three directions. For precision exterior dimension, matched metal molds can be used during the resin matrix curing process. The following are the general steps involved in the braiding process:

1. Set the feed speed, cop speed, and weave pattern (3D braiding).
2. Run the braiding machine until the product is finished.
3. If prepreg material is not being used, use an appropriate resin impregnation process - RTM, wet resin impregnation, etc.
4. Cure according to the appropriate process determined by the impregnation method - autoclave cure, vacuum bag, RTM, etc.
5. Remove the part from the mold or mandrel.

2.7.5 Filament winding

Filament winding is an automated process in which a continuous fiber bundle (or tape), either preimpregnated or wet impregnated with resin, is wound on a removable mandrel in a pattern. The filament winding process consists of winding onto a male mandrel that is rotating while the winding head moves along the mandrel. The speed of the winding head as it moves along the mandrel in relation to the rotation of the mandrel controls the angular orientation of the fiber reinforcement. Filament winding can be done using wet resin winding, preimpregnated yarns and tapes. The following general steps are used for filament winding:

The construction of the mandrel is critical to the process and the materials of choice are dependent upon the use and geometry of the finished part. The mandrel must be capable of withstanding the applied winding tension, retaining sufficient strength during intermediate vacuum compaction procedures. In addition, if the outer surface of the part is dimensionally critical, the part is generally transferred from the male winding mandrel to a female tool for cure. If the internal surface of the part is dimensionally critical, the part is usually cured using the male winding mandrel as the cure tool. Metal is used in segmented collapsible mandrels or in cases where the domes are removed to leave a cylindrical part. Other mandrel material choices are low melt alloys, soluble or frangible plaster, eutectic salts, sand and inflatables.

The following general steps are used for filament winding:

1. The winder is programmed to provide correct winding pattern.
2. The required number of dry fiber or prepreg roving/slit tape spools for the specified band width are installed on the winding machine
3. When wet winding, the fiber bundle is pulled through the resin bath.
4. The fiber bundle is pulled through the eye, attached to the mandrel, the winding tension is set and the winding program is initiated..
5. When winding is complete, the mandrel is disassembled as required and removed from the part if the part is to be cured on a female tool., otherwise the part is trimmed and prepared for cure on the male mandrel.
6. Elevated temperature cure of thermosets resin parts is usually performed in an oven or autoclave, room temperature cure resin parts are usually placed under vacuum to provide compaction during cure. During cure the male mandrel or female tool is often rotated to maintain resin distribution.
7. After cure the mandrel is removed from the part (for male tooled parts)

Cured product characteristics can be affected by both the winding process and design features such as:

1. Uniformity of the fiber to resin ratio (primarily wet winding)
2. Wind angle
3. Layer sequence

4. Effective fiber bandwidth (tight fiber weave or loose/open fiber weave pattern)
5. End closure.

The cure cycle and compaction procedure affects such cured product characteristics as described in the applicable cure and consolidation process section - 2.8.1 (for vacuum bag molding for room temperature cure resins), 2.8.2 (for oven cure), or 2.8.3 (for autoclave cure).

2.7.6 Pultrusion

The pultrusion process consists of passing a continuous resin-impregnated fiber bundle through a heated die for part shape and cure. This process is limited to constant cross-sections such as rods, tubes, I-beams, and channels. The pultrusion process works well with quick-curing resins and is a very low-cost method for high-production parts with constant cross-sections. For a discussion of cure and consolidation during pultrusion, see Section 2.8.6 below.

2.7.7 Sandwich construction

Sandwich construction, as applied to polymer matrix composites, is a structural panel concept consisting in its simplest form of two relatively thin, parallel sheets of structural laminated materials bonded to and separated by a relatively thick, lightweight core. The following information is limited to non-metallic sandwich construction used for structural applications. Sandwich construction provides a method to obtain high bending stiffness at minimal weight in comparison to monolithic laminate construction. This advantage must be weighed against the risk of increased processing difficulty that can increase production costs over monolithic construction. Damage tolerance and ease of repair should also be considered when selecting sandwich panel or monolithic laminate construction. Good structural practice requires selection of skin, core and adhesive materials to be strategically based on overall part quality considerations including:

1. Surface quality (pinholes, mark-off, etc.)
2. Skin quality (porosity, consolidation, waviness, resin loss)
3. Adhesive bond and fillet quality (strength, fillet size)
4. Core strength, cell size, bonding preparation
5. Resistance to moisture ingress

Polymer matrix composite sandwich construction is most often fabricated using autoclave cure, press cure or vacuum bag cure. Skin laminates may be pre-cured and subsequently bonded to core, co-cured to core in one operation, or a combination of the two methods. Pre-cured skin sandwich construction insures a high quality surface, but adequate fit-up to core must be addressed. Co-curing often results in poor panel surface quality which is prevented by using a secondary surfacing material co-cured in the standard cure cycle or a subsequent "fill-and-fair" operation. Co-cured skins may also have poorer mechanical properties, and this may require the use of reduced design values.

Cure cycles can be developed to reliably produce good quality sandwich panels. For co-cured sandwich construction, this is essential. Some primary cure cycle considerations are transport of volatiles, core evacuation and/or pressurization, adhesive and prepreg resin viscosity profiles, and compatibility to monolithic structure co-cured with the sandwich structure.

Skin materials for co-cure processing have a "low flow" resin material system that prevents resin running down the cell walls into the core. A compatible adhesive must be selected that develops an adequate fillet bond to the selected core whether co-cured or secondarily bonded. For co-cured construction, prepreg resin to adhesive compatibility must be demonstrated.

Core should be selected according to the required characteristics of the application often including surface quality, shear stiffness and strength, compressive strength, weight, water absorption, and damage tolerance. Currently available core materials include metallic and non-metallic honeycomb core and a variety of non-metallic foams. Honeycomb core selection can be made from a range of common carbon, glass or aramid fiber reinforced matrix materials including phenolics, epoxies, polyimides, or thermoplastics.

Additional information may be found in References 2.7.7(a)-(d).

2.7.8 Adhesive bonding

Three types of adhesive bonding are commonly employed with composite structures. These are cocuring, secondary bonding and cobonding. A typical cocure application is the simultaneous cure of a stiffener and a skin. Adhesive film is frequently placed into the interface between the stiffener and the skin to increase fatigue and peel resistance. Principal advantages derived from the cocure process are excellent fit between bonded components and guaranteed surface cleanliness

Secondary bonding utilizes precured composite detail parts. Honeycomb sandwich assemblies commonly use a secondary bonding process to ensure optimal structural performance. Laminates cocured over honeycomb core may have distorted plies which have dipped into the core cells. As a result, compressive stiffness and strength can be reduced as much as 10 and 20 percent, respectively. While secondary bonding avoids this performance loss, care must be exercised prior to bonding in order to ensure proper fit and surface cleanliness. In some applications, aluminum foil layers or an adhesive sandwiched between two layers of polyester release film is placed into the bonded joint. The assembly is then bagged and run through a simulated bonding cycle using the same temperatures and pressures as those in the actual cycle. The foil or film is removed, and its thickness is measured. Based upon these measurements, additional adhesive can be added to the bondline to ensure proper fit; or detail parts can be reworked to eliminate interference fits.

Precured laminates undergoing secondary bonding usually have a thin nylon or fiberglass peel ply cured onto the bonding surfaces. While the peel ply sometimes hampers nondestructive inspection of the precured laminate, it has been found to be the most effective means of ensuring surface cleanliness prior to bonding. When the peel ply is stripped away, a pristine surface becomes available. Light scuff sanding removes high resin peak impressions, produced by the peel ply weave which, if they fracture, create cracks in the bondline.

In-service secondary bond failures are usually interfacial, with all of the adhesive on one side of the interface and all of the resin on the other. One well-known cause of this condition is transfer of silicone from released peel plies. Another cause of this weakness, which cannot be detected by ultrasonic inspections, is pre-bond moisture. Adhesion relies on the surface energy of the substrate being higher than that of the uncured adhesive. Water at the interface lowers the surface energy of the substrate, making it more difficult or even impossible for the glue to adhere. As little as 0.2 percent pre-bond moisture in undried reinforced epoxy laminates has been found to reduce the shear strength of the bond by as much as 80 percent. The moisture is driven to the interface by the heat applied to cure the adhesive and is prevented from escaping by the typical ridged texture left by removal of even uncoated peel plies. Pre-bond moisture can also be present as the result of the hygroscopic nature of adhesive films left too long in an ambient environment. Condensate on adhesive that had not been properly stored in a sealed bag in the refrigerator has also resulted in kissing bonds that separate because of close to zero peel strength. The mechanical interlock achieved by filling the cavities in peel ply surfaces creates a ‘Velcro’-type bond with sufficient strength to pass initial inspections, but without the durability to last in service.

