2 Materials

Major constituents in a fiber-reinforced composite material are the reinforcing fibers and a matrix, which acts as a binder for the fibers. Other constituents that may also be found are coupling agents, coatings, and fillers. Coupling agents and coatings are applied on the fibers to improve their wetting with the matrix as well as to promote bonding across the fiber–matrix interface. Both in turn promote a better load transfer between the fibers and the matrix. Fillers are used with some polymeric matrices primarily to reduce cost and improve their dimensional stability.

Manufacturing of a composite structure starts with the incorporation of a large number of fibers into a thin layer of matrix to form a *lamina* (ply). The thickness of a lamina is usually in the range of 0.1–1 mm (0.004–0.04 in.). If continuous (long) fibers are used in making the lamina, they may be arranged either in a unidirectional orientation (i.e., all fibers in one direction, Figure 2.1a), in a bidirectional orientation (i.e., fibers in two directions, usually normal to each other, Figure 2.1b), or in a multidirectional orientation (i.e., fibers in more than two directions, Figure 2.1c). The bi- or multidirectional orientation of fibers is obtained by weaving or other processes used in the textile industry. The bidirectional orientations in the form of fabrics are shown in Appendix A.1. For a lamina containing unidirectional fibers, the composite material has the highest strength and modulus in the longitudinal direction of the fibers. However, in the transverse direction, its strength and modulus are very low. For a lamina containing bidirectional fibers, the strength and modulus can be varied using different amounts of fibers in the longitudinal and transverse directions. For a balanced lamina, these properties are the same in both directions.

A lamina can also be constructed using discontinuous (short) fibers in a matrix. The discontinuous fibers can be arranged either in unidirectional orientation (Figure 2.1c) or in random orientation (Figure 2.1d). Discontinuous fiber-reinforced composites have lower strength and modulus than continuous fiber composites. However, with random orientation of fibers (Figure 2.1e), it is possible to obtain equal mechanical and physical properties in all directions in the plane of the lamina.

The thickness required to support a given load or to maintain a given deflection in a fiber-reinforced composite structure is obtained by stacking several laminas in a specified sequence and then consolidating them to form a *laminate*. Various laminas in a laminate may contain fibers either all in one

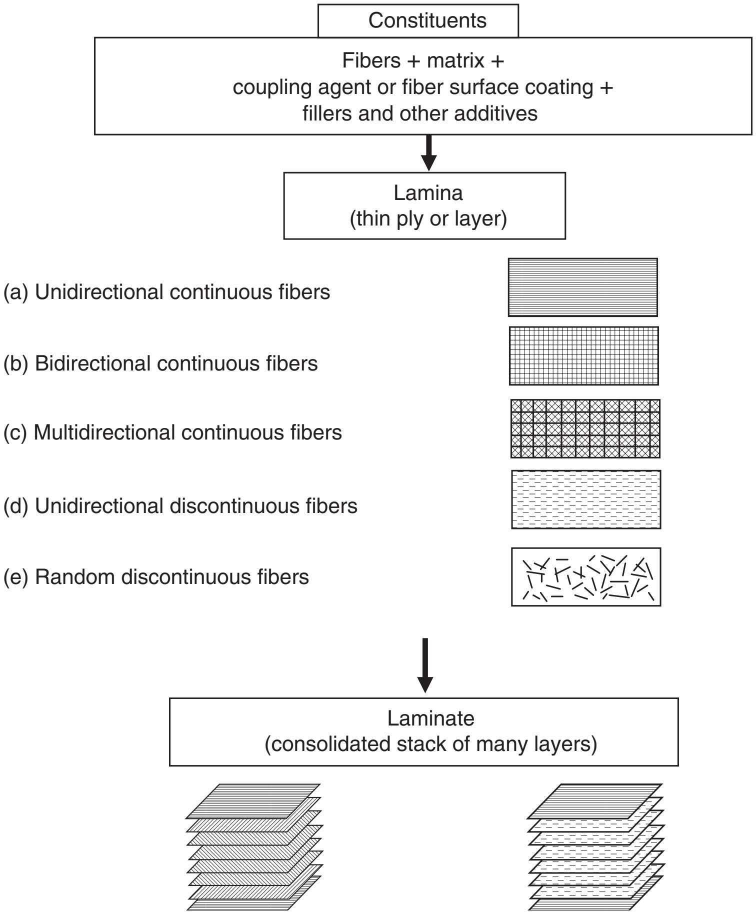


FIGURE 2.1 Basic building blocks in fiber-reinforced composites.

direction or in different directions. It is also possible to combine different kinds of fibers to form either an interply or an intraply hybrid laminate. An *interply* hybrid laminate consists of different kinds of fibers in different laminas, whereas an *intraply* hybrid laminate consists of two or more different kinds of fibers interspersed in the same lamina. Generally, the same matrix is used throughout the laminate so that a coherent interlaminar bond is formed between the laminas.

Fiber-reinforced polymer laminas can also be combined with thin aluminum or other metallic sheets to form metal–composite hybrids, commonly known as *fiber metal laminates* (FML). Two such commercial metal–composite hybrids are ARALL and GLARE. *ARALL* uses alternate layers of aluminum sheets and unidirectional aramid fiber–epoxy laminates

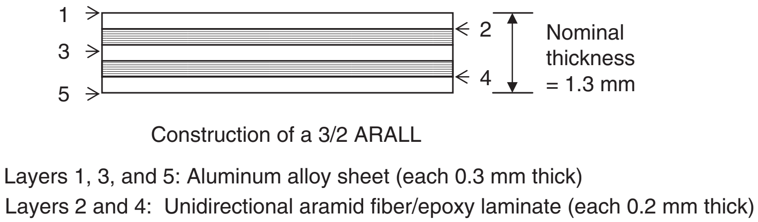


FIGURE 2.2 Construction of an ARALL laminate.

(Figure 2.2). *GLARE* uses alternate layers of aluminum sheets and either unidirectional or bidirectional S-glass fiber–epoxy laminates. Both metal–composite hybrids have been primarily developed for aircraft structures such as wing panels and fuselage sections.

2.1 FIBERS

Fibers are the principal constituents in a fiber-reinforced composite material. They occupy the largest volume fraction in a composite laminate and share the major portion of the load acting on a composite structure. Proper selection of the fiber type, fiber volume fraction, fiber length, and fiber orientation is very important, since it influences the following characteristics of a composite laminate:

1. Density
2. Tensile strength and modulus
3. Compressive strength and modulus
4. Fatigue strength as well as fatigue failure mechanisms
5. Electrical and thermal conductivities
6. Cost

A number of commercially available fibers and their properties are listed in Table 2.1. The first point to note in this table is the extremely small filament diameter for the fibers. Since such small sizes are difficult to handle, the useful form of commercial fibers is a bundle, which is produced by gathering a large number of continuous filaments, either in untwisted or twisted form. The untwisted form is called *strand* or *end* for glass and Kevlar fibers and *tow* for carbon fibers (Figure 2.3a). The twisted form is called *yarn* (Figure 2.3b).

Tensile properties listed in Table 2.1 are the average values reported by the fiber manufacturers. One of the test methods used for determining the tensile properties of filaments is the single filament test. In this test method, designated as ASTM D3379, a single filament is mounted along the centerline of a slotted

TABLE 2.1
Properties of Selected Commercial Reinforcing Fibers

Fiber	Typical Diameter (μm)[a]	Density (g/cm^3)	Tensile Modulus GPa (Msi)	Tensile Strength GPa (ksi)	Strain-to-Failure (%)	Coefficient of Thermal Expansion ($10^{-6}/°\text{C}$)[b]	Poisson's Ratio
Glass							
E-glass	10 (round)	2.54	72.4 (10.5)	3.45 (500)	4.8	5	0.2
S-glass	10 (round)	2.49	86.9 (12.6)	4.30 (625)	5.0	2.9	0.22
PAN carbon							
T-300[c]	7 (round)	1.76	231 (33.5)	3.65 (530)	1.4	−0.6 (longitudinal) 7–12 (radial)	0.2
AS-1[d]	8 (round)	1.80	228 (33)	3.10 (450)	1.32		
AS-4[d]	7 (round)	1.80	248 (36)	4.07 (590)	1.65		
T-40[c]	5.1 (round)	1.81	290 (42)	5.65 (820)	1.8	−0.75 (longitudinal)	
IM-7[d]	5 (round)	1.78	301 (43.6)	5.31 (770)	1.81		
HMS-4[d]	8 (round)	1.80	345 (50)	2.48 (360)	0.7		
GY-70[e]	8.4 (bilobal)	1.96	483 (70)	1.52 (220)	0.38		
Pitch carbon							
P-55[c]	10	2.0	380 (55)	1.90 (275)	0.5	−1.3 (longitudinal)	
P-100[c]	10	2.15	758 (110)	2.41 (350)	0.32	−1.45 (longitudinal)	
Aramid							
Kevlar 49[f]	11.9 (round)	1.45	131 (19)	3.62 (525)	2.8	−2 (longitudinal) 59 (radial)	0.35
Kevlar 149[f]		1.47	179 (26)	3.45 (500)	1.9		
Technora[g]		1.39	70 (10.1)	3.0 (435)	4.6	−6 (longitudinal)	

Extended chain polyethylene							
Spectra 900[h]	38	0.97	117 (17)	2.59 (375)	3.5		
Spectra 1000[h]	27	0.97	172 (25)	3.0 (435)	2.7		
Boron	140 (round)	2.7	393 (57)	3.1 (450)	0.79	5	0.2
SiC							
Monofilament	140 (round)	3.08	400 (58)	3.44 (499)	0.86	1.5	
Nicalon[i] (multifilament)	14.5 (round)	2.55	196 (28.4)	2.75 (399)	1.4		
Al_2O_3							
Nextel 610[j]	10–12 (round)	3.9	380 (55)	3.1 (450)		8	
Nextel 720[j]	10–12	3.4	260 (38)	2.1 (300)		6	
Al_2O_3–SiO_2							
Fiberfrax (discontinuous)	2–12	2.73	103 (15)	1.03–1.72 (150–250)			

[a] 1 μm = 0.0000393 in.

[b] m/m per °C = 0.556 in./in. per °F.

[c] Amoco.

[d] Hercules.

[e] BASF.

[f] DuPont.

[g] Teijin.

[h] Honeywell.

[i] Nippon carbon.

[j] 3-M.

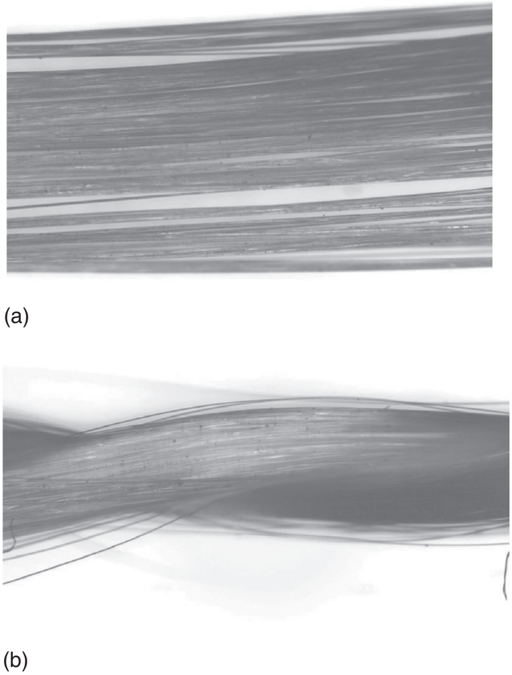


FIGURE 2.3 (a) Untwisted and (b) twisted fiber bundle.

tab by means of a suitable adhesive (Figure 2.4). After clamping the tab in the grips of a tensile testing machine, its midsection is either cut or burned away. The tension test is carried out at a constant loading rate until the filament

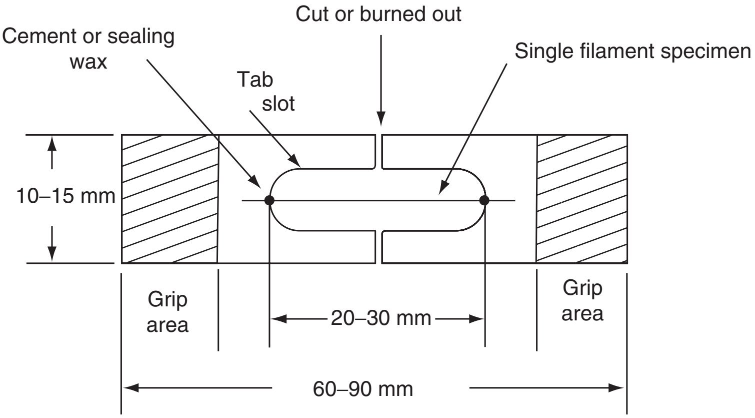


FIGURE 2.4 Mounting tab for tensile testing of single filament.

fractures. From the load-time record of the test, the following tensile properties are determined:

$$\text{Tensile strength } \sigma_{\mathrm{fu}} = \frac{F_{\mathrm{u}}}{A_{\mathrm{f}}} \tag{2.1}$$

and

$$\text{Tensile modulus } E_{\mathrm{f}} = \frac{L_{\mathrm{f}}}{CA_{\mathrm{f}}}, \tag{2.2}$$

where

F_{u} = force at failure
A_{f} = average filament cross-sectional area, measured by a planimeter from the photomicrographs of filament ends
L_{f} = gage length
C = true compliance, determined from the chart speed, loading rate, and the system compliance

Tensile stress–strain diagrams obtained from single filament test of reinforcing fibers in use are almost linear up to the point of failure, as shown in Figure 2.5. They also exhibit very low strain-to-failure and a brittle failure mode. Although the absence of yielding does not reduce the load-carrying capacity of the fibers, it does make them prone to damage during handling as well as during contact with other surfaces. In continuous manufacturing operations, such as filament winding, frequent fiber breakage resulting from such damages may slow the rate of production.

The high tensile strengths of the reinforcing fibers are generally attributed to their filamentary form in which there are statistically fewer surface flaws than in the bulk form. However, as in other brittle materials, their tensile strength data exhibit a large amount of scatter. An example is shown in Figure 2.6.

The experimental strength variation of brittle filaments is modeled using the following Weibull distribution function [1]:

$$f(\sigma_{\mathrm{fu}}) = \alpha\sigma_{\mathrm{o}}^{-\alpha}\sigma_{\mathrm{fu}}^{\alpha-1}\left(\frac{L_{\mathrm{f}}}{L_{\mathrm{o}}}\right)\exp\left[-\left(\frac{L_{\mathrm{f}}}{L_{\mathrm{o}}}\right)\left(\frac{\sigma_{\mathrm{fu}}}{\sigma_{\mathrm{o}}}\right)^{\alpha}\right], \tag{2.3}$$

where

$f(\sigma_{\mathrm{fu}})$ = probability of filament failure at a stress level equal to σ_{fu}
σ_{fu} = filament strength
L_{f} = filament length
L_{o} = reference length
α = shape parameter
σ_{o} = scale parameter (the filament strength at $L_{\mathrm{f}} = L_{\mathrm{o}}$)

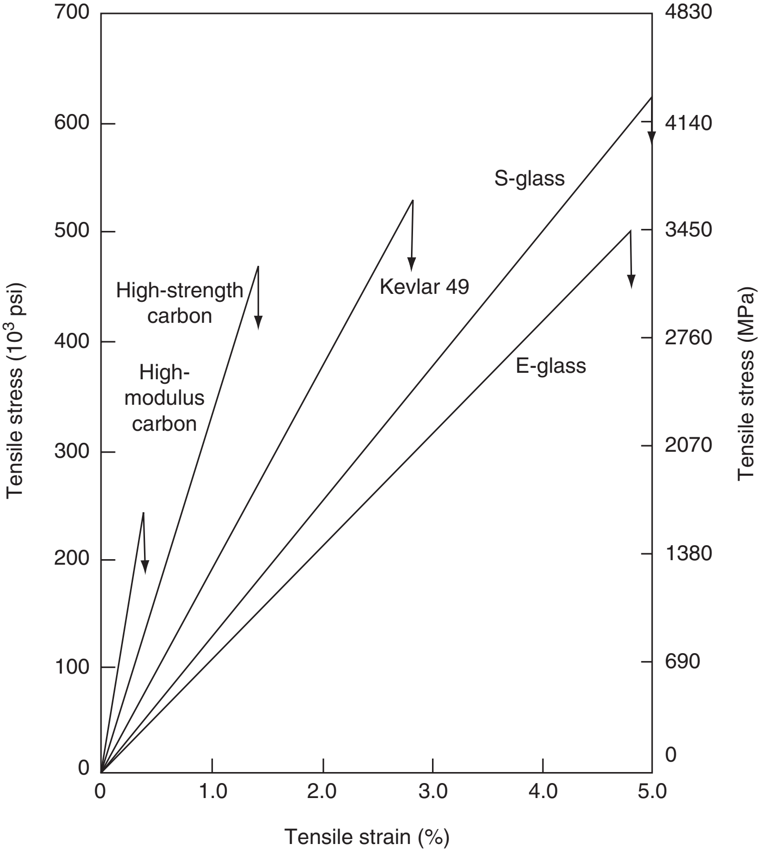


FIGURE 2.5 Tensile stress–strain diagrams for various reinforcing fibers.

The cumulative distribution of strength is given by the following equation:

$$F(\sigma_{\mathrm{fu}}) = 1 - \exp\left[-\left(\frac{L_{\mathrm{f}}}{L_{\mathrm{o}}}\right)\left(\frac{\sigma_{\mathrm{fu}}}{\sigma_{\mathrm{o}}}\right)^{\alpha}\right], \tag{2.4}$$

where $F(\sigma_{\mathrm{fu}})$ represents the probability of filament failure at a stress level lower than or equal to σ_{fu}. The parameters α and σ_{o} in Equations 2.3 and 2.4 are called the Weibull parameters, and are determined using the experimental data. α can be regarded as an inverse measure of the coefficient of variation. The higher the value of α, the narrower is the distribution of filament strength. The scale parameter σ_{o} may be regarded as a reference stress level.

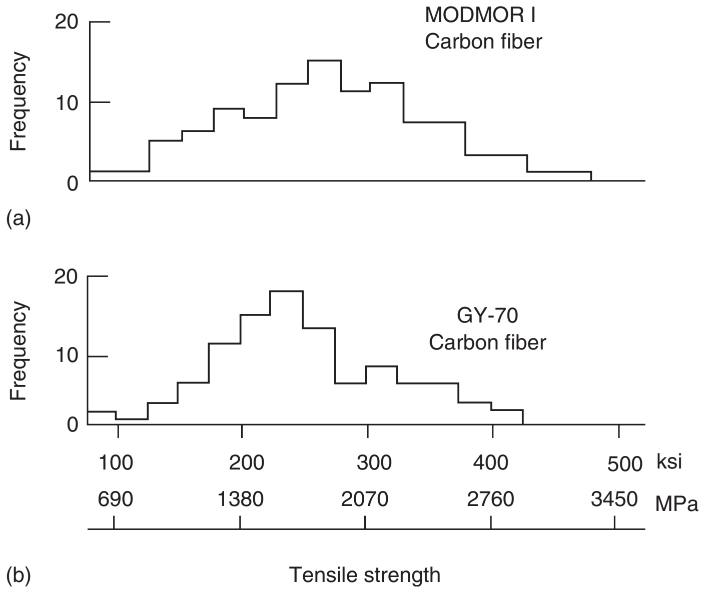


FIGURE 2.6 Histograms of tensile strengths for (a) Modmor I carbon fibers and (b) GY-70 carbon fibers. (After McMahon, P.E., *Analysis of the Test Methods for High Modulus Fibers and Composites, ASTM STP*, 521, 367, 1973.)

The mean filament strength $\bar{\sigma}_{\mathrm{fu}}$ is given by

$$\bar{\sigma}_{\mathrm{fu}} = \sigma_{\mathrm{o}} \left(\frac{L_{\mathrm{f}}}{L_{\mathrm{o}}} \right)^{-1/\alpha} \Gamma\left(1 + \frac{1}{\alpha}\right), \tag{2.5}$$

where Γ represents a gamma function. Equation 2.5 clearly shows that the mean strength of a brittle filament decreases with increasing length. This is also demonstrated in Figure 2.7.

Tensile properties of fibers can also be determined using fiber bundles. It has been observed that even though the tensile strength distribution of individual filaments follows the Weibull distribution, the tensile strength distribution of fiber bundles containing a large number of parallel filaments follows a normal distribution [1]. The maximum strength, σ_{fm}, that the filaments in the bundle will exhibit and the mean bundle strength, $\bar{\sigma}_{\mathrm{b}}$, can be expressed in terms of the Weibull parameters determined for individual filaments. They are given as follows:

$$\begin{aligned} \sigma_{\mathrm{fm}} &= \sigma_{\mathrm{o}} \left[\left(\frac{L_{\mathrm{f}}}{L_{\mathrm{o}}} \right) \alpha \right]^{-1/\alpha}, \\ \bar{\sigma}_{\mathrm{b}} &= \sigma_{\mathrm{o}} \left[\left(\frac{L_{\mathrm{f}}}{L_{\mathrm{o}}} \right) \alpha \right]^{-1/\alpha} \mathrm{e}^{-1/\alpha}. \end{aligned} \tag{2.6}$$

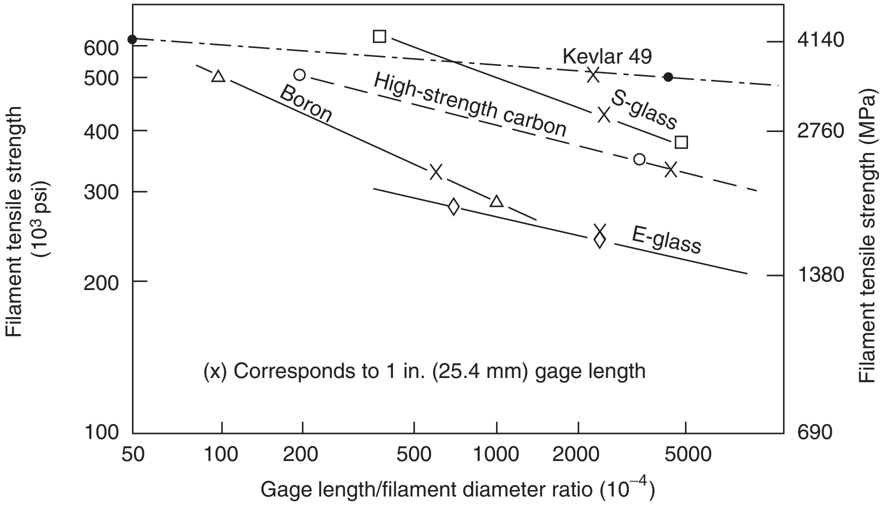


FIGURE 2.7 Filament strength variation as a function of gage length-to-diameter ratio. (After Kevlar 49 Data Manual, E. I. duPont de Nemours & Co., 1975.)

The fiber bundle test method is similar to the single filament test method. The fiber bundle can be tested either in dry or resin-impregnated condition. Generally, the average tensile strength and modulus of fiber bundles are lower than those measured on single filaments. Figure 2.8 shows the stress–strain diagram of a dry glass fiber bundle containing 3000 filaments. Even though a single glass filament shows a linear tensile stress–strain diagram until failure, the glass fiber strand shows not only a nonlinear stress–strain diagram before reaching the maximum stress, but also a progressive failure after reaching the maximum stress. Both nonlinearity and progressive failure occur due to the statistical distribution of the strength of glass filaments. The weaker filaments in the bundle fail at low stresses, and the surviving filaments continue to carry the tensile load; however, the stress in each surviving filament becomes higher. Some of them fail as the load is increased. After the maximum stress is reached, the remaining surviving filaments continue to carry even higher stresses and start to fail, but not all at one time, thus giving the progressive failure mode as seen in Figure 2.8. Similar tensile stress–strain diagrams are observed with carbon and other fibers in fiber bundle tests.

In addition to tensile properties, compressive properties of fibers are also of interest in many applications. Unlike the tensile properties, the compressive properties cannot be determined directly by simple compression tests on filaments or strands. Various indirect methods have been used to determine the compressive strength of fibers [2]. One such method is the loop test in which a filament is bent into the form of a loop until it fails. The compressive strength

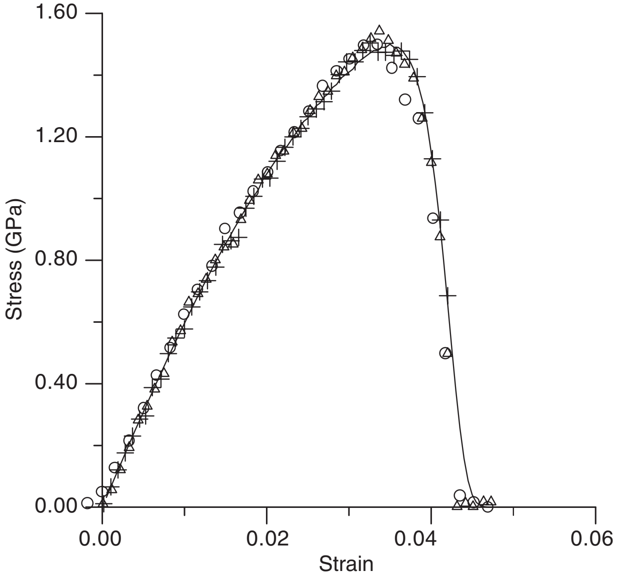


FIGURE 2.8 Tensile stress–strain diagram of an untwisted E-glass fiber bundle containing 3000 filaments.

of the fiber is determined from the compressive strain at the fiber surface. In general, compressive strength of fibers is lower than their tensile strength, as is shown in Table 2.2. The compressive strength of boron fibers is higher than that of carbon and glass fibers. All organic fibers have low compressive

TABLE 2.2
Compressive Strength of a Few Selected Reinforcing Fibers

Fiber	Tensile Strength[a] (GPa)	Compressive Strength[a] (GPa)
E-glass fiber	3.4	4.2
T-300 carbon fiber	3.2	2.7–3.2
AS 4 carbon fiber	3.6	2.7
GY-70 carbon fiber	1.86	1.06
P100 carbon fiber	2.2	0.5
Kevlar 49 fiber	3.5	0.35–0.45
Boron	3.5	5

Source: Adapted from Kozey, V.V., Jiang, H., Mehta, V.R., and Kumar, S., *J. Mater. Res.*, 10, 1044, 1995.