In a particularly illuminating series of tests, using a peel ply known to be free of release agents, the first panel tested failed prematurely because of condensate on the adhesive film that not been properly stored. When the tests were repeated with no change other than to have stored the adhesive properly, the test specimens failed interlaminarly, in the resin between the interface and the nearest fibers in the top ply. In neither case were the adherends abraded. The change was clearly the result of the presence or absence of pre-bond moisture at the interface. The series production program with which these tests were associated has a requirement to severely restrict the out time of the components between curing and bonding to a matter of only hours, instead of days or weeks, and there have been no in-service failures. An interruption to the manufacturing process would require thorough drying of the cured details before bonding.

Another relevant incident involved metal bonding, with condensate known to be on the adhesive film prior to bonding. In one tool, the molded rubber bag on one side of the bonded assembly prevented any of the moisture from escaping; the stiffeners were held on by only the fillet of adhesive squeezed out along the edges. There was intimate contact but absolutely no adhesion on the faying surfaces. On another tool, using beady balls to simplify bagging, the moisture was easily able to escape through the cavities between the beady balls, and none of these bonds were found to be defective, despite the known presence of moisture before bonding. The difference between these two cases was simply the opposite ends of the spectrum in terms of venting of volatiles during cure. The moisture was able to escape when it had to migrate less than an inch to a huge vent path, but unable to escape when it would need to travel as much as three feet, escaping past as many as six knife-edge rubber seals.

There are not yet any tests in which composite bond surfaces have been grit-blasted, to remove the peel-ply texture to facilitate venting, in combination with the deliberate introduction of moisture to see if it could escape during the cure cycle. These are planned, however.

Experience with adhesive bonding of composite structures has made it clear that pre-bond moisture that is unable to escape easily during the cure has a disastrous effect on the strength and durability of the bonds. It is most important to dry composite laminates made sufficiently long before bonding that they could have absorbed even a small amount of moisture. It is also important to keep moisture away from uncured adhesive films. It is also clear that good venting can increase the tolerance of the bonding process to any pre-bond moisture that may occur accidentally.

Peel plies are generally not useful for thermoplastic composite laminates. Instead, plasma technologies such as flame spray are employed to remove minor amounts of contaminants and to increase surface reactivity. Thermosetting adhesives are sometimes used with pre-consolidated thermoplastic composites, but more commonly melt fusible thermoplastic films are utilized. Amorphous thermoplastics (e.g., polyetherimide) are superior choices for an adhesive film because of their wide processing latitude. In some instances, nichrome wire or ferromagnetic particles are placed into the film to resistively heat the film and effect flow within the bondline. Reference 2.7.8(a) provides an excellent overview of this technology.

Cobonding is a combination of secondary bonding and cocuring in which one detail part, usually a skin or spar web, is precured. Adhesive is placed into the bondline and additional composite plies for another detail part (e.g., a blade or hat stiffener) are laid up over the adhesive. The adhesive and composite plies are then concurrently cured together. The cobonding process has the advantage of avoiding expensive matched metal tooling that may be required for a cocured integrally stiffened composite part having the same geometry.

Whether cobonded joints develop the same structural performance levels as cocured joints is a matter of conjecture. The high cost of matched metal tooling has made conclusive testing prohibitive. Presently, there is no proof that cobonding is inferior to cocuring.

Historically, secondary bonding has been very susceptible to bondline failure as a result of improper cleaning and contamination (e.g., silicones). Cocured joints have demonstrated significantly less susceptibility to shop contaminants; therefore, it is anticipated that cobonding will be somewhat less susceptible to improper surface preparation than secondary bonding.

In many applications, composites are secondarily bonded or cocured with metals. Common examples are stepped lap splices and closure ribs and spars. Special attention must be given to minimizing thermal mismatch in composite to metal bonding. Carbon/epoxy and aluminum have been successfully bonded using adhesives which cure at 250°F (121°C) or less. With 350°F (177°C) curing adhesives, titanium is recommended because its coefficient of thermal expansion more closely matches that of carbon fiber composites.

Surface cleanliness is more critical for metals than composites in a bonded assembly. Aluminum, stainless steel and titanium detail parts require solvent vapor degreasing, alkaline cleaning and acid etch to produce an oxide layer with a controlled thickness and reactivity. The Forest Products Laboratory (FPL) etch, phosphoric acid anodize and chromic acid anodize processes are commonly employed as aluminum surface pre-treatments. Titanium pre-treatments include chromic acid anodize or chromated hydrofluoric acid etch processes. Phosphate solutions have proven successful in pretreating stainless steel surfaces.

In all instances, metal surfaces must be sprayed with a thin coat of adhesive bonding primer within few hours of pre-treatment. For best environmental resistance and bondline durability, a chromated epoxy primer is recommended. However, environmental regulations will restrict both the usage of chromium containing compounds and the application of primers with high volatile solvent contents. The challenge then for the coming decade is to develop environmentally friendly pre-treatment processes and primers while retaining or improving bondline durability under adverse environmental conditions and cyclic loading.

Additional information on joint design, adhesive materials selection processing, testing and quality assurance may be found in MIL-HDBK-691, Adhesive Bonding (Reference 2.7.8(b)).

2.7.9 Prebond moisture

This section is reserved for future use.

2.8 CURE AND CONSOLIDATION PROCESSES

Resin consolidation and cure processes are required to ensure that the individual sections or layers of a composite part are properly bonded, and that the matrix is intact and capable of maintaining the placement of the fibrous reinforcement which will carry the loads applied to the part. These processes are among the most sensitive in the materials processing pipeline. As a thermosetting composite part is formed during cure, the material is undergoing extensive chemical and morphological change. As a result, there are many actions occurring simultaneously. Some of these actions can be controlled directly, others only indirectly, and some of them interact. Such actions as evolution of voids or shifting of reinforcing fibers during matrix flow may result in large changes in properties of the cured composite.

In the case of a thermoplastic matrix composite, the matrix is not intended to undergo chemical change, during consolidation, but changes such as chain scissions resulting in production of volatiles may occur inadvertently. In addition, resin flow is required for consolidation, and semicrystalline thermoplastics may undergo morphological changes such as changes in the degree of crystallinity upon melting, flow and recrystallization, particularly in the fiber/matrix interphase. These changes can cause significant changes in mechanical and physical properties of the consolidated composite. In amorphous thermoplastics, segregation of varying molecular weight materials in the interphase may also result in changes in composite properties.

2.8.1 Vacuum bag molding

Vacuum bag molding is a process in which the lay-up is cured under pressure generated by drawing a vacuum in the space between the lay-up and a flexible sheet placed over it and sealed at the edges. In the vacuum bag molding process, the reinforcement is generally placed in the mold by hand lay-up using prepreg or wet resin. High flow resins are preferred for vacuum bag molding. The following steps are used in vacuum bag molding:

1. Place composite material for part into mold.
2. Install bleeder and breather material.
3. Place vacuum bag over part.
4. Seal bag and check for leaks.

5. Place tool and part in oven and cure as required at elevated temperature.
6. Remove part from mold.

Parts fabricated using vacuum bag oven cure have lower fiber volumes and higher void contents. Vacuum bag molding is a low-cost method of fabrication and uses low-cost tooling for short production runs.

2.8.2 Oven cure

Composite material can be cured in ovens using various pressure application methods. Vacuum bagging, as described in the above section, can be used to remove volatiles and trapped air, and utilize atmospheric pressure for consolidation. Another method of pressure application for oven cures is the use of shrink wrapping or shrink tape. This method is commonly used with parts that have been filament wound, because some of the same rules for application apply. The tape is wrapped around the completed lay-up, usually with only a layer of release material between the tape and the lay-up. Heat is applied to the tape, usually using a heat gun, to make the tape shrink, and can apply a tremendous amount of pressure to the lay-up. After shrinking the part is placed in the oven for cure. High quality parts can be made inexpensively using shrink tape, with a couple of caveats. First, the part must be of a configuration where the tape can apply pressure at all points. Second, flow of the resin during cure must be limited, because the tape will not continue to shrink in the oven. If the resin flows excessively, the pressure applied by the shrink tape will be reduced substantially.

2.8.3 Autoclave curing processing

2.8.3.1 General description

Autoclave curing is the process of curing materials using relatively high heat and high pressure in an autoclave. An autoclave is a heated pressure vessel typically capable of 300 psi (2 MPa) internal pressure and temperatures up to 700°F (370°C). Thermoset composite materials are generally processed at less than 100 psi and at temperatures ranging from 250 to 400°F (120 to 200°C). Thermoplastic composites may require higher temperatures and pressures. Due to the high temperatures in the autoclave during processing, the atmosphere within the vessel is generally purged of oxygen using an inert gas, such as nitrogen, to displace the oxygen thereby preventing thermal combustion or charring of the materials being cured.