[a] In the longitudinal direction.

strength. This includes Kevlar 49, which has a compressive strength almost 10 times lower than its tensile strength.

2.1.1 GLASS FIBERS

Glass fibers are the most common of all reinforcing fibers for polymeric matrix composites (PMC). The principal advantages of glass fibers are low cost, high tensile strength, high chemical resistance, and excellent insulating properties. The disadvantages are relatively low tensile modulus and high density (among the commercial fibers), sensitivity to abrasion during handling (which frequently decreases its tensile strength), relatively low fatigue resistance, and high hardness (which causes excessive wear on molding dies and cutting tools).

The two types of glass fibers commonly used in the fiber-reinforced plastics (FRP) industry are E-glass and S-glass. Another type, known as C-glass, is used in chemical applications requiring greater corrosion resistance to acids than is provided by E-glass. E-glass has the lowest cost of all commercially available reinforcing fibers, which is the reason for its widespread use in the FRP industry. S-glass, originally developed for aircraft components and missile casings, has the highest tensile strength among all fibers in use. However, the compositional difference and higher manufacturing cost make it more expensive than E-glass. A lower cost version of S-glass, called S-2-glass, is also available. Although S-2-glass is manufactured with less-stringent nonmilitary specifications, its tensile strength and modulus are similar to those of S-glass.

The chemical compositions of E- and S-glass fibers are shown in Table 2.3. As in common soda-lime glass (window and container glasses), the principal ingredient in all glass fibers is silica (SiO_2). Other oxides, such as B_2O_3 and Al_2O_3, are added to modify the network structure of SiO_2 as well as to improve its workability. Unlike soda-lime glass, the Na_2O and K_2O content in E- and S-glass fibers is quite low, which gives them a better corrosion resistance to water as well as higher surface resistivity. The internal structure of glass fibers is a three-dimensional, long network of silicon, oxygen, and other atoms arranged in a random fashion. Thus, glass fibers are amorphous (noncrystalline) and isotropic (equal properties in all directions).

TABLE 2.3
Typical Compositions of Glass Fibers (in wt%)

Type	SiO_2	Al_2O_3	CaO	MgO	B_2O_3	Na_2O
E-glass	54.5	14.5	17	4.5	8.5	0.5
S-glass	64	26	—	10	—	—

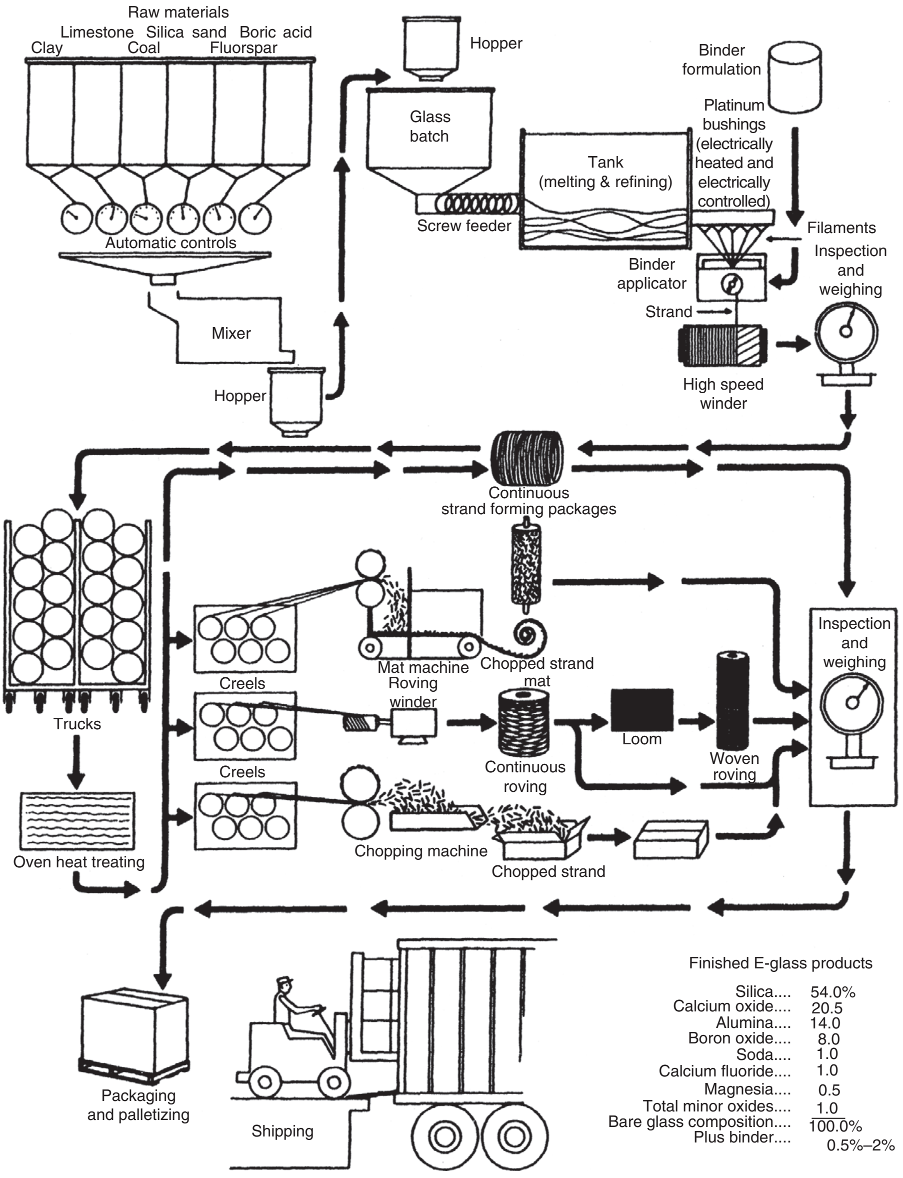


FIGURE 2.9 Flow diagram in glass fiber manufacturing. (Courtesy of PPG Industries. With permission.)

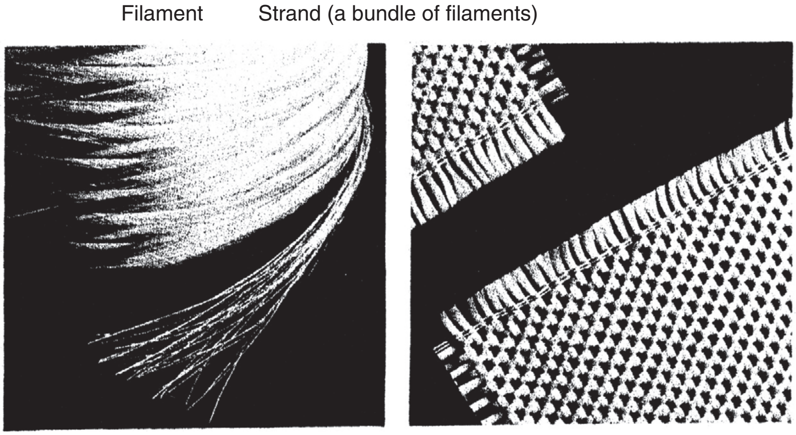
The manufacturing process for glass fibers is depicted in the flow diagram in Figure 2.9. Various ingredients in the glass formulation are first dry-mixed and melted in a refractory furnace at about 1370°C. The molten glass is exuded through a number of orifices contained in a platinum bushing and rapidly drawn into filaments of ~10 μm in diameter. A protective coating (size) is then applied on individual filaments before they are gathered together into a strand and wound on a drum. The coating or size is a mixture of lubricants (which prevent abrasion between the filaments), antistatic agents (which reduce static friction between the filaments), and a binder (which packs the filaments together into a strand). It may also contain small percentages of a coupling agent that promotes adhesion between fibers and the specific polymer matrix for which it is formulated.

The basic commercial form of continuous glass fibers is a *strand*, which is a collection of parallel filaments numbering 204 or more. Other common forms of glass fibers are illustrated in Figure 2.10. A *roving* is a group of untwisted parallel strands (also called *ends*) wound on a cylindrical *forming package*. Rovings are used in continuous molding operations, such as filament winding and pultrusion. They can also be preimpregnated with a thin layer of polymeric resin matrix to form *prepregs*. Prepregs are subsequently cut into required dimensions, stacked, and cured into the final shape in batch molding operations, such as compression molding and hand layup molding.

Chopped strands are produced by cutting continuous strands into short lengths. The ability of the individual filaments to hold together during or after the chopping process depends largely on the type and amount of the size applied during fiber manufacturing operation. Strands of high integrity are called "hard" and those that separate more readily are called "soft." Chopped strands ranging in length from 3.2 to 12.7 mm (0.125–0.5 in.) are used in injection-molding operations. Longer strands, up to 50.8 mm (2 in.) in length, are mixed with a resinous binder and spread in a two-dimensional random fashion to form chopped strand mats (CSMs). These mats are used mostly for hand layup moldings and provide nearly equal properties in all directions in the plane of the structure. *Milled glass fibers* are produced by grinding continuous strands in a hammer mill into lengths ranging from 0.79 to 3.2 mm (0.031–0.125 in.). They are primarily used as a filler in the plastics industry and do not possess any significant reinforcement value.

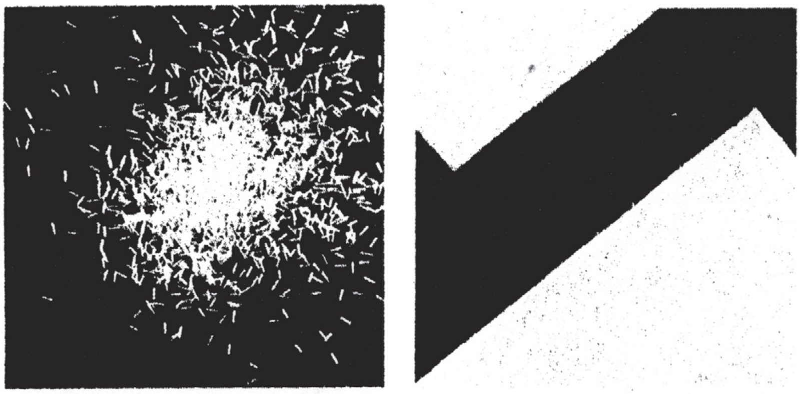
Glass fibers are also available in woven form, such as *woven roving* or *woven cloth*. Woven roving is a coarse drapable fabric in which continuous rovings are woven in two mutually perpendicular directions. Woven cloth is weaved using twisted continuous strands, called *yarns*. Both woven roving and cloth provide bidirectional properties that depend on the style of weaving as well as relative fiber counts in the length (*warp*) and crosswise (*fill*) directions (See Appendix A.1). A layer of woven roving is sometimes bonded with a layer of CSM to produce a woven roving mat. All of these forms of glass fibers are suitable for hand layup molding and liquid composite molding.

The average tensile strength of freshly drawn glass fibers may exceed 3.45 GPa (500,000 psi). However, surface damage (flaws) produced by abrasion, either by rubbing against each other or by contact with the processing



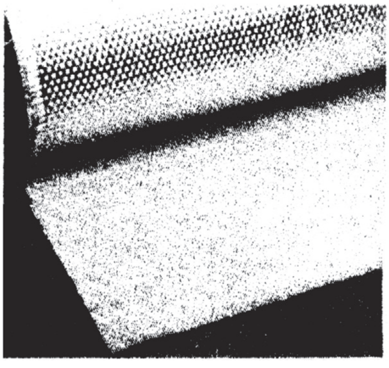
Continuous strand roving

Woven roving



Chopped strands

Chopped strand mat



Woven roving mat

FIGURE 2.10 Common forms of glass fibers. (Courtesy of Owens Corning Fiberglas Corporation.)

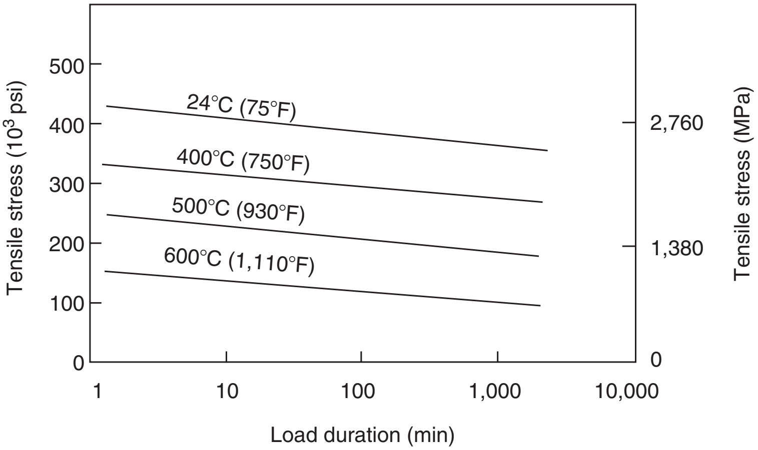


FIGURE 2.11 Reduction of tensile stress in E-glass fibers as a function of time at various temperatures. (After Otto, W.H., Properties of glass fibers at elevated temperatures, Owens Corning Fiberglas Corporation, AD 228551, 1958.)

equipment, tends to reduce it to values that are in the range of 1.72–2.07 GPa (250,000–300,000 psi). Strength degradation is increased as the surface flaws grow under cyclic loads, which is one of the major disadvantages of using glass fibers in fatigue applications. Surface compressive stresses obtained by alkali ion exchange [3] or elimination of surface flaws by chemical etching may reduce the problem; however, commercial glass fibers are not available with any such surface modifications.