Materials that are to be cured in an autoclave are located onto tooling providing the eventual shape of the cured material. The tooling, frequently referred to as the mold, may be comprised of an assembly of mandrels or tool details to accommodate complex geometry. The mold may also include features such as locating devices, tooling tabs or net-molding details to enhance the subsequent processing of the final product or material. Typically, an impervious layer of bagging film or a reusable elastic bladder is located over the material being cured and sealed against the mold. Vacuum is applied between the bagging material and the material being cured such that the plies of material are compressed through the thickness against the mold. In some instances, an autoclave or oven is used to apply heat and pressure to only a portion of the material being cured as an interim debulk step to enhance the quality of the finished product through improved consolidation. As the temperature in the autoclave is raised, the viscosity of the curing material is generally lowered to a fluid state and the gasses within and between the layers escape as the material consolidates. A porous "bleeder" layer and/or a "breather" in the form of sheet, strips or strands may be utilized under the bagging material to help enable the evacuation of gasses. Surface films or in-mold coatings may also be included against the tool surface to improve the surface finish of the cured material. Rigid caul plates or intensifiers may also be incorporated under the bagging material to locally control the thickness and quality of the finished product. In some cases, pre-cured or stage-cured components may be co-cured or co-bonded with the material being cured in the autoclave. For issues regarding specific resins, refer to Volume 3, Section 2.4.2. Also, see Volume 3, Section 2.10 for process control during autoclave curing.

2.8.3.2 Sources of variability

The primary sources of variability in the autoclave curing process are listed below:

- Tooling or mold surface finish; poor surface finish will transfer to finished product.
- Tooling materials, density, and spacing of tools in the autoclave; more, denser tools closer together will act as a heat sink and affect degree of cure.
- Part geometry; the more complex the geometry the more difficult to achieve uniform consolidation and avoid wrinkling.
- Lay-up symmetry; non-symmetrical geometry and/or lay-up cause part warpage or springback.
- Material location and alignment tolerances; non-symmetrical lay-up causes part warpage.
- Bagging technique and bagging materials including bleeder materials and cauls, etc.; vacuum bagging material movement or restriction from complete contact against curing material (i.e., bridging) causes non-uniformity in material compaction and resin flow affecting the quality of the finished product.
- Number of interim debulk cycles and debulk time, temperature and pressure (vacuum); insufficient debulking causes thickness and surface finish variability as well as wrinkles in the finished part.
- Raw material variability (including batch-to-batch variability) and material shelf life; materials are typically time and temperature dependent.
- Moisture content of materials being cured or processed; moisture in material affects laminate quality causing porosity as it turns to steam during cure.
- Number of vacuum ports, location of vacuum ports, and vacuum integrity during cure cycles; materials are consolidated through the thickness during cure as the resin flows and gels. Vacuum integrity affects the level of compaction.
- Autoclave temperature, pressure and time; variations in cure cycle affect the resin flow prior to cure, level of cure, and finished product thickness.
- Part thickness variations; thickness variations may affect consolidation and curing uniformity.

For special issues with respect to thick composites, see Volume 3, Chapter 7. For processing concerns with respect to sandwich construction, see Volume 3, Sections 2.7.7 and 2.7.8.

2.8.4 Press molding

Press curing uses heated platens to apply both pressure and heat to the part. Presses, in general, operate at 20 - 1000 psi (140 - 7000 kPa) and up to 600°F (320°C). Press curing is very economical for flat parts and high production rates. Tooling requires matched die molds for contoured parts. The following steps are used in press molding:

1. Composite material is placed in the mold cavity.
2. Cure monitoring devices are installed.
3. Parts are placed into press and cured. Pressure, temperature, and time are monitored during the cure cycle to ensure curing parameters are met.

Press curing produces high quality parts with low void content.

2.8.5 Integrally heated tooling

With integrally heated tooling the heat required for cure is provided through the tool itself, rather than through the use of external heating in an oven or autoclave. This can be used to make high quality parts without using an autoclave if matched mold tools are used. The heat is usually provided by imbedding electrical resistance elements or hot oil circulation channels within the tool. This can result in hot and cold spots within the tool. Heat surveys are necessary to ensure that all parts of the tool perform with a heat profile that allows the part to be cured completely and with high quality.

2.8.6 Pultrusion die cure and consolidation

Pultrusion is an automated process for the continuous manufacture of composites with a constant cross-sectional area. A continuous reinforcing fiber is integral to the process and the finished product. Pultrusion can be dry, employing prepreg thermosets or thermoplastics, or wet, where the continuous fiber bundle is resin-impregnated in a resin bath. The wet resin process was developed around the rapid addition reaction chemistry exhibited by thermoset polyester resins, although advances in resin and catalyst systems has made the use of epoxy systems commonplace.

In pultrusion the material is cured in a continuous process that can provide large quantities of high quality cured shapes. The material is drawn through a heated die that is specially designed for the shape being made. The tool is designed such that the volume of the cavity for cure causes the resin pressure to build, allowing consolidation of the material to occur. This cure cavity pressure is built up against the cured material that is downstream of it, and induced by the new material upstream which is continuously being drawn into the cavity. As a result this process can be very sensitive to variation in the tow and rate used for pultrusion.

The resins used for pultrusion are also very specialized. There is little time for volatile removal, consolidation, and other activities that can take considerably longer using other cure processes. The resin must be able to cure very rapidly, sometimes in less than a second, when exposed to the proper temperature. The resin must also be very consistent. Disruptions to this process can be very time consuming and expensive. Like most continuous processes, much of the operating expenses are associated with starting up and stopping the line.

The key elements in the process consist of a reinforcement delivery platform, resin bath (for wet pultrusion), preform dies, a heated curing die, a pulling system and a cut-off station. A wide range of solid and hollow profiles can be produced by the process and stitched fabrics, random mats and bidirectional reinforcements can be used in the process. The die employs a bell section opening to help reduce hydraulic resin pressures which build up in the die. The die is also plated to help eliminate die wall adhesion as well as hardened to counteract the abrasive action of the fibers.

In general the following process is used:

1. The reinforcements are threaded though the reinforcement delivery station.
2. The fiber bundle is pulled through the resin bath (if using a wet process) and die preforms.
3. A strap is used to initiate the process by pulling the resin impregnated bundle through the preheated die.
4. As the impregnated fiber bundle is pulled through the heated die, the die temperature and pulling rate are controlled such that the cure of the product (for thermosets) is completed prior to exiting the heated die.
5. The composite parts are cut off by the saw at the desired length as the continuous pultruded product exits the heated die.

The most critical process variable in pultrusion is the temperature control of the product which is a function of the temperature profile of the heated die and the line speed. Temperature control is critical because the product must achieve full cure just prior to exiting the pultrusion die. Other variables which affect cured properties are fiber tension which directly influences the fiber alignment of the final product, and resin bath viscosity which contributes to the completeness of fiber wet-out and the uniformity of the fiber to resin ratio of the final product.

2.8.7 Resin transfer molding (RTM)

RTM is a process which combines a dry fibrous reinforcement material or mixture of materials, generally referred to as a "preform", with liquid resin during the molding process, whereby the combined materials are cured to produce a 3-dimensional component. RTM is a term which is broadly applied to describe a number of variations of this general manufacturing approach throughout the aerospace and nonaerospace industries with extremely different results in terms of the quality of the end product. The conventional RTM process employs closed “hard” tooling, similar to that used for injection molding, which completely encloses the preform and precisely controls all surfaces of the component. A variation of the conventional RTM process is vacuum assisted RTM (VARTM), which employs a single-sided tooling approach with a flexible film barrier (vacuum bag) to define the "non-tooled" surface. Likewise, some variations may loosely define the preform as simple ply shapes which are placed onto the molding tool surface with little regard to orientation or location control, while others employ additional materials, tools and interim processing steps to precisely control these features of the preform. Components used in critical structural applications generally warrant a more sophisticated and well controlled version of the RTM process in order to obtain a repeatable and reliable end product. It is important that the designer or end user of an RTM component have an appreciation of these variations, as the applicability or validity of material allowables generated for RTM material combinations, and furthermore, the ability to "certify" the component for critical applications is heavily influenced by the degree of control or sophistication employed in the manufacture of the component.

RTM is applied as a cost effective means by which to produce a component due to its use of constituent materials in their simplest, and thus least expensive forms by the producer of the component. Furthermore, in conventional closed mold RTM, due to the nature of the process, extremely complex shapes and 3-dimensional load paths can be obtained, enabling the designer to combine what would otherwise be numerous individual components produced by alternative processes, thereby reducing overall part count, and therefore minimizing the cost of the end product. Unlike conventional RTM which has the capability to produce very complex part details, VARTM produces part details similar to open molding techniques since similar one-sided tools are used. Since the VARTM process usually does not require elevated pressure or heat greater than 200°F, tooling costs are far lower than for autoclave cured open molding or conventional RTM. Probably the most well-known VARTM process is SCRIMP™ (Seemann Composites Resin Infusion Molding Process) which has successfully been applied to numerous marine structures, primarily pleasure boat hulls. Other proprietary VARTM processes include the Marco Method, Paddle Lite, Prestovac, Resin Injection Recirculation Molding (RIRM), and Ultraviolet (UV) VARTM . Careful consideration must be given, however, when designing the component or specifying the RTM process, to determine those features which are necessary for the application so as not to misuse the fabrication approach when an alternative or variation may be more cost effective.

The conventional RTM process begins with the fabrication of the preform whereby the fibrous reinforcement material or materials are formed and/or assembled to produce the geometry and load paths warranted by the application. These fibrous materials may be woven into broadgoods, braided into tubular goods or applied directly onto tooling, or otherwise combined and/or processed with additional materials such as binders or tackifiers which will define the geometry of the reinforcement in the end product. Likewise, 3-dimensional reinforcement may be incorporated into the preform as part of the weaving or braiding process, or as secondary processes such as stitching or alternative fiber insertion techniques. The preform is then located onto the tooling or into the mold and impregnated with the liquid resin, and subsequently cured while contained within the tooling to produce the as-molded geometry of the end product. Depending on the resin being utilized and the desired end product material properties, the cure cycle may require the application of elevated temperatures to produce the final cure state of the product. The cured component must then be removed from the tooling for trimming, machining, finishing and final inspection as applicable. The following general steps are employed for any RTM process:

1. Produce the fibrous reinforcement preform (weaving, braiding, cutting, forming, assembling).
2. Locate the preform onto the tooling or into the mold (this may also entail further assembly of preforms or reinforcement materials).
3. Impregnate the preform with liquid resin (this may require preheating of the assembled tooling and preform, heating of the resin, application of vacuum and/or pressure).
4. Cure (room temperature, elevated temperature, or alternative cure techniques).
5. Remove cured component from tooling for further processing.
6. Post cure (if required).

Variations of (or processes which resemble) the RTM process are Vacuum Assisted RTM (VARTM) and Resin Film Infusion (RFI), in that they incorporate the basic philosophy of combining the dry reinforcement preform and the resin during the molding process which produces the final cured component geometry. An almost endless variety of reinforcement materials, resins and combinations thereof may be employed in the RTM process, offering a large degree of freedom to the designer.

In the VARTM process, the preform is usually fabricated directly onto the tool. Each layer of reinforcement is applied and held in place using a binder or tackifier. Resin inlet tubes are positioned above the part in optimum locations to enable the resin to fully wet out the part prior to the resin gel. Vacuum tubes connected to a vacuum manifold are positioned around the perimeter of the part. The part is vacuum bagged with conventional nylon vacuum bagging film and sealant tape, allowing the resin and vacuum lines to penetrate the bag along its edges. Vacuum is applied to the part, the bag is positioned so as to prevent bridging, and a leak test is performed. The resin lines are inserted into an open container of mixed liquid resin. When the lines are opened the resin is forced through the part by the pressure differential between the resin and the vacuum bag. After it is fully wetted out, the part is allowed to initially cure at room temperature or at an elevated temperature in a convection oven. Alternate methods of cure including ultraviolet, electron beam and microwave have also been employed. The part is then removed from the tool, the process materials are removed, the part is post cured (if required), and finally trimmed.

RFI is a type of RTM in which resin infusion is accomplished by placing resin against the preform. Resin form and placement vary with the resin and tool. Parts have been fabricated using resin in the form of tiles, films, and liquid, with placement either above or below the preform. Resin flows through the preform during cure and vent holes are located at the high points of the tool. Any gaps in the tooling will allow resin leakage that will produce localized dry areas. Generally, parts are bagged and cured using procedures similar to the autoclave cure process.

The benefit of RFI over other resin transfer processes is lower tooling cost because matched metal tooling is not needed. Also, resin is transferred relatively short distances (essentially through the thickness), so part size is not dependent on resin flow capacity and very large parts can be produced. The short transfer distance also increases the number of potential resins, including higher performance resins. Another potential advantage of the process is improved damage tolerance due to the capability to produce unitized structure using stitched preforms. Continuous fiber volume is typically 55-60% by weight and, therefore, other mechanical properties such as tension and compression, are close to those achieved with hand lay-up.

The RFI process has been demonstrated with a variety of resins including epoxies (Hexcel 3501-6, Fiberite 977-3), bismaleimide (Cytec 5250-4RTM) and versions of Dupont K3Bresins. Unitized panels have been successfully fabricated with blade, “J,” and hat stiffeners with the above resins. A wing stub box, 1220 pounds and 12 foot long, has been fabricated and tested by NASA to validate the process.

The degree of control of the following variables within the RTM process and how they may affect the end product are as follows:

1. Constituent materials from suppliers - affect laminate strength, stiffness, processability, porosity, surface finish.
2. Reinforcement materials production (weaving, braiding, etc.) - affect laminate strength, stiffness due to fiber orientation, fiber damage, areal weight/fiber volume.
3. Reinforcement materials processing (application of binders or tackifiers and other materials) - affect ability to form materials/define shapes, ability to form multiple layers simultaneously, permeability changes which affect ability to impregnate preform, could affect laminate structural properties if materials are incompatible with each other.
4. Cutting and stacking of plies - affect orientation of materials or lay-up sequence which establishes structural properties, ply drop-offs within the component which define local fiber volumes.
5. Forming of shapes/preforming - affect ply orientation, ply drop-offs, local fiber volumes.
6. Assembly of preforms/tooling - affect ply/fiber orientation and alignment, ply drop-offs, fiber volumes, part geometry, ability to flow resin and impregnate preform.

7. Liquid resin processing/cure parameters (time/temperature profile, vacuum, pressure, flow rate, viscosity of resin) - affect laminate porosity level, glass transition temperature (T_g), laminate surface finish quality.
8. Demolding and tool cleaning (removing part from tooling) - affect laminate integrity due to possible delamination, surface finish (scratches, gouges).
9. Tooling design and tooling materials selection (coefficient of thermal expansion (CTE) considerations) - affect tool life, part surface finish, part integrity (which could be affected by CTE mismatch causing laminate damage), and processability.

2.8.8 Thermoforming

Thermoforming fiber-reinforced thermoplastics. The thermoforming process, as applied to thermoplastic composite materials, is generally divided into two categories: melt-phase forming (MPF) and solid-phase forming (SPF). Thermoforming capitalizes on the rapid processing characteristics of thermoplastics. The composite thermoforming process can be broken down to four basic steps:

1. The material is heated to its processing temperature external to the forming tool. This can be accomplished with radiant heat.
2. The oven-heated material is rapidly and accurately transferred to the forming tool.
3. The heated material is pressure-formed with matched die set tooling into desired shape.
4. The formed laminate is cooled and its shape is set by sinking the heat into the tooling.

MPF is performed at the melting point of the thermoplastic matrix and requires sufficient pressure and/or vacuum application during the forming process to provide complete consolidation. The MPF process is preferred when sharp contour changes requiring some level of resin flow are a characteristic of the part geometry.

SPF is generally performed at temperatures between the onset of crystallization and below the peak melting point. This temperature range provides sufficient formability while the material remains in a solid form. SPF allows forming of preconsolidated sheet to be performed without a consolidation phase, but it is limited to part geometries exhibiting gentle curvatures.

The processing time for thermoforming is governed by the rates at which heat can be added to the material and then removed. This is primarily a function of the material thermal properties, material thickness, forming temperature, and tooling temperature. The pressures required to shape the material are dependent on various factors including part geometry, material thickness, and formability. The general deformability behavior of thermoplastics also depends on the strain-rate used during forming and the thermal history of the thermoplastic matrix. The forming process can affect such final properties as:

1. Degree of crystallinity,
2. Glass transition temperature,
3. Fiber orientation/alignment,
4. Uniformity of the fiber to resin ratio,
5. Residual stress,
6. Dimensional tolerances, and
7. Mechanical Properties.

The forming process has s significant effect on the quality of the finished part. High quality parts with predictable engineering properties require that a well controlled thermoforming process developed for specific applications be utilized.