The tensile strength of glass fibers is also reduced in the presence of water or under sustained loads (static fatigue). Water bleaches out the alkalis from the surface and deepens the surface flaws already present in fibers. Under sustained loads, the growth of surface flaws is accelerated owing to stress corrosion by atmospheric moisture. As a result, the tensile strength of glass fibers is decreased with increasing time of load duration (Figure 2.11).

2.1.2 CARBON FIBERS

Carbon fibers are commercially available with a variety of tensile modulus values ranging from 207 GPa (30×10^6 psi) on the low side to 1035 GPa (150×10^6 psi) on the high side. In general, the low-modulus fibers have lower density, lower cost, higher tensile and compressive strengths, and higher tensile strains-to-failure than the high-modulus fibers. Among the advantages of carbon fibers are their exceptionally high tensile strength–weight ratios as well as tensile modulus–weight ratios, very low coefficient of linear thermal expansion (which provides dimensional stability in such applications as space antennas), high fatigue strengths, and high thermal conductivity (which is even

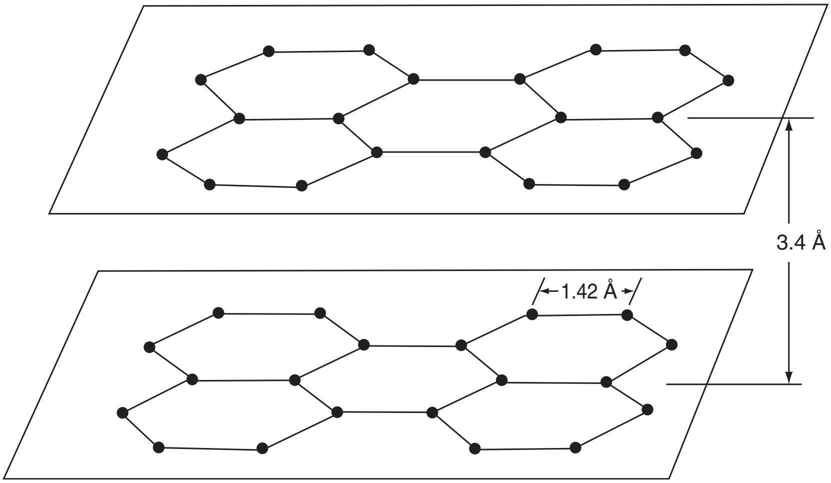


FIGURE 2.12 Arrangement of carbon atoms in a graphite crystal.

higher than that of copper). The disadvantages are their low strain-to-failure, low impact resistance, and high electrical conductivity, which may cause "shorting" in unprotected electrical machinery. Their high cost has so far excluded them from widespread commercial applications. They are used mostly in the aerospace industry, where weight saving is considered more critical than cost.

Structurally, carbon fibers contain a blend of amorphous carbon and graphitic carbon. Their high tensile modulus results from the graphitic form, in which carbon atoms are arranged in a crystallographic structure of parallel planes or layers. The carbon atoms in each plane are arranged at the corners of interconnecting regular hexagons (Figure 2.12). The distance between the planes (3.4 Å) is larger than that between the adjacent atoms in each plane (1.42 Å). Strong covalent bonds exist between the carbon atoms in each plane, but the bond between the planes is due to van der Waals-type forces, which is much weaker. This results in highly anisotropic physical and mechanical properties for the carbon fiber.

The basal planes in graphite crystals are aligned along the fiber axis. However, in the transverse direction, the alignment can be either circumferential, radial, random, or a combination of these arrangements (Figure 2.13). Depending on which of these arrangements exists, the thermoelastic properties, such as modulus (E) and coefficient of thermal expansion (α), in the radial (r) and circumferential (θ) directions of the fiber can be different from those in the axial (a) or longitudinal direction. For example, if the arrangement is circumferential, $E_a = E_\theta > E_r$, and the fiber is said to be circumferentially orthotropic. For the radial arrangement, $E_a = E_r > E_\theta$, and the fiber is radially orthotropic. When there is a random arrangement, $E_a > E_\theta = E_r$, the fiber is transversely isotropic. In commercial fibers, a two-zone structure with circumferential

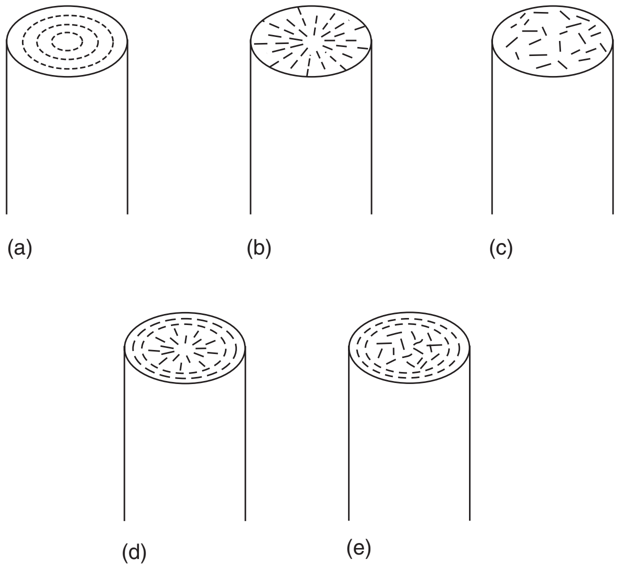


FIGURE 2.13 Arrangement of graphite crystals in a direction transverse to the fiber axis: (a) circumferential, (b) radial, (c) random, (d) radial–circumferential, and (e) random–circumferential.

arrangement in the skin and either radial or random arrangement in the core is commonly observed [4].

Carbon fibers are manufactured from two types of precursors (starting materials), namely, textile precursors and pitch precursors. The manufacturing process from both precursors is outlined in Figure 2.14. The most common textile precursor is polyacrylonitrile (PAN). The molecular structure of PAN, illustrated schematically in Figure 2.15a, contains highly polar CN groups that are randomly arranged on either side of the chain. Filaments are wet spun from a solution of PAN and stretched at an elevated temperature during which the polymer chains are aligned in the filament direction. The stretched filaments are then heated in air at 200°C–300°C for a few hours. At this stage, the CN groups located on the same side of the original chain combine to form a more stable and rigid ladder structure (Figure 2.15b), and some of the CH_2 groups are oxidized. In the next step, PAN filaments are carbonized by heating them at a controlled rate at 1000°C–2000°C in an inert atmosphere. Tension is maintained on the filaments to prevent shrinking as well as to improve molecular orientation. With the elimination of oxygen and nitrogen atoms, the filaments now contain mostly carbon atoms, arranged in aromatic ring patterns in parallel planes. However, the carbon atoms in the neighboring planes are not yet perfectly ordered, and the filaments have a relatively low tensile modulus. As the carbonized filaments are subsequently heat-treated at or above 2000°C,

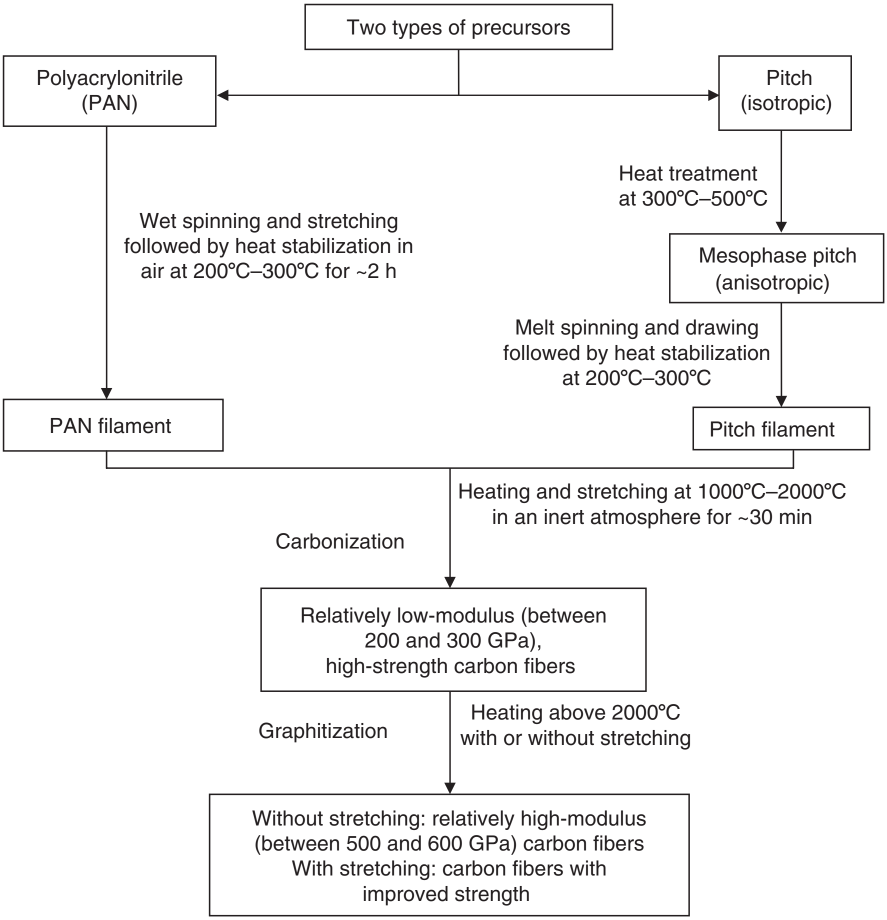


FIGURE 2.14 Flow diagram in carbon fiber manufacturing.

their structure becomes more ordered and turns toward a true graphitic form with increasing heat treatment temperature. The graphitized filaments attain a high tensile modulus, but their tensile strength may be relatively low (Figure 2.16). Their tensile strength can be increased by hot stretching them above 2000°C, during which the graphitic planes are aligned in the filament direction. Other properties of carbon fibers (e.g., electrical conductivity, thermal conductivity, longitudinal coefficient of thermal expansion, and oxidation resistance) can be improved by controlling the amount of crystallinity and eliminating the defects, such as missing carbon atoms or catalyst impurities. Tensile strength and tensile modulus are also affected by the amount of crystallinity and the presence of defects (Table 2.4).

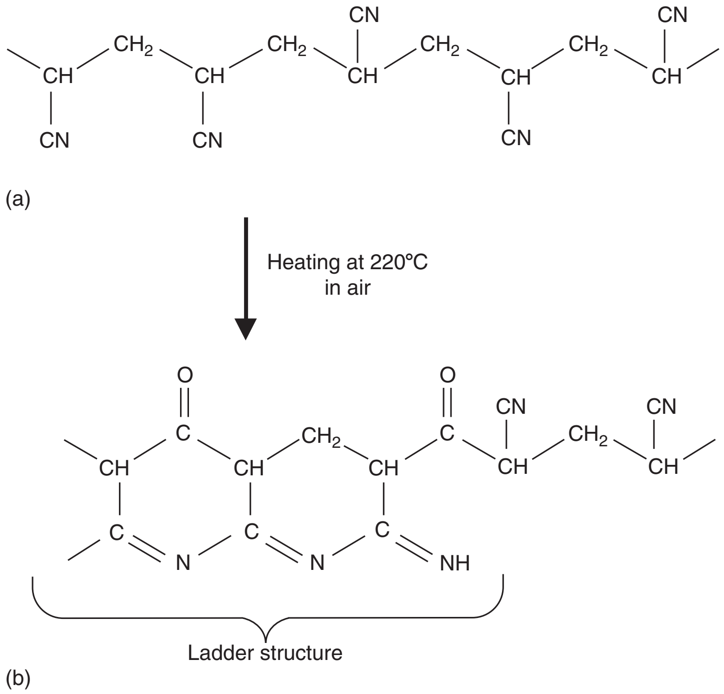


FIGURE 2.15 Ladder structure in an oxidized PAN molecule. (a) Molecular structure of PAN and (b) rigid ladder structure.

Pitch, a by-product of petroleum refining or coal coking, is a lower cost precursor than PAN. The carbon atoms in pitch are arranged in low-molecular-weight aromatic ring patterns. Heating to temperatures above 300°C polymerizes (joins) these molecules into long, two-dimensional sheetlike structures. The highly viscous state of pitch at this stage is referred to as "mesophase." Pitch filaments are produced by melt spinning mesophase pitch through a spinneret (Figure 2.17). While passing through the spinneret die, the mesophase pitch molecules become aligned in the filament direction. The filaments are cooled to freeze the molecular orientation, and subsequently heated between 200°C and 300°C in an oxygen-containing atmosphere to stabilize them and make them infusible (to avoid fusing the filaments together). In the next step, the filaments are carbonized at temperatures around 2000°C. The rest of the process of transforming the structure to graphitic form is similar to that followed for PAN precursors.

PAN carbon fibers are generally categorized into high tensile strength (HT), high modulus (HM), and ultrahigh modulus (UHM) types. The high tensile strength PAN carbon fibers, such as T-300 and AS-4 in Table 2.1, have the

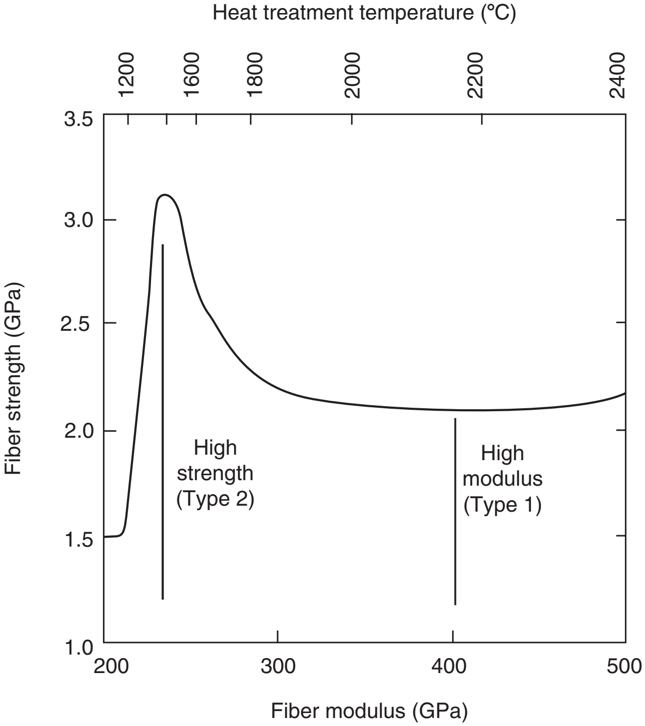


FIGURE 2.16 Influence of heat treatment temperature on strength and modulus of carbon fibers. (After Watt, W., *Proc. R. Soc. Lond.*, A319, 5, 1970.)

lowest modulus, while the ultrahigh-modulus PAN carbon fibers, such as GY-70, have the lowest tensile strength as well as the lowest tensile strain-to-failure. A number of intermediate modulus (IM) high-strength PAN carbon fibers, such as T-40 and IM-7, have also been developed that possess the highest strain-to-failure among carbon fibers. Another point to note in Table 2.1 is that the pitch carbon fibers have very high modulus values, but their tensile strength and strain-to-failure are lower than those of the PAN carbon fibers. The high modulus of pitch fibers is the result of the fact that they are more graphitizable; however, since shear is easier between parallel planes of a graphitized fiber and graphitic fibers are more sensitive to defects and flaws, their tensile strength is not as high as that of PAN fibers.

The axial compressive strength of carbon fibers is lower than their tensile strength. The PAN carbon fibers have higher compressive strength than pitch carbon fibers. It is also observed that the higher the modulus of a carbon fiber, the lower is its compressive strength. Among the factors that contribute to the reduction in compressive strength are higher orientation, higher graphitic order, and larger crystal size [5,6].

TABLE 2.4
Structural Features and Controlling Parameters Affecting the Properties of Carbon Fibers

		Properties	
Structural Feature	**Controlling Parameters**	**Increase**	**Decrease**
Increasing orientation of crystallographic basal planes parallel to the fiber axis	Fiber drawing, fiber structure, restraint against shrinkage during heat treatment	Longitudinal strength and modulus, longitudinal negative CTE, thermal and electrical conductivities	Transverse strength and modulus
Increasing crystallinity (larger and perfect crystals)	Precursor chemistry, heat treatment	Thermal and electrical conductivities, longitudinal negative CTE, oxidation resistance	Longitudinal tensile and compressive strengths, transverse strength and modulus
Decreasing defect content	Precursor purity, fiber handling	Tensile strength, thermal and electrical conductivities, oxidation resistance	

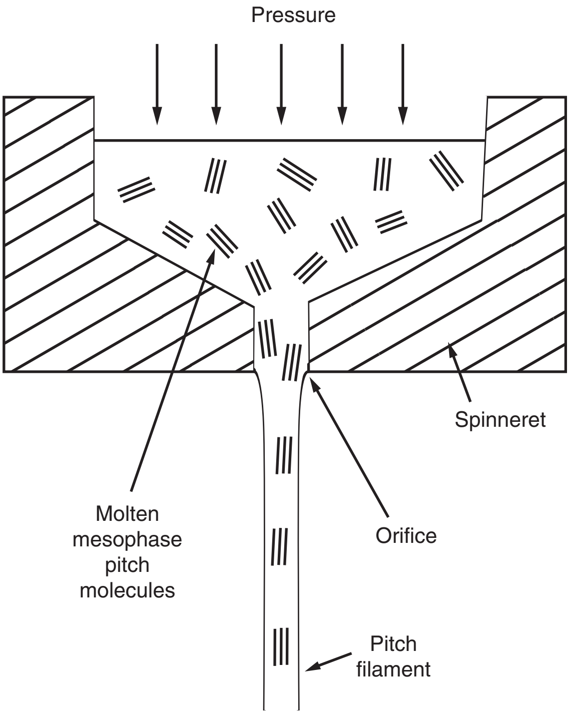


FIGURE 2.17 Alignment of mesophase pitch into a pitch filament. (After *Commercial Opportunities for Advanced Composites, ASTM STP*, 704, 1980.)

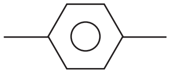
The PAN carbon fibers have lower thermal conductivity and electrical conductivity than pitch carbon fibers [6]. For example, thermal conductivity of PAN carbon fibers is in the range of 10–100 W/m °K compared with 20–1000 W/m °K for pitch carbon fibers. Similarly, electrical conductivity of PAN carbon fibers is in the range of 10^4–10^5 S/m compared with 10^5–10^6 S/m for pitch carbon fibers. For both types of carbon fibers, the higher the tensile modulus, the higher are the thermal and electrical conductivities.

Carbon fibers are commercially available in three basic forms, namely, long and continuous tow, chopped (6–50 mm long), and milled (30–3000 μm long). The long and continuous tow, which is simply an untwisted bundle of 1,000–160,000 parallel filaments, is used for high-performance applications. The price of carbon fiber tow decreases with increasing filament count. Although high filament counts are desirable for improving productivity in continuous molding operations, such as filament winding and pultrusion, it becomes increasingly difficult to wet them with the matrix. "Dry" filaments are not conducive to good mechanical properties.

Carbon fiber tows can also be weaved into two-dimensional fabrics of various styles (see Appendix A.1). Hybrid fabrics containing commingled or coweaved carbon and other fibers, such as E-glass, Kevlar, PEEK, PPS, and so on, are also available. Techniques of forming three-dimensional weaves with fibers running in the thickness direction have also been developed.

2.1.3 ARAMID FIBERS

Aramid fibers are highly crystalline aromatic polyamide fibers that have the lowest density and the highest tensile strength-to-weight ratio among the current reinforcing fibers. Kevlar 49 is the trade name of one of the aramid fibers available in the market. As a reinforcement, aramid fibers are used in many marine and aerospace applications where lightweight, high tensile strength, and resistance to impact damage (e.g., caused by accidentally dropping a hand tool) are important. Like carbon fibers, they also have a negative coefficient of thermal expansion in the longitudinal direction, which is used in designing low thermal expansion composite panels. The major disadvantages of aramid fiber-reinforced composites are their low compressive strengths and difficulty in cutting or machining.

The molecular structure of aramid fibers, such as Kevlar 49 fibers, is illustrated in Figure 2.18. The repeating unit in its molecules contains an amide (–NH) group (which is also found in nylons) and an aromatic ring represented by  in Figure 2.18. The aromatic ring gives it a higher chain stiffness (modulus) as well as better chemical and thermal stability over other commercial organic fibers, such as nylons.

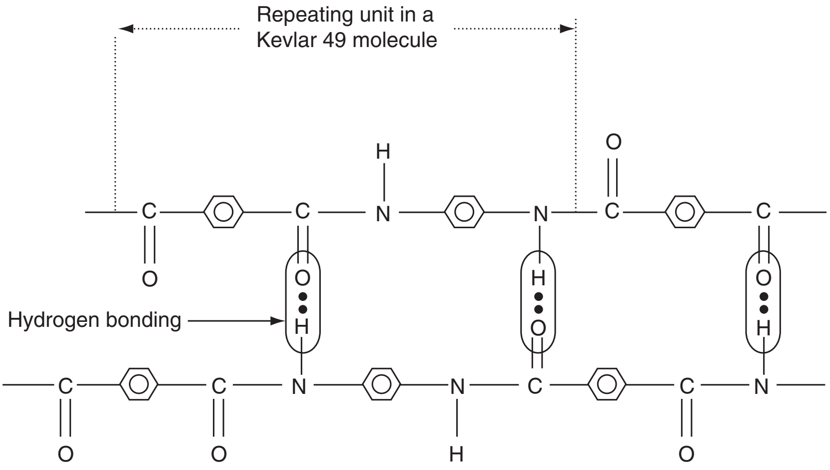


FIGURE 2.18 Molecular structure of Kevlar 49 fiber.

Kevlar 49 filaments are manufactured by extruding an acidic solution of a proprietary precursor (a polycondensation product of terephthaloyol chloride and *p*-phenylene diamine) from a spinneret. During the filament drawing process, Kevlar 49 molecules become highly oriented in the direction of the filament axis. Weak hydrogen bonds between hydrogen and oxygen atoms in adjacent molecules hold them together in the transverse direction. The resulting filament is highly anisotropic, with much better physical and mechanical properties in the longitudinal direction than in the radial direction.

Although the tensile stress–strain behavior of Kevlar 49 is linear, fiber fracture is usually preceded by longitudinal fragmentation, splintering, and even localized drawing. In bending, Kevlar 49 fibers exhibit a high degree of yielding on the compression side. Such a noncatastrophic failure mode is not observed in glass or carbon fibers, and gives Kevlar 49 composites superior damage tolerance against impact or other dynamic loading. One interesting application of this characteristic of Kevlar 49 fibers is found in soft lightweight body armors and helmets used for protecting police officers and military personnel.

Kevlar 49 fibers do not melt or support combustion but will start to carbonize at about 427°C. The maximum long-term use temperature recommended for Kevlar 49 is 160°C. They have very low thermal conductivity, but a very high vibration damping coefficient. Except for a few strong acids and alkalis, their chemical resistance is good. However, they are quite sensitive to ultraviolet lights. Prolonged direct exposure to sunlight causes discoloration and significant loss in tensile strength. The problem is less pronounced in composite laminates in which the fibers are covered with a matrix. Ultraviolet light-absorbing fillers can be added to the matrix to further reduce the problem.

Kevlar 49 fibers are hygroscopic and can absorb up to 6% moisture at 100% relative humidity and 23°C. The equilibrium moisture content (i.e., maximum moisture absorption) is directly proportional to relative humidity and is attained in 16–36 h. Absorbed moisture seems to have very little effect on the tensile properties of Kevlar 49 fibers. However, at high moisture content, they tend to crack internally at the preexisting microvoids and produce longitudinal splitting [7].

A second-generation Kevlar fiber is Kevlar 149, which has the highest tensile modulus of all commercially available aramid fibers. The tensile modulus of Kevlar 149 is 40% higher than that of Kevlar 49; however, its strain-to-failure is lower. Kevlar 149 has the equilibrium moisture content of 1.2% at 65% relative humidity and 22°C, which is nearly 70% lower than that of Kevlar 49 under similar conditions. Kevlar 149 also has a lower creep rate than Kevlar 49.

2.1.4 EXTENDED CHAIN POLYETHYLENE FIBERS

Extended chain polyethylene fibers, commercially available under the trade name Spectra, are produced by gel spinning a high-molecular-weight polyethylene. Gel spinning yields a highly oriented fibrous structure with exceptionally high crystallinity (95%–99%) relative to melt spinning used for conventional polyethylene fibers.

Spectra polyethylene fibers have the highest strength-to-weight ratio of all commercial fibers available to date. Two other outstanding features of Spectra fibers are their low moisture absorption (1% compared with 5%–6% for Kevlar 49) and high abrasion resistance, which make them very useful in marine composites, such as boat hulls and water skis.

The melting point of Spectra fibers is 147°C; however, since they exhibit a high level of creep above 100°C, their application temperature is limited to 80°C–90°C. The safe manufacturing temperature for composites containing Spectra fibers is below 125°C, since they exhibit a significant and rapid reduction in strength as well as increase in thermal shrinkage above this temperature. Another problem with Spectra fibers is their poor adhesion with resin matrices, which can be partially improved by their surface modification with gas plasma treatment.

Spectra fibers provide high impact resistance for composite laminates even at low temperatures and are finding growing applications in ballistic composites, such as armors, helmets, and so on. However, their use in high-performance aerospace composites is limited, unless they are used in conjunction with stiffer carbon fibers to produce hybrid laminates with improved impact damage tolerance than all-carbon fiber laminates.

2.1.5 NATURAL FIBERS

Examples of natural fibers are jute, flax, hemp, remi, sisal, coconut fiber (coir), and banana fiber (abaca). All these fibers are grown as agricultural plants in various parts of the world and are commonly used for making ropes, carpet backing, bags, and so on. The components of natural fibers are cellulose microfibrils dispersed in an amorphous matrix of lignin and hemicellulose [8]. Depending on the type of the natural fiber, the cellulose content is in the range of 60–80 wt% and the lignin content is in the range of 5–20 wt%. In addition, the moisture content in natural fibers can be up to 20 wt%. The properties of some of the natural fibers in use are given in Table 2.5.