2.9 ASSEMBLY PROCESSES

Assembly processes are not conventionally covered within composite material characterization, but can have a profound influence on the properties obtained in service. As seen with test coupons, edge and hole quality can dramatically affect the results obtained. While these effects are not usually covered as material properties, it should be noted that there is an engineering trade-off between part performance and the time and effort expended toward edge and hole quality. These effects need to be considered along with the base material properties.

2.10 PROCESS CONTROL

Composite structures have the potential to provide higher performance in many applications. In order for this potential to be fulfilled, it must be possible to cost effectively manufacture parts of high, uniform quality. During cure of composite parts, the material is being made at the same time as the part. As a result, there are many actions happening at the same time. Some of these actions can be controlled directly, others only indirectly, and some of them interact. Process control is one of the methods used to manage the variability associated with composites.

2.10.1 Common process control schemes

Process control is used to attempt to direct these many changes during cure to reach many objectives. The manufacture of high quality parts is one objective. Others include exotherm avoidance, minimization of cure times, and addressing part specific manufacturing problems. Several different approaches to process control can be pursued: empirical, active, and passive. The most common is empirical, or trial and error. Many different sets of cure conditions are attempted, with the cure conditions providing the best results being picked for manufacturing. The second is active, or real-time process control. Here data is acquired during the cure from the part in question. Data that can be acquired includes temperature, pressure, resin viscosity, resin chemical characteristics (degree of cure), and average ply thickness. An expert system is used to analyze the cure information, and direct the autoclave how to proceed with the cure. The third is passive, or off-line process control. Here mathematical models are used to predict the response of the part during cure. Many different cure approaches can be simulated, and the one that best meets the needs at hand are applied.

Each of these process control approaches benefit from an understanding of the effects and interrelationships that are occurring during the cure of the resin. This understanding is referred to as a process control model. The model remains the same regardless of which particular type of process control is attempted for a particular application.

2.10.1.1 Empirical methods

This section is reserved for future use.

2.10.1.2 Active sensor-based control

This section is reserved for future use.

2.10.1.3 Passive model-based control

This section is reserved for future use.

2.10.2 Example - autoclave cure of a thermoset composite

A generic process control model can be used to evaluate and develop composite cures that produce high quality parts. When the resin is heated and has begun to flow, the system can be divided into gas (volatiles or trapped air), liquid (resin), and solid (reinforcement) phases. All void producing gas phase material should be either eliminated or absorbed by the liquid phase. The liquid phase should be uniformly distributed throughout the part, maintaining or producing the desired resin content. The solid phase should maintain its selected orientation. There are several initial factors that must be determined in order to cure parts, and which are used as input for the process model. These initial factors have been broken down into the following categories: resin, time, heat, applied pressure, process materials, design, and reinforcement. It is well known that different resins, even within the same general material family, do not always provide equivalent results when processed in the same manner. The cure times and temperatures, including dwell(s) and heat up rates, usually control heat flow. For thick structures heat from resin exotherm can be dominant. The pressure to be used during cure must be determined, and may be changed substantially during the cure. Vacuum bagging or other process materials may be used to perform actions such as resin bleed, but can also have other effects, especially when they fail. Design choices such as the use of sandwich construction and radii affect the results obtained with the cure. Finally, although the reinforcement is usually intended to just maintain its orientation, it does influence gas and liquid flow, and picks up some of the applied pressure.

The number of initial factors alone makes composite processing difficult. What makes it even more complicated is that these initial factors affect the desired results and interact with each other in complex, non-linear relationships. Because of this, adjusting one factor in a seemingly logical fashion often does not obtain the desired results. A diagram of such a process model is shown in Figure 2.10.2. This particular model was designed for autoclave cure of thermoset composites. However, this model would also be largely applicable to most other composite and adhesive cure processes with slight modification. The initial factors are shown at the top of the figure, and the desired output at the bottom. The center area between the initial factors and the desired outputs represents the process interactions. These process interactions are: degree of cure, viscosity, resin pressure, void prevention, and flow. By using this model, cure process changes and optimization can be performed in a logical progression rather than a hit-or-miss fashion. Each of these process interactions is discussed in turn.

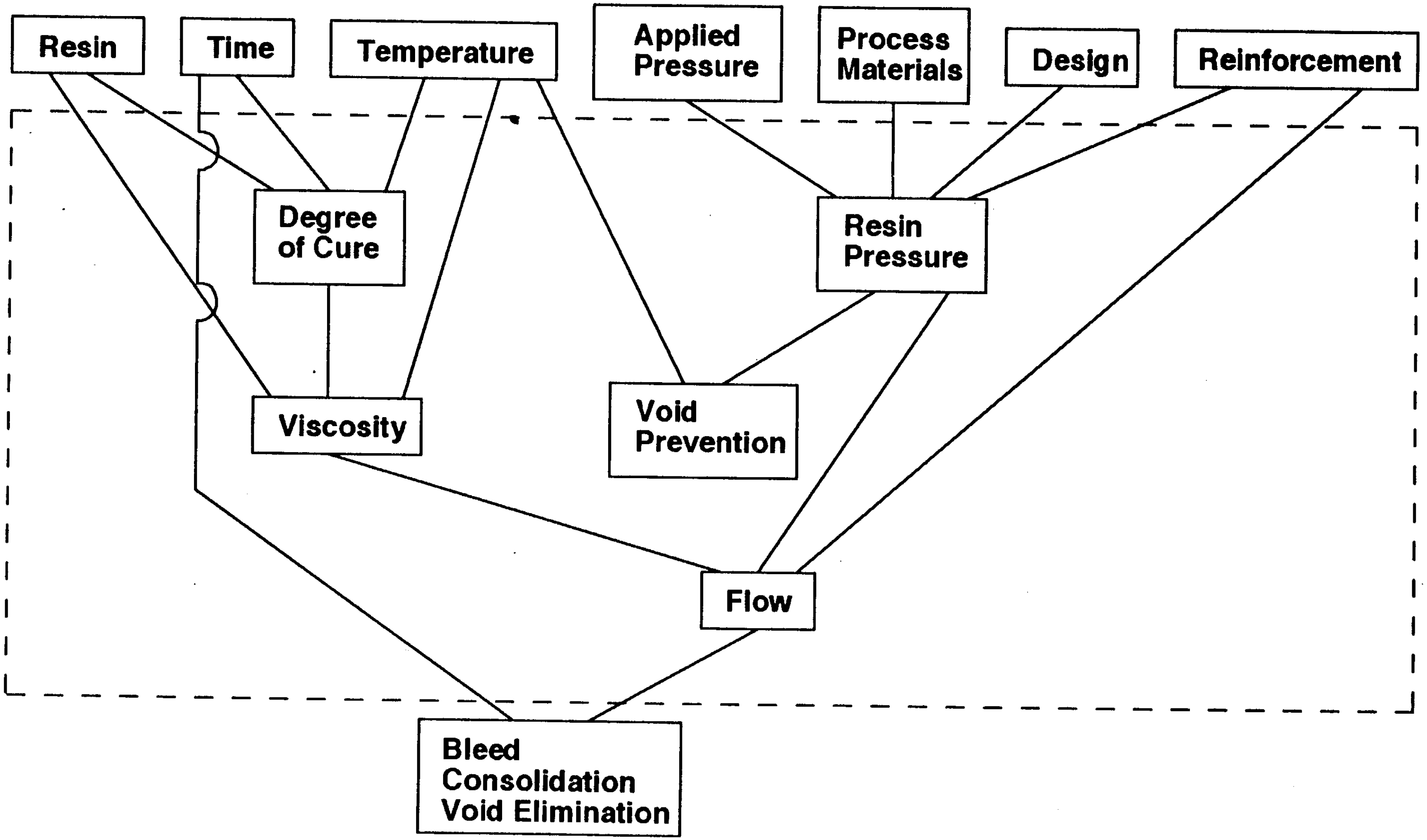
2.10.2.1 Degree of cure

The resin degree of cure acts primarily as an input to the viscosity interaction. Determining the rate of change of degree of cure for a resin requires a knowledge of the particular response for the individual resin and the temperature history for the resin. The resin heat of reaction is used as an index of degree of cure. The rate of change of degree of cure is then calculated as a function of the current degree of cure and the temperature. The rate of change of degree of cure is often not linear, which is why it is difficult to estimate the response of a resin to a new temperature profile without a model. In addition, in thick structures the heat of reaction may contribute significantly to the temperature of the resin, in turn affecting the degree of cure, and the viscosity. After the resin has gelled , the glass transition temperature is often used as an index of degree of cure.