TABLE 2.5
Properties of Selected Natural Fibers

Property	Hemp	Flax	Sisal	Jute
Density (g/cm^3)	1.48	1.4	1.33	1.46
Modulus (GPa)	70	60–80	38	10–30
Tensile strength (MPa)	550–900	800–1500	600–700	400–800
Elongation to failure (%)	1.6	1.2–1.6	2–3	1.8

Source: Adapted from Wambua, P., Ivens, J., and Verpoest, I., *Compos. Sci. Tech.*, 63, 1259, 2003.

Recently, natural fiber-reinforced polymers have created interest in the automotive industry for the following reasons. The applications in which natural fiber composites are now used include door inner panel, seat back, roof inner panel, and so on.

1. They are environment-friendly, meaning that they are biodegradable, and unlike glass and carbon fibers, the energy consumption to produce them is very small.
2. The density of natural fibers is in the range of 1.25−1.5 g/cm^3 compared with 2.54 g/cm^3 for E-glass fibers and 1.8–2.1 g/cm^3 for carbon fibers.
3. The modulus–weight ratio of some natural fibers is greater than that of E-glass fibers, which means that they can be very competitive with E-glass fibers in stiffness-critical designs.
4. Natural fiber composites provide higher acoustic damping than glass or carbon fiber composites, and therefore are more suitable for noise attenuation, an increasingly important requirement in interior automotive applications.
5. Natural fibers are much less expensive than glass and carbon fibers.

However, there are several limitations of natural fibers. The tensile strength of natural fibers is relatively low. Among the other limitations are low melting point and moisture absorption. At temperatures higher than 200°C, natural fibers start to degrade, first by the degradation of hemicellulose and then by the degradation of lignin. The degradation leads to odor, discoloration, release of volatiles, and deterioration of mechanical properties.

2.1.6 Boron Fibers

The most prominent feature of boron fibers is their extremely high tensile modulus, which is in the range of 379–414 GPa ($55–60 \times 10^6$ psi). Coupled with their relatively large diameter, boron fibers offer excellent resistance to buckling, which in turn contributes to high compressive strength for boron fiber-reinforced composites. The principal disadvantage of boron fibers is their high cost, which is even higher than that of many forms of carbon fibers. For this reason, its use is at present restricted to a few aerospace applications.

Boron fibers are manufactured by chemical vapor deposition (CVD) of boron onto a heated substrate (either a tungsten wire or a carbon monofilament). Boron vapor is produced by the reaction of boron chloride with hydrogen:

$$2BCl_3 + 3H_2 = 2B + 6HCl$$

The most common substrate used in the production of boron fibers is tungsten wire, typically 0.0127 mm (0.0005 in.) in diameter. It is continuously pulled through a reaction chamber in which boron is deposited on its surface at 1100°C–1300°C. The speed of pulling and the deposition temperature can be varied to control the resulting fiber diameter. Currently, commercial boron fibers are produced in diameters of 0.1, 0.142, and 0.203 mm (0.004, 0.0056, and 0.008 in.), which are much larger than those of other reinforcing fibers.

During boron deposition, the tungsten substrate is converted into tungsten boride by diffusion and reaction of boron with tungsten. The core diameter increases in diameter from 0.0127 mm (0.0005 in.) to 0.0165 mm (0.00065 in.), placing boron near the core in tension. However, near the outer surface of the boron layer, a state of biaxial compression exists, which makes the boron fiber less sensitive to mechanical damage [9]. The adverse reactivity of boron fibers with metals is reduced by chemical vapor deposition of silicon carbide on boron fibers, which produces borsic fibers.

2.1.7 CERAMIC FIBERS

Silicon carbide (SiC) and aluminum oxide (Al_2O_3) fibers are examples of ceramic fibers notable for their high-temperature applications in metal and ceramic matrix composites. Their melting points are 2830°C and 2045°C, respectively. Silicon carbide retains its strength well above 650°C, and aluminum oxide has excellent strength retention up to about 1370°C. Both fibers are suitable for reinforcing metal matrices in which carbon and boron fibers exhibit adverse reactivity. Aluminum oxide fibers have lower thermal and electrical conductivities and have higher coefficient of thermal expansion than silicon carbide fibers.

Silicon carbide fibers are available in three different forms [10]:

1. Monofilaments that are produced by chemical vapor deposition of β-SiC on a 10–25 μm diameter carbon monofilament substrate. The carbon monofilament is previously coated with ~1 μm thick pyrolitic graphite to smoothen its surface as well as to enhance its thermal conductivity. β-SiC is produced by the reaction of silanes and hydrogen gases at around 1300°C. The average fiber diameter is 140 μm.
2. Multifilament yarn produced by melt spinning of a polymeric precursor, such as polycarbosilane, at 350°C in nitrogen gas. The resulting polycarbosilane fiber is first heated in air to 190°C for 30 min to cross-link the polycarbosilane molecules by oxygen and then heat-treated to 1000°C–1200°C to form a crystalline structure. The average fiber diameter in the yarn is 14.5 μm and a commercial yarn contains 500 fibers. Yarn fibers have a considerably lower strength than the monofilaments.
3. Whiskers, which are 0.1–1 μm in diameter and around 50 μm in length. They are produced from rice hulls, which contain 10–20 wt% SiO_2. Rice hulls are first heated in an oxygen-free atmosphere to 700°C–900°C to remove the volatiles and then to 1500°C–1600°C for 1 h to produce SiC

whiskers. The final heat treatment is at 800°C in air, which removes free carbon. The resulting SiC whiskers contain 10 wt% of SiO_2 and up to 10 wt% Si_3N_4. The tensile modulus and tensile strength of these whiskers are reported as 700 GPa and 13 GPa (101.5×10^6 psi and 1.88×10^6 psi), respectively.

Many different aluminum oxide fibers have been developed over the years, but many of them at present are not commercially available. One of the early aluminum oxide fibers, but not currently available in the market, is called the Fiber FP [11]. It is a high-purity (>99%) polycrystalline α-Al_2O_3 fiber, dry spun from a slurry mix of alumina and proprietary spinning additives. The spun filaments are fired in two stages: low firing to control shrinkage, followed by flame firing to produce a suitably dense α-Al_2O_3. The fired filaments may be coated with a thin layer of silica to improve their strength (by healing the surface flaws) as well as their wettability with the matrix. The filament diameter is 20 μm. The tensile modulus and tensile strength of Fiber FP are reported as 379 GPa and 1.9 GPa (55×10^6 psi and 275,500 psi), respectively. Experiments have shown that Fiber FP retains almost 100% of its room temperature tensile strength after 300 h of exposure in air at 1000°C. Borsic fiber, on the other hand, loses 50% of its room temperature tensile strength after only 1 h of exposure in air at 500°C. Another attribute of Fiber FP is its remarkably high compressive strength, which is estimated to be about 6.9 GPa (1,000,000 psi).

Nextel 610 and Nextel 720, produced by 3 M, are two of the few aluminum oxide fibers available in the market now [12]. Both fibers are produced in continuous multifilament form using the sol–gel process. Nextel 610 contains greater than 99% Al_2O_3 and has a single-phase structure of α-Al_2O_3. The average grain size is 0.1 μm and the average filament diameter is 14 μm. Because of its fine-grained structure, it has a high tensile strength at room temperature; but because of grain growth, its tensile strength decreases rapidly as the temperature is increased above 1100°C. Nextel 720, which contains 85% Al_2O_3 and 15% SiO_2, has a lower tensile strength at room temperature, but is able to retain about 85% of its tensile strength even at 1400°C. Nextel 720 also has a much lower creep rate than Nextel 610 and other oxide fibers at temperatures above 1000°C. The structure of Nextel 720 contains α-Al_2O_3 grains embedded in mullite grains. The strength retention of Nextel 720 at high temperatures is attributed to reduced grain boundary sliding and reduced grain growth.

Another ceramic fiber, containing approximately equal parts of Al_2O_3 and silica (SiO_2), is available in short, discontinuous lengths under the trade name Fiberfrax. The fiber diameter is 2–12 μm and the fiber aspect ratio (length to diameter ratio) is greater than 200. It is manufactured either by a melt blowing or by a melt spinning process. Saffil, produced by Saffil Ltd., is also a discontinuous aluminosilicate fiber, containing 95% Al_2O_3 and 5% SiO_2. Its diameter is 1–5 μm. It is produced by blow extrusion of partially hydrolyzed solution of aluminum salts with a small amount of SiO_2. It contains mainly δ-Al_2O_3 grains of 50 nm size, but it also contains some larger size α-Al_2O_3. These two fibers are mostly used for high temperature insulation.

2.2 MATRIX

The roles of the matrix in a fiber-reinforced composite are: (1) to keep the fibers in place, (2) to transfer stresses between the fibers, (3) to provide a barrier against an adverse environment, such as chemicals and moisture, and (4) to protect the surface of the fibers from mechanical degradation (e.g., by abrasion). The matrix plays a minor role in the tensile load-carrying capacity of a composite structure. However, selection of a matrix has a major influence on the compressive, interlaminar shear as well as in-plane shear properties of the composite material. The matrix provides lateral support against the possibility of fiber buckling under compressive loading, thus influencing to a large extent, the compressive strength of the composite material. The interlaminar shear strength is an important design consideration for structures under bending loads, whereas the in-plane shear strength is important under torsional loads. The interaction between fibers and matrix is also important in designing damage-tolerant structures. Finally, the processing and defects in a composite material depend strongly on the processing characteristics of the matrix. For example, for epoxy polymers used as matrix in many aerospace composites, the processing characteristics include the liquid viscosity, the curing temperature, and the curing time.

Table 2.6 lists various matrix materials that have been used either commercially or in research. Among these, thermoset polymers, such as epoxies, polyesters, and vinyl esters, are more commonly used as matrix material in continuous or long fiber-reinforced composites, mainly because of the ease of processing due to their low viscosity. Thermoplastic polymers are more commonly used with short fiber-reinforced composites that are injection-molded; however, the interest in continuous fiber-reinforced thermoplastic matrix is growing. Metallic and ceramic matrices are primarily considered for high-temperature applications. We briefly discuss these three categories of matrix in this section.

2.2.1 POLYMER MATRIX

A polymer is defined as a long-chain molecule containing one or more repeating units of atoms (Figure 2.19), joined together by strong covalent bonds. A polymeric material (commonly called a plastic) is a collection of a large number of polymer molecules of similar chemical structure (but not of equal length). In the solid state, these molecules are frozen in space, either in a random fashion in amorphous polymers or in a mixture of random fashion

TABLE 2.6
Matrix Materials

Polymeric

Thermoset polymers

- Epoxies: principally used in aerospace and aircraft applications
- Polyesters, vinyl esters: commonly used in automotive, marine, chemical, and electrical applications
- Phenolics: used in bulk molding compounds
- Polyimides, polybenzimidazoles (PBI), polyphenylquinoxaline (PPQ): for high-temperature aerospace applications (temperature range: 250°C–400°C)
- Cyanate ester

Thermoplastic polymers

- Nylons (such as nylon 6, nylon 6,6), thermoplastic polyesters (such as PET, PBT), polycarbonate (PC), polyacetals: used with discontinuous fibers in injection-molded articles
- Polyamide-imide (PAI), polyether ether ketone (PEEK), polysulfone (PSUL), polyphenylene sulfide (PPS), polyetherimide (PEI): suitable for moderately high temperature applications with continuous fibers

Metallic

- Aluminum and its alloys, titanium alloys, magnesium alloys, copper-based alloys, nickel-based superalloys, stainless steel: suitable for high-temperature applications (temperature range: 300°C–500°C)

Ceramic

- Aluminum oxide (Al_2O_3), carbon, silicon carbide (SiC), silicon nitride (Si_3N_4): suitable for high-temperature applications

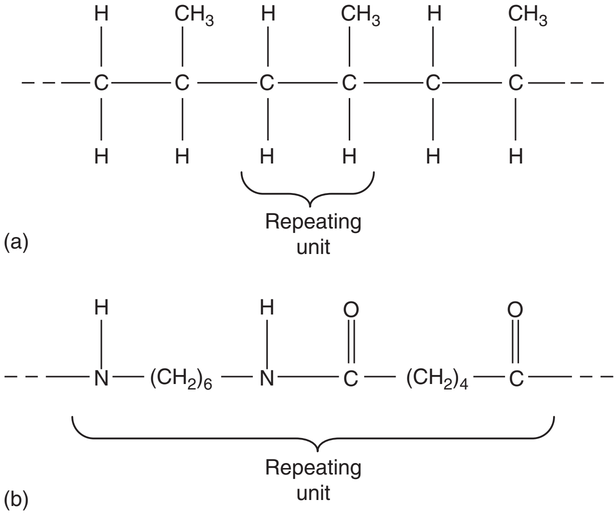


FIGURE 2.19 Examples of repeating units in polymer molecules. (a) A polypropylene molecule. (b) A nylon 6,6 molecule.

and orderly fashion (folded chains) in semicrystalline polymers (Figure 2.20). However, on a submicroscopic scale, various segments in a polymer molecule may be in a state of random excitation. The frequency, intensity, and number of these segmental motions increase with increasing temperature, giving rise to the temperature-dependent properties of a polymeric solid.

2.2.1.1 Thermoplastic and Thermoset Polymers

Polymers are divided into two broad categories: thermoplastics and thermosets. In a thermoplastic polymer, individual molecules are not chemically joined together (Figure 2.21a). They are held in place by weak secondary bonds or intermolecular forces, such as van der Waals bonds and hydrogen bonds. With the application of heat, these secondary bonds in a solid thermoplastic polymer can be temporarily broken and the molecules can now be moved relative to each other or flow to a new configuration if pressure is applied on them. On cooling, the molecules can be frozen in their new configuration and the secondary bonds are restored, resulting in a new solid shape. Thus, a thermoplastic polymer can be heat-softened, melted, and reshaped (or postformed) as many times as desired.