2.10.2.2 Viscosity

The resin viscosity is a function of the resin degree of cure and temperature. The resin viscosity response function does vary from resin to resin. Thermoplastic resins do not chemically react during the fabrication process ("cure"), but do flow upon melting of the resin. Because the chemical makeup of the resin is not changing, the viscosity of a thermoplastic resin is strictly a function of the temperature. In other words, the viscosity effects are entirely physical, and no chemical interactions come into play. However, two different thermoplastic resins may have different viscosities at the same temperature due to chain length or other chemical differences.

A thermoset resin does react, so its chemical makeup is constantly changing during cure. Because of increases in chain length and crosslink density, the viscosity of the resin at a given temperature will increase over time. This is because there is increased interaction between the chains, and they become increasingly entangled with each other. Once chain extension and cross-linking have extended sufficiently, a thermoset resin will gel. The reason that viscosity effects for thermoset resins are much more difficult to predict than for thermoplastics is this continuous, sometimes rapid, change in the chemical makeup of the system.



7

FIGURE 2.10.2 *Composite cure process model.*

2.10.2.3 Resin pressure

The pressure applied to a laminate is usually not the same as that which is experienced by the resin, referred to as resin pressure. The concept of resin pressure is frequently conceptualized with a spring and dashpot type model, with resin as the fluid, and the fiber pack as the spring. If the spring is completely surrounded by the fluid, it cannot pick up any of the applied load. If there is not enough resin to surround the spring, due perhaps to resin bleed, the spring (fiber pack) will pick up an increasing percentage of the load. The resin loses the corresponding amount of pressure. A diagram of this model can be seen in Figure 2.10.2.3.

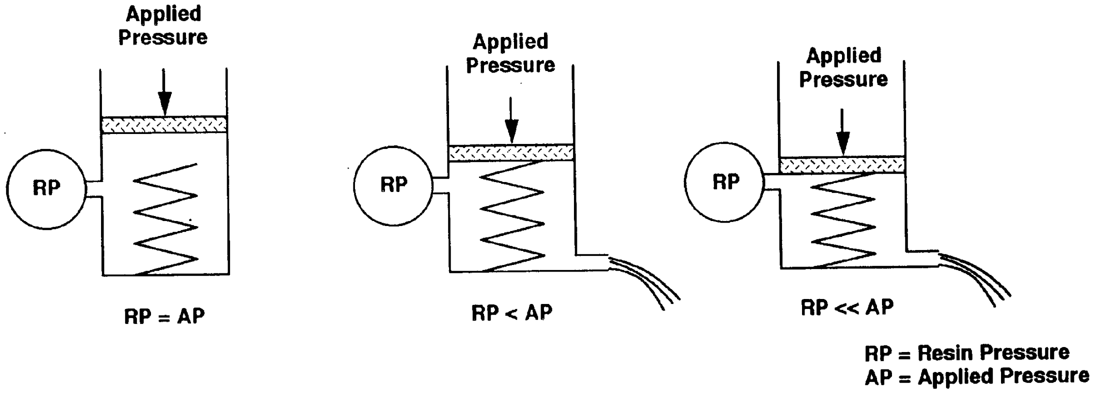


FIGURE 2.10.2.3 *Spring and dashpot model for resin pressure.*

Resin pressure is important because it is the driving force for moving resin and gas phase material from one place to another, and because it helps prevent formation of voids. Resin pressure is a function of the applied pressure, how and what process materials are used for cure, the design, and the reinforcement. If there is not sufficient resin to completely surround the reinforcement, then the reinforcement will pick up some or all of the load.

Just as the reinforcement can pick up applied pressure, so can the other process materials, especially the breather and bleeder. These items act as additional springs in the dashpot/spring model, and can absorb a significant amount of the applied pressure, especially for lower pressure cures. One of the design factors affecting the resin pressure is the use of materials such as honeycomb and some types of foam core. With co-cured skins, if a force is applied to the tool or bag side of the skin, resin pressure will be created, but all the resin has to do is flow slightly into the cell to relieve this pressure. This results in quality problems with honeycomb parts, especially if the skins are fairly thin, such as less than five plies. If the skins are fairly thick, then through the thickness resin pressure variations could be present. This would allow the surface of the parts at the tools surface to be under appreciable resin pressure, while at the honeycomb side the resin pressure would be near zero. Given an infinite amount of time, these pressures would equalize, but not in the time frame for many cures. When the skins are thin, the resin pressure is near zero. Thus the skins on thin skin honeycomb are cured with near zero resin pressure, essentially a contact lay-up, and the quality of the skins is often reduced. Because of the resistance that the reinforcement provides, some interesting resin pressure effects can be noted, along with their consequences on part quality. Just as through the thickness variations in resin pressure can be established, they can also be present in the plane of the reinforcement. This helps explain why widely different laminate quality can be present on the same part cured at the same time. Consider the bridging of the fiber reinforcement in a tight corner. Unless the plies can slide past each other to contact the tool in this corner, the reinforcement is, by definition, picking up all of the pressure applied by the autoclave, and the resin pressure is zero. At the location of bridges it can often be seen that increased porosity has occurred, voids at the tool interface are present, and excess resin has built up. These are all due to the fact that the resin pressure in this location is near zero.

Areas surrounding this bridging may have adequate resin pressure. A series of experiments on honeycomb panels revealed that while the resin pressure in the skins (co-cured) was near zero, the resin pressure in the edge band (laminate) was significantly higher. The quality of the laminate in the edge band area was significantly higher even though the two points were only inches apart. This demonstrates the concept of differing resin pressures in close proximity.

2.10.2.4 Void prevention

Some resin systems, especially the higher temperature systems such as polyimides and phenolics, produce volatiles as a part of the cure reaction chemistry. While these byproducts are being evolved, the applied pressure should be minimal, and vacuum applied. As soon as all the volatiles have been created, then resin pressure can be used to drive out any volatile products remaining prior to gel. Once the resin has gelled, flow of the resin has been completed, and issues such as resin content, bleed, volatile content have been settled. The continuing cure advances the cure of the resin, but the physical configuration of the resin is locked in.

Some volatiles may be present in the prepreg, the most common being absorbed moisture. If resin pressure is maintained above the volatile vapor pressure until gel, these compounds cannot volatilize, increasing their volume many-fold, and forming additional voids and/or porosity. This functions in the same manner as a car radiator, as diagramed in Figure 2.10.2.4.

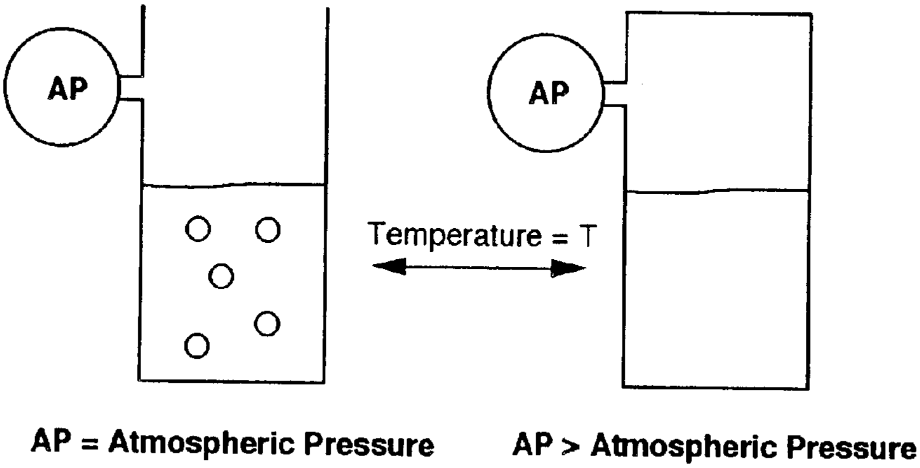


FIGURE 2.10.2.4 *Void prevention resin pressure model.*

2.10.2.5 Flow

The viscosity, resin pressure and reinforcement factors feed into the flow factor. The viscosity and reinforcement can be thought of as resistances to flow, while the resin pressure can be thought of as the driving force for flow. The amount of flow that occurs due to these factors is then a function of time. This is consistent with experience. If the resin is more viscous, less flow would be expected with the same resin pressure and reinforcement. If the reinforcement is changed, perhaps to a tighter weave, then the resistance to resin and gas phase flow is increased. Once these flow characteristics have been established, then they and the time available for flow determine how bleed of the laminate takes place, how the laminate is consolidated, and the elimination of voids present in the lay-up or formed during the cure.

2.11 PREPARING MATERIAL AND PROCESSING SPECIFICATIONS

Requirements for materials and processes are frequently so specific and extensive, a special type of engineering drawing format was developed. Material and process specifications are one of the ways used to control composite material variability. Specifications are usually E-sized engineering drawings (see MIL-STD-961D (Reference 2.11)). They are part of the engineering package that defines a particular product, whether an airplane or a golf club.

2.11.1 Types of specifications

Material and process specifications are similar but do have some differing requirements.

2.11.1.1 Material specifications

The primary purpose of material specifications is to control the purchase of critical materials. The properties and values contained in the specification will relate to, but not necessarily be identical to, the properties used for activities such as design and structure testing. The properties and values contained in the specification are used to assure that the material does not change substantially with time. This is especially critical for materials used in primary applications, and which have undergone expensive qualifications. Material specifications are included in relevant contracts, and are part of the purchase order requirements to purchase material.

2.11.1.2 Process specs - controls end product

Process specifications establish the procedures that are required to control the end product. The more process dependent the materials and/or end product are, the more detailed and complex the process requirements. On the other hand, if there is a wide window of acceptable product produced by the process, the requirements may be minimal. Composite and adhesive bonding processing specifications are usually detailed because the materials are very sensitive to process variations, and the aerospace end item requirements are usually very stringent.

2.11.2 Format for specifications

Most specifications follow a similar format, based on guidelines contained in documents such as MIL-STD-961D (Reference 2.11). The sections of a material or process specification are generally as follows: scope, applicable documents, technical requirements or process controls, receiving inspection and quality control, delivery, notes, and approved sources and other. Each is covered in more detail in the following sections.

2.11.2.1 Scope

The first section is the scope, which generally describes the materials or processes covered by the specification in a few sentences. Also covered in this first section are any types, classes, or forms, of the materials that are governed by the specification. Another method for handling different material configurations is the use of slash sheets. These slash sheets are part of the base document, but provide the additional information that is specific to that particular material. For example, one material specification may cover several different thicknesses of the same film adhesive, each thickness being a different class. The scope section establishes the shorthand terminology, or callout, which is used to identify the material on other engineering and procurement documents. A process specification may cover multiple processes, such as anodizing, with minor process variations based on the type of alloy being processed.

2.11.2.2 Applicable documents

The second section identifies all the other documents that are referenced within the specification. Testing procedures, and other material and process specifications may be called out. A trade-off is made between a specification being self contained, and redundancy between multiple specifications for similar materials or processes. For example, if a change to a testing procedure is required, only a change to the referenced testing specification is required. If the specifications are all self contained, the test procedure within each specification must be revised. The time and expense associated with changes to common materials and procedures can be substantial. However, when only a limited amount of information is required, the modular approach can bring along a great deal of unused information. These configuration management issues are discussed in more detail in a following section.

2.11.2.3 Technical requirements/process controls

The third section covers the technical requirements for the material or controls for the process. For a materials specification, these requirements can include physical, chemical, mechanical, shelf and work life, toxicity, environmental stability, and many other characteristics. The requirements can be minimum values, maximum values, and/or ranges. Sometimes it is only required that the data obtained from the test be submitted. Only the test result requirements are contained in this section. The test procedure used to obtain this result is covered in the next section. For a process specification, the controls required to ensure the product produced is consistent are specified.

2.11.2.4 Receiving inspection and qualification testing

The fourth section covers testing. Receiving inspection testing is that which is performed each time a quantity of the material is purchased, or a lot of product is processed. Although it is required that all the requirements of the specification be met at all times, only a fraction of the tests are performed routinely. Qualification testing usually involves testing to all of the requirements of the specification to insure that the supplier or processor is capable of meeting the requirements, and is performed only once unless there is cause.

Responsibility for the testing required is also delineated. The manufacturer may do all their receiving inspection testing, or the user may perform additional testing upon receipt of the material. Required reports are defined, as well as requirements for resampling and retesting if a requirement is initially failed.

Sampling and the specific test procedures to be used to determine conformance to the technical requirements are contained in this section. Testing procedures can be critical. In most cases, the value obtained cannot be used unless the specific test used to generate the value is documented. Test results can change when test procedures change, even though the material being tested has not changed itself. Also important is the preparation of the test specimens. Test results can vary widely depending on the configuration and condition of the test specimens. The conditions under which the test is performed can dramatically change the results. Preconditioning of the specimen prior to test is also important, such as exposure to elevated temperature and humidity prior to test.

2.11.2.5 Delivery

Delivery requirements are covered in the fifth section. Issues such as packaging and identification, storage, shipping and documentation must be established. Packaging is especially critical for temperature sensitive materials such as prepreg and film adhesive.

2.11.2.6 Notes

The sixth section is usually notes, although sixth and later section formats can vary substantially. Notes are additional information for reference, and are not requirements unless specifically stated in the requirements section.

2.11.2.7 Approved sources and other

Seventh and additional sections can include information such as what materials are qualified to the specification. This section may reference a separate document that lists the qualified materials. Because of the substantial expense that can be experienced as a result of qualification, normally only materials that are currently qualified are used for production applications.

2.11.3 Specification examples

Specifications in common use are generally released by industry associations or the military. Industry associations common to composite and adhesive bonded structure are SAE, ASTM, and SACMA. In addition, companies may develop their own internal specifications for materials or processes that are not adequately covered by industry/military specifications, or to protect proprietary information. Company specifications may be similar in style and content to industry and military specifications, but can vary widely in approach and level of control. Each has advantages and disadvantages.

2.11.3.1 Industry

Examples of industry specifications are as follows:

AMS 3897	Cloth, Carbon Fiber, Resin Impregnated
AMS 3894	Carbon Fiber Tape and Sheet, Epoxy Resin Impregnated

AMS specifications are available from SAE, 400 Commonwealth Drive, Warrendale, PA 15096-001.

2.11.3.2 Military

Examples of military specifications are as follows.

MIL-A-83377	Adhesive Bonding (Structural) for Aerospace and Other Systems, Requirements for
MIL-P-9400	Plastic Laminate and Sandwich Construction Parts and Assembly, Aircraft Structural, Process Specification Requirements
MIL-T-29586	Thermosetting Polymer Matrix, Unidirectional Carbon Fiber Reinforced Prepreg Tape (Widths up to 60 Inches), General Specification for

Military specifications are available from DODSSP, Standardization Document Order Desk, 700 Robbins Ave., Bldg. 4D, Philadelphia, PA 19111-5094.

2.11.4 Configuration management

Most major aerospace companies use many materials and process specifications to control and define their products, and those made by their subcontractors. Many companies prefer to have a company controlled specification for some materials and processes, even when equivalent industry or military specifications are available. Industry and military specifications are, by definition, consensus documents. Reaching this consensus can take a good deal of time, and may conflict with a specific company's objectives. With company control, tailoring of the specification to company requirements can be relatively easily effected. Company specifications do allow tailoring, but at the cost of standardization. Company specific tests and procedures incur additional expense. There may be many specifications that govern essentially the same material. Sometimes this is because different specifications offer different levels of control (testing). The amount and complexity of testing required for procurement of material can soon account for a large percentage of the total cost of the material. If only minor changes to the specification are made, amendments or supplements can be released. Some specification changes may only be in effect for limited periods of time, or restricted to certain facilities. Control of the current and prior versions of specifications is an important issue. Specification changes can have a great influence on manufacturing operations, and if additional expenses are associated with the changes in the revision, prices and timing for implementation may have to be negotiated. Not all operations and subcontractors may start work per a new revision of a specification at the same time. In addition, confusion frequently arises from different parties unintentionally using different revisions, or versions, of the same specification.

REFERENCES

2.4.1.1 Multicomponent Polymer Systems, I. Miles and S. Rostami ed., Longmore Scientific and Technical, 1992.

2.4.1.1.1 Engineered Material Handbook Volume 1: Composites, ASM International, 1987.

2.4.1.1.3.1.3 Technology of Carbon and Graphite Fiber Composites, J. Delmonte, Krieger, 1987.

2.4.1.2(a) *Data Manual for Kevlar™49 Aramid*, E.I. Du Pont de Nemours & Co., Wilmington, DE 1989.

2.4.1.2(b) Krueger, W.H., et al., "High Performance Composites of J2 Thermoplastic Matrix Reinforced with Kevlar™ Aramid Fiber," *Proceedings of the 33rd International SAMPE Symposium*, March 1988, pp. 181-193.

2.4.1.2(c) Gruber, M.B., "Thermoplastic Tape Laydown and Consolidation," SME Technical Paper EM86-590.

2.4.1.2(d) Okine, R.K., et al., "Properties and Formability of a Novel Advanced Thermoplastic Composite Sheet Product," *Proceedings of the 32nd International SAMPE Symposium*, April 1987, pp. 1413-1425.