In a thermoset polymer, on the other hand, the molecules are chemically joined together by cross-links, forming a rigid, three-dimensional network structure (Figure 2.21b). Once these cross-links are formed during the polymerization reaction (also called the curing reaction), the thermoset polymer

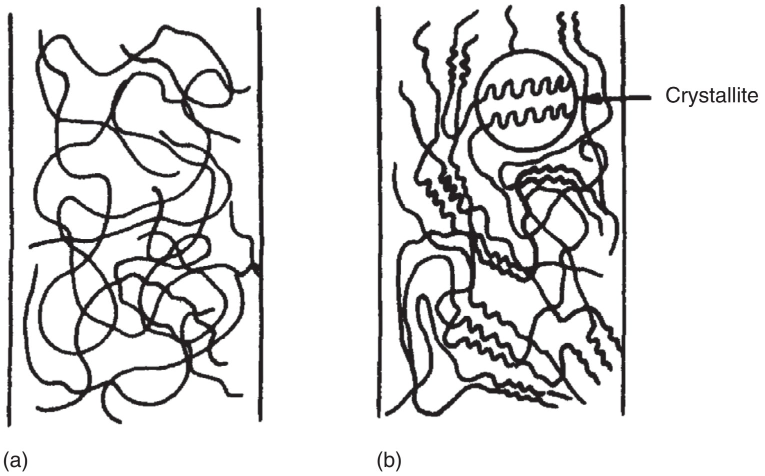


FIGURE 2.20 Arrangement of molecules in (a) amorphous polymers and (b) semicrystalline polymers.

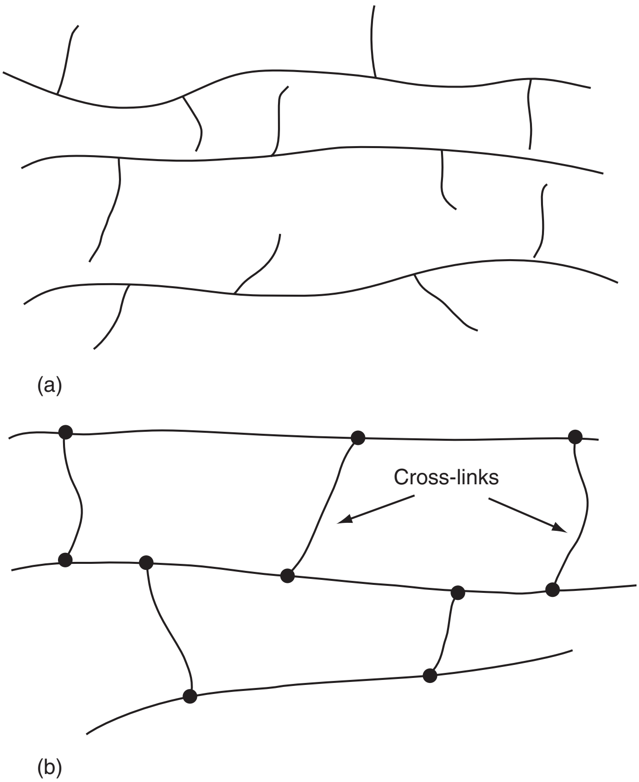


FIGURE 2.21 Schematic representation of (a) thermoplastic polymer and (b) thermoset polymer.

cannot be melted by the application of heat. However, if the number of cross-links is low, it may still be possible to soften them at elevated temperatures.

2.2.1.2 Unique Characteristics of Polymeric Solids

There are two unique characteristics of polymeric solids that are not observed in metals under ordinary conditions, namely, that their mechanical properties depend strongly on both the ambient temperature and the loading rate. Figure 2.22 schematically shows the general trends in the variation of tensile modulus of various types of polymers with temperature. Near the glass transition temperature, denoted by T_g in this diagram, the polymeric solid changes from a hard, sometimes brittle (glass-like) material to a soft, tough (leather-like) material. Over a temperature range around T_g, its modulus is reduced by as much as five orders of magnitude. Near this temperature, the material is also highly viscoelastic. Thus, when an external load is applied, it exhibits an

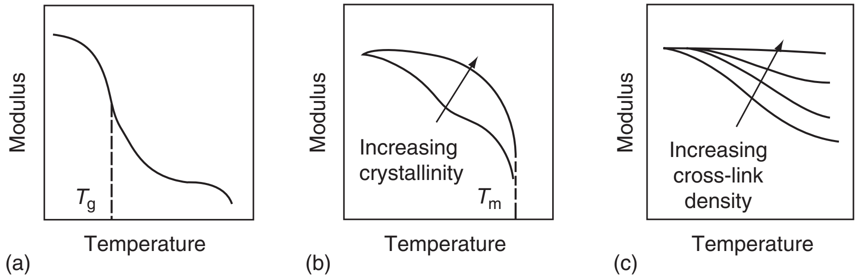


FIGURE 2.22 Variation of tensile modulus with temperature for three different types of polymers: (a) amorphous thermoplastic, (b) semicrystalline thermoplastic, and (c) thermoset.

instantaneous elastic deformation followed by a slow viscous deformation. With increasing temperature, the polymer changes into a rubber-like solid capable of undergoing large, elastic deformations under external loads. As the temperature is increased further, both amorphous and semicrystalline thermoplastics achieve highly viscous liquid states, with the latter showing a sharp transition at the crystalline melting point, denoted by T_m. However, for a thermoset polymer, no melting occurs; instead, it chars and finally burns at very high temperatures. The glass transition temperature of a thermoset polymer can be controlled by varying the amount of cross-linking between the molecules. For very highly cross-linked polymers, the glass transition and the accompanying softening may not be observed.

The mechanical characteristics of a polymeric solid depend on the ambient temperature relative to the glass transition temperature of the polymer. If the ambient temperature is above T_g, the polymeric solid exhibits low surface hardness, low modulus, and high ductility. At temperatures below T_g, the segmental motion in a polymer plays an important role. If the molecular structure of a polymer allows many segmental motions, it behaves in a ductile manner even below T_g. Polycarbonate (PC), polyethylene terephthalate (PET), and various nylons fall into this category. If, on the other hand, the segmental motions are restricted, as in polymethyl methacrylate (PMMA), polystyrene (PS), and many thermoset polymers, it shows essentially a brittle failure.

Figure 2.23 shows the effects of temperature and loading rate on the stress–strain behavior of polymeric solids. At low temperatures, the stress–strain behavior is much like that of a brittle material. The polymer may not exhibit any signs of yielding and the strain-to-failure is low. As the temperature is increased, yielding may occur; but the yield strength decreases with increasing temperature. The strain-to-failure, on the other hand, increases with increasing temperature, transforming the polymer from a brittle material at low temperatures to a ductile material at elevated temperatures.

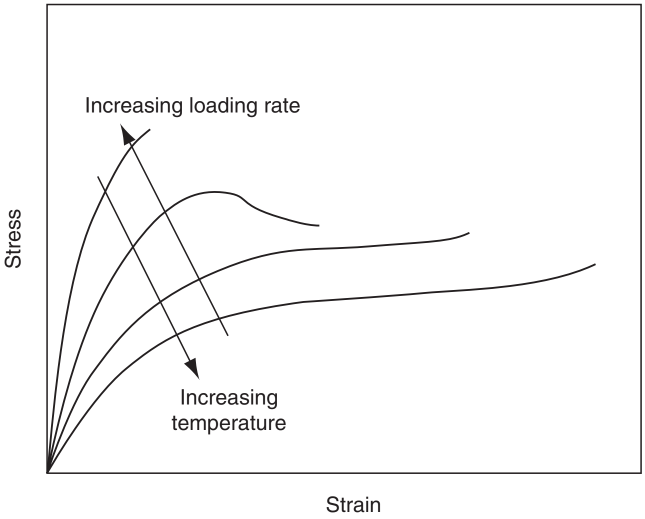


FIGURE 2.23 Effects of loading rate and temperature on the stress–strain behavior of polymeric solids.

The effect of loading rate on the stress–strain behavior is opposite to that due to temperature (Figure 2.23). At low loading rates or long durations of loading, the polymer may behave in a ductile manner and show high toughness. At high loading rates or short durations of loading, the same polymer behaves in a rigid, brittle (glass-like) manner.

2.2.1.3 Creep and Stress Relaxation

The viscoelastic characteristic of a polymeric solid is best demonstrated by creep and stress relaxation tests. In creep tests, a constant stress is maintained on a specimen while its deformation (or strain) is monitored as a function to time. As the polymer creeps, the strain increases with time. In stress relaxation tests, a constant deformation (strain) is maintained while the stress on the specimen is monitored as a function of time. In stress relaxation, stress decreases with time. Both tests are performed at various ambient temperatures of interest. Typical creep and stress relaxation diagrams, shown schematically in Figure 2.24, exhibit an instantaneous elastic response followed by a delayed viscous response. In general, thermoset polymers exhibit lower creep and stress relaxation than thermoplastic polymers.

2.2.1.4 Heat Deflection Temperature

Softening characteristics of various polymers are often compared on the basis of their heat deflection temperatures (HDT). Measurement of HDT is

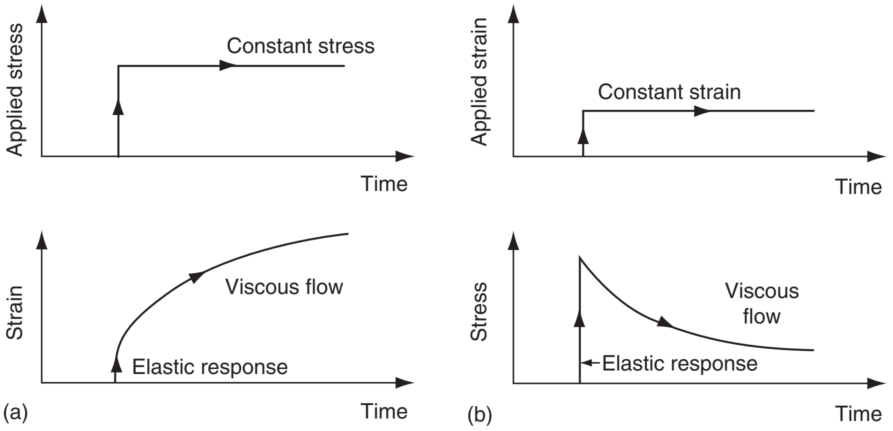


FIGURE 2.24 (a) Creep and (b) stress relaxation in solid polymers.

described in ASTM test method D648. In this test, a polymer bar of rectangular cross section is loaded as a simply supported beam (Figure 2.25) inside a suitable nonreacting liquid medium, such as mineral oil. The load on the bar is adjusted to create a maximum fiber stress of either 1.82 MPa (264 psi) or 0.455 MPa (66 psi). The center deflection of the bar is monitored as the temperature of the liquid medium is increased at a uniform rate of 2 ± 0.2°C/min. The temperature at which the bar deflection increases by 0.25 mm

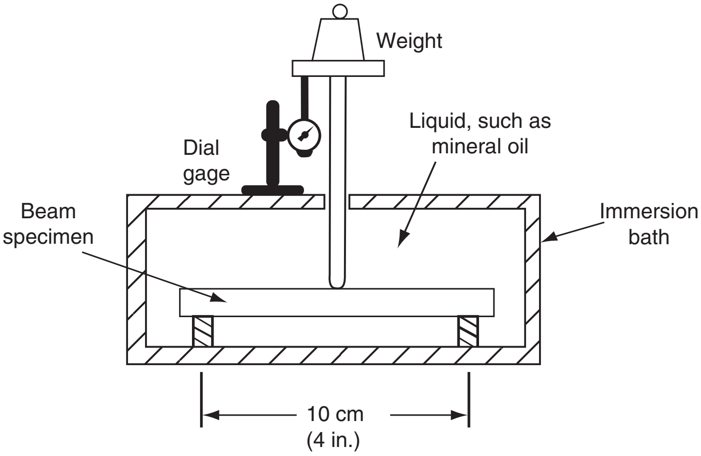


FIGURE 2.25 Test setup for measuring heat deflection temperature (HDT).

(0.01 in.) from its initial room temperature deflection is called the HDT at the specific fiber stress.

Although HDT is widely reported in the plastics product literature, it should not be used in predicting the elevated temperature performance of a polymer. It is used mostly for quality control and material development purposes. It should be pointed out that HDT is not a measure of the glass transition temperature. For glass transition temperature measurements, such methods as differential scanning calorimetry (DSC) or differential thermal analysis (DTA) are used [13].

2.2.1.5 Selection of Matrix: Thermosets vs. Thermoplastics

The primary consideration in the selection of a matrix is its basic mechanical properties. For high-performance composites, the most desirable mechanical properties of a matrix are

1. High tensile modulus, which influences the compressive strength of the composite
2. High tensile strength, which controls the intraply cracking in a composite laminate
3. High fracture toughness, which controls ply delamination and crack growth

For a polymer matrix composite, there may be other considerations, such as good dimensional stability at elevated temperatures and resistance to moisture or solvents. The former usually means that the polymer must have a high glass transition temperature T_g. In practice, the glass transition temperature should be higher than the maximum use temperature. Resistance to moisture and solvent means that the polymer should not dissolve, swell, crack (craze), or otherwise degrade in hot–wet environments or when exposed to solvents. Some common solvents in aircraft applications are jet fuels, deicing fluids, and paint strippers. Similarly, gasoline, motor oil, and antifreeze are common solvents in the automotive environment.