2.4.1.2(e) Egerton, M.W. and Gruber, M.B., "Thermoplastic Filament Winding Demonstrating Economics and Properties via In-Situ Consolidation," *Proceedings of the 33rd International SAMPE Symposium*, March 1988, pp. 35-46.

2.4.1.2(f) Khan, S., "Environmental Effects on Woven Thermoplastic Composites," *Proceedings, Materials Week™, 87*, ASM International, Cincinnati, OH, October 10-15, 1987.

2.4.1.3.1(a) "PPG Fiber Glass Yarn Products/Handbook," PPG Industries, Inc., 1984

2.4.1.3.1(b) *Engineered Materials Handbook*, ASM, International, Metals Park, Ohio, 1987, pp. 107-100.

2.4.1.3.1(c) "Textile Fibers for Industry," Owens-Corning Fiberglas Corporation, Pub. No. 5-TOD-8285-C, September 1985.

2.4.1.3.2(a) ASTM Specification D 579, "Greige Woven Glass Fabrics Fiber Yarns," Annual Book of ASTM Standards, Vol 7.01, American Society for Testing and Materials, West Conshohocken, PA.

2.4.1.3.2(b) ASTM Specification D 578, "Glass Fiber Yarns," Annual Book of ASTM Standards, Vol 7.01, American Society for Testing and Materials, West Conshohocken, PA.

2.4.1.3.4(a) "Discover S-2 Glass Fiber," Owens-Corning Fiberglas Corp., Pub. No. 5-ASP-13101-A, 1986.

2.4.1.3.4(b) "Industrial Fabrics," Clark - Schwebel Fiber Glass Corp.

2.4.1.3.4(c) "Product Bulletin," Stratifils H_R/P109.

2.4.1.4(a) Shoenberg, T., "Boron and Silicon Carbide Fibers," *Engineered Materials Handbook, Volume 1, Composites*, ASM International, Metals Park, Ohio, 1987, pp. 58-59.

2.4.1.4(b) Bascom, W.D., "Other Continuous Fiber," *Engineered Materials Handbook, Volume 1, Composites*, ASM International, Metals Park, Ohio, 1987, pp. 117-118.

2.4.1.4(c) Krukonis, V., "Boron Filaments," *Handbook of Fillers and Reinforcements for Plastics*, H. Katz and J. Milewski, eds., Van Nostrand Reinhold, Co., 1978.

2.4.1.4(d) DeBolt, H.E., "Boron and Other High Strength, High Modulus Low-Density Filamentary Reinforcing Agents," *Handbook of Composites*, G. Lubin, ed., Van Nostrand Reinhold Co., 1982, pp. 171-195.

2.4.1.4(e) MIL-HDBK-727, *Design Guide for Producibility*, Chapter 6.

2.4.1.4(f) "Boron Monofilament, Continuous, Vapor Deposited," MIL-B-83353.

2.4.1.4(g) "Filaments, Boron - Tungsten Substrate, Continuous," AMS 3865B.

2.4.1.6(a) *Advanced Materials*, Carrol-Porczynski, Chemical Publishing, 1962, pp. 117,118.

2.4.1.6(b) *Engineered Materials Handbook*, ASM International, Vol I, Metals Park, Ohio, 1987, p.58-59.

2.4.1.6(c) Lynch, et al., "Engineered Properties of Selected Ceramic Materials," *Journal of American Ceramic Society*, 1966, pp. 5.2.3-5.2.6.

2.4.1.6(d) *Advanced Materials and Processes*, "Guide to Selected Engineered Materials," Vol 2, No 1, June 1987, pp. 42-114.

2.4.1.6(e) BP Chemical, Advanced Materials Division, Carborundum.

2.4.1.7 "Quartz Yarn of High Purity," AMS 3846A.

2.4.1.8(a) Spectra® fiber properties product data of Allied Signal Inc., Petersburg, VA, May 1996.

2.4.1.8(b) Strong, A.B., *Fundamentals of Composites Manufacturing: Materials, Methods, and Applications,* SME, Dearborn, Michigan, 1989.

2.4.1.8(c) Billmeyer, Jr., F.W., *Textbook of Polymer Science,* 3rd Ed., John Wiley & Sons, New York, 1984.

2.4.1.8(d) Ladizesky, N.H., and Ward, I.M., "A Study of the Adhesion of Drawn Polyethylene Fibre/ Polymeric Resin System," *Journal of Material Science*, Vol. 18, 1983, pp. 533-544.

2.4.1.8(e) Adams, D.F., Zimmerman, R.S., and Chang, H.-W., "Properties of a Polymer-Matrix Composite Incorporating Allied A-900 Polyethylene Fiber," *SAMPE Journal*, September/October 1985.

2.4.2.7.1(a) Hertzberg, R.W., *Deformation and Fracture Mechanics of Engineering Materials*, John Wiley & Sons, New York, 1976 p. 190.

2.4.2.7.1(b) Kaufman, H.S., "Introduction to Polymer Science and Technology," Lecture Notes.

2.4.2.7.1(c) "The Place for Thermoplastics in Structural Components," Contract MDA 903-86-K0220, pp. 1-2, 20, 29.

2.4.2.7.1(d) Murtha, T.P., Pirtle, J., Beaulieu, W.B., Waldrop, J.R., Wood, H.D., "New High Performance Field Installed Sucker Rod Guides," *62 Annual Technical Conference and Exhibition of SPE*, Dallas, Texas, September 1987, pp. 423-429.

2.4.2.7.1(e) Brown, J.E., Loftus, J.J., Dipert, R.A., "Fire Characteristics of Composite Materials - a Review of the Literature," NAVSEA 05R25, Washington, DC, August 1986.

2.4.2.7.1(f) "The Place for Thermoplastics in Structural Compounds," contract MOA 903-86-K-0Z20, Table 3-5, p. 1.

2.4.2.7.1(g) Horton, R.E., McCarty, J.E., "Damage Tolerance of Composites," *Engineered Materials Handbook*, Volume 1, Composites, ASTM International, 1987, pp. 256-267.

2.4.2.7.1(h) Silverman, E.M., Griese, R.A., Wright, W.F., "Graphite and Kevlar Thermoplastic Composites for Space Craft Applications," *Technical Proceedings, 34th International SAMPE Symposium*, May 8-11, 1989, pp. 770-779.

2.4.2.7.1(i) Shahwan, E.J., Fletcher, P.N., Sims, D.F., "The Design, Manufacture, and Test of One-Piece Thermoplastic Wing Rib for a Tiltrotor Aircraft," *Seventh Industry/Government Review of Thermoplastic Matrix Composites*, San Diego, California, February 26-March 2, 1991, pp. III-C-1 - III-C-19.

2.4.2.7.1(j) Lower Leading Edge Fairing to AH-64A Apache Helicopter-Phillips 66-McDonnell Douglas Helicopter Prototype Program.

2.4.2.7.2(a) *Modern Plastics Encyclopedia*, Materials, McGraw-Hill, 1986-1987, p. 6-112.

2.4.2.7.2(b) Koch, S., Bernal, R., "Design and Manufacture of Advanced Thermoplastic Structures," *Seventh Industry/Government Review of Thermoplastic Matrix Composites Review*, San Diego, California, February 26-March 1, 1991, pp. II-F1 - II-F-22.

2.4.2.7.2(c) Stone, R.H., Paul, M.L., Gersten, H.E., "Manufacturing Science of Complex Shape Thermoplastics," *Eighth Thermoplastic Matrix Composites Review*," San Diego, California, January 29-31, 1991, pp. I-B-1 - I-B-20.

2.7.7(a) Lubin, G., *Handbook of Composites*, Van Nostrand Reinholt, 1982, Chapter 21, "Sandwich Construction".

2.7.7(b) MIL-P-9400C, *Plastic Laminate and Sandwich Construction, Parts and Assembly, Aircraft Structural, Process Specification Requirements*.

2.7.7(c) MIL-HDBK-23 (Canceled), *Structural Sandwich Construction*.

2.7.7(d) MIL-STD-401, *Sandwich Constructions and Core Materials: General Test Methods*.

2.7.8(a) Kinloch, A.J., Kodokian, G.K.A., and Watts, J.F., "The Adhesion of Thermoplastic Fiber Composites," *Phil. Trans. Royal Soc: London A*, Vol. 338, pp. 83-112, 1992.

2.7.8(b) MIL-HDBK-691B, Adhesive Bonding, Defense Automation and Production Service, Philadelphia, PA, 1987.

2.11 MIL-STD-961D(1), DoD Standard Practice, Defense Specification, Executive Agent for the Defense Standardization Program, Falls Church, 1995.