Traditionally, thermoset polymers (also called resins) have been used as a matrix material for fiber-reinforced composites. The starting materials used in the polymerization of a thermoset polymer are usually low-molecular-weight liquid chemicals with very low viscosities. Fibers are either pulled through or immersed in these chemicals before the polymerization reaction begins. Since the viscosity of the polymer at the time of fiber incorporation is very low, it is possible to achieve a good wet-out between the fibers and the matrix without the aid of either high temperature or pressure. Fiber surface wetting is extremely important in achieving fiber–matrix interaction in the composite, an essential requirement for good mechanical performance. Among other

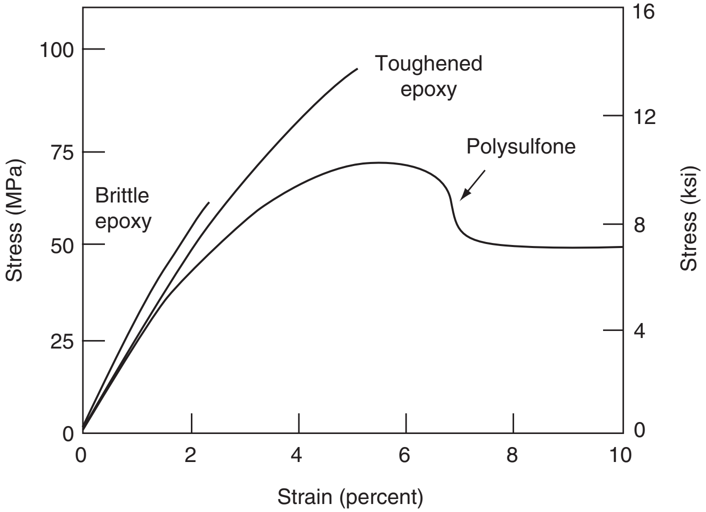


FIGURE 2.26 Tensile stress–strain diagrams of a thermoset polymer (epoxy) and a thermoplastic polymer (polysulfone).

advantages of using thermoset polymers are their thermal stability and chemical resistance. They also exhibit much less creep and stress relaxation than thermoplastic polymers. The disadvantages are

1. Limited storage life (before the final shape is molded) at room temperature
2. Long fabrication time in the mold (where the polymerization reaction, called the curing reaction or simply called *curing*, is carried out to transform the liquid polymer to a solid polymer)
3. Low strain-to-failure (Figure 2.26), which also contributes to their low impact strengths

The most important advantage of thermoplastic polymers over thermoset polymers is their high impact strength and fracture resistance, which in turn impart an excellent damage tolerance characteristic to the composite material. In general, thermoplastic polymers have higher strain-to-failure (Figure 2.25) than thermoset polymers, which may provide a better resistance to matrix microcracking in the composite laminate. Other advantages of thermoplastic polymers are

1. Unlimited storage (shelf) life at room temperature
2. Shorter fabrication time
3. Postformability (e.g., by thermoforming)

TABLE 2.7
Maximum Service Temperature for Selected Polymeric Matrices

Polymer	T_g, °C	Maximum Service Temperature, °C (°F)
Thermoset matrix		
DGEBA epoxy	180	125 (257)
TGDDM epoxy	240–260	190 (374)
Bismaleimides (BMI)	230–290	232 (450)
Acetylene-terminated polyimide (ACTP)	320	280 (536)
PMR-15	340	316 (600)
Thermoplastic matrix		
Polyether ether ketone (PEEK)	143	250 (482)
Polyphenylene sulfide (PPS)	85	240 (464)
Polysulfone	185	160 (320)
Polyetherimide (PEI)	217	267 (512)
Polyamide-imide (PAI)	280	230 (446)
K-III polyimide	250	225 (437)
LARC-TPI polyimide	265	300 (572)

4. Ease of joining and repair by welding, solvent bonding, and so on
5. Ease of handling (no tackiness)
6. Can be reprocessed and recycled

In spite of such distinct advantages, the development of continuous fiber-reinforced thermoplastic matrix composites has been much slower than that of continuous fiber-reinforced thermoset matrix composites. Because of their high melt or solution viscosities, incorporation of continuous fibers into a thermoplastic matrix is difficult. Commercial engineering thermoplastic polymers, such as nylons and polycarbonate, are of very limited interest in structural applications because they exhibit lower creep resistance and lower thermal stability than thermoset polymers. Recently, a number of thermoplastic polymers have been developed that possess high heat resistance (Table 2.7) and they are of interest in aerospace applications.

2.2.2 METAL MATRIX

Metal matrix has the advantage over polymeric matrix in applications requiring a long-term resistance to severe environments, such as high temperature [14]. The yield strength and modulus of most metals are higher than those for polymers, and this is an important consideration for applications requiring high transverse strength and modulus as well as compressive strength for the composite. Another advantage of using metals is that they can be plastically deformed and strengthened by a variety of thermal and mechanical treatments. However, metals have a number of disadvantages, namely, they have high densities, high melting points (therefore, high process temperatures), and a tendency toward corrosion at the fiber–matrix interface.

The two most commonly used metal matrices are based on aluminum and titanium. Both of these metals have comparatively low densities and are available in a variety of alloy forms. Although magnesium is even lighter, its great affinity toward oxygen promotes atmospheric corrosion and makes it less suitable for many applications. Beryllium is the lightest of all structural metals and has a tensile modulus higher than that of steel. However, it suffers from extreme brittleness, which is the reason for its exclusion as a potential matrix material. Nickel- and cobalt-based superalloys have also been used as matrix; however, the alloying elements in these materials tend to accentuate the oxidation of fibers at elevated temperatures.

Aluminum and its alloys have attracted the most attention as matrix material in metal matrix composites. Commercially, pure aluminum has been used for its good corrosion resistance. Aluminum alloys, such as 201, 6061, and 1100, have been used for their higher tensile strength–weight ratios. Carbon fiber is used with aluminum alloys; however, at typical fabrication temperatures of 500°C or higher, carbon reacts with aluminum to form aluminum carbide (Al_4C_3), which severely degrades the mechanical properties of the composite. Protective coatings of either titanium boride (TiB_2) or sodium has been used on carbon fibers to reduce the problem of fiber degradation as well as to improve their wetting with the aluminum alloy matrix [15]. Carbon fiber-reinforced aluminum composites are inherently prone to galvanic corrosion, in which carbon fibers act as a cathode owing to a corrosion potential of 1 V higher than that of aluminum. A more common reinforcement for aluminum alloys is SiC.

Titanium alloys that are most useful in metal matrix composites [16] are α, β alloys (e.g., Ti-6Al-9V) and metastable β-alloys (e.g., Ti-10V-2Fe-3Al). These titanium alloys have higher tensile strength–weight ratios as well as better strength retentions at 400°C–500°C over those of aluminum alloys. The thermal expansion coefficient of titanium alloys is closer to that of reinforcing fibers, which reduces the thermal mismatch between them. One of the problems with titanium alloys is their high reactivity with boron and Al_2O_3 fibers at normal fabrication temperatures. Borsic (boron fibers coated with silicon carbide) and silicon carbide (SiC) fibers show less reactivity with titanium. Improved tensile strength retention is obtained by coating boron and SiC fibers with carbon-rich layers.

2.2.3 CERAMIC MATRIX

Ceramics are known for their high temperature stability, high thermal shock resistance, high modulus, high hardness, high corrosion resistance, and low density. However, they are brittle materials and possess low resistance to crack propagation, which is manifested in their low fracture toughness. The primary reason for reinforcing a ceramic matrix is to increase its fracture toughness.

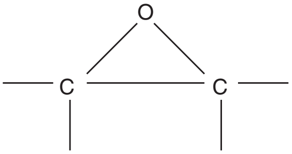
Structural ceramics used as matrix materials can be categorized as either oxides or nonoxides. Alumina (Al_2O_3) and mullite (Al_2O_3–SiO_2) are the two most commonly used oxide ceramics. They are known for their thermal and chemical stability. The common nonoxide ceramics are silicon carbide (SiC), silicon nitride (Si_3N_4), boron carbide (B_4C), and aluminum nitride (AlN). Of these, SiC has found wider applications, particularly where high modulus is desired. It also has an excellent high temperature resistance. Si_3N_4 is considered for applications requiring high strength and AlN is of interest because of its high thermal conductivity.

The reinforcements used in ceramic matrix composites are SiC, Si_3N_4, AlN, and other ceramic fibers. Of these, SiC has been the most commonly used reinforcement because of its thermal stability and compatibility with a broad range of both oxide and nonoxide ceramic matrices. The forms in which the reinforcement is used in ceramic matrix composites include whiskers (with length to diameter ratio as high as 500), platelets, particulates, and both monofilament and multifilament continuous fibers.

2.3 THERMOSET MATRIX

2.3.1 EPOXY

Starting materials for epoxy matrix are low-molecular-weight organic liquid resins containing a number of epoxide groups, which are three-member rings of one oxygen atom and two carbon atoms:



A common starting material is diglycidyl ether of bisphenol A (DGEBA), which contains two epoxide groups, one at each end of the molecule (Figure 2.27a). Other ingredients that may be mixed with the starting liquid are diluents to reduce its viscosity and flexibilizers to improve the impact strength of the cured epoxy matrix.

The polymerization (curing) reaction to transform the liquid resin to the solid state is initiated by adding small amounts of a reactive curing agent just before incorporating fibers into the liquid mix. One such curing agent is diethylene triamine (DETA, Figure 2.27b). Hydrogen atoms in the amine (NH_2) groups of a DETA molecule react with the epoxide groups of DGEBA molecules in the manner illustrated in Figure 2.28a. As the reaction continues, DGEBA molecules form cross-links with each other (Figure 2.28b) and a three-dimensional network structure is slowly formed (Figure 2.28c). The resulting material is a solid epoxy polymer.

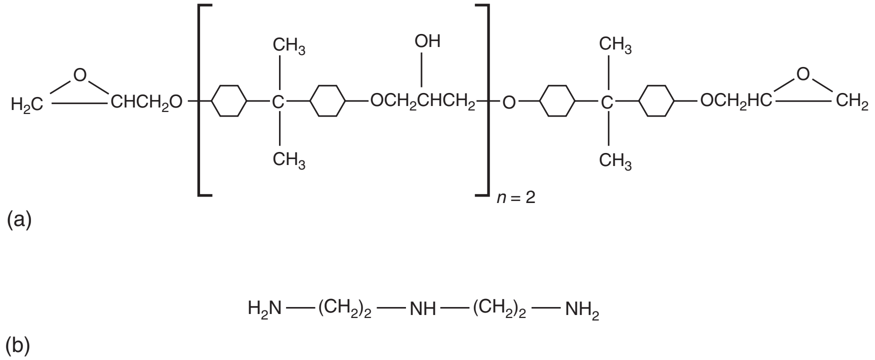


FIGURE 2.27 Principal ingredients in the preparation of an epoxy matrix. (a) A molecule of diglycidyl ether of bisphenol A (DGEBA) epoxy resin. (b) A molecule of diethylene triamine (DETA) curing agent.

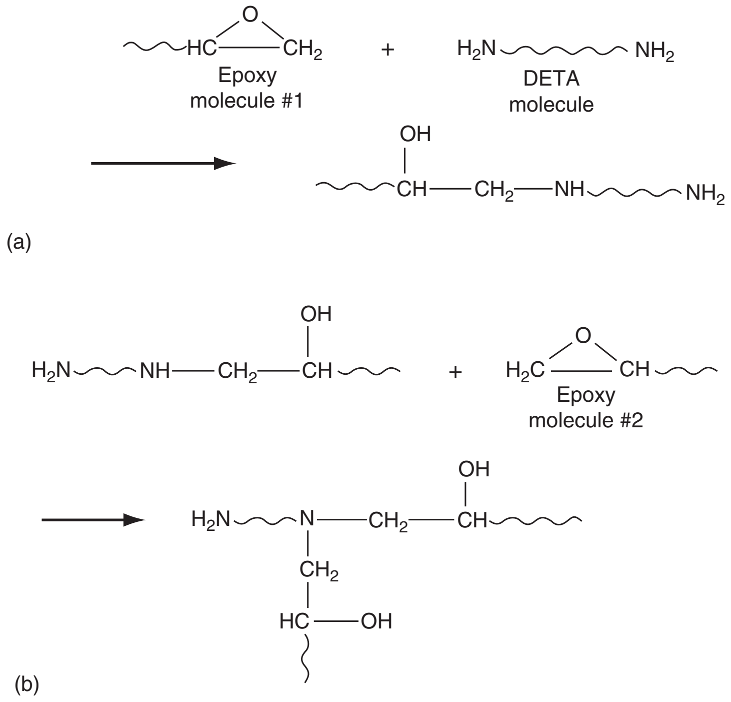


FIGURE 2.28 Schematic representation of a cross-linked epoxy resin. (a) Reaction of epoxide group with DETA molecule; (b) formation of cross-links; and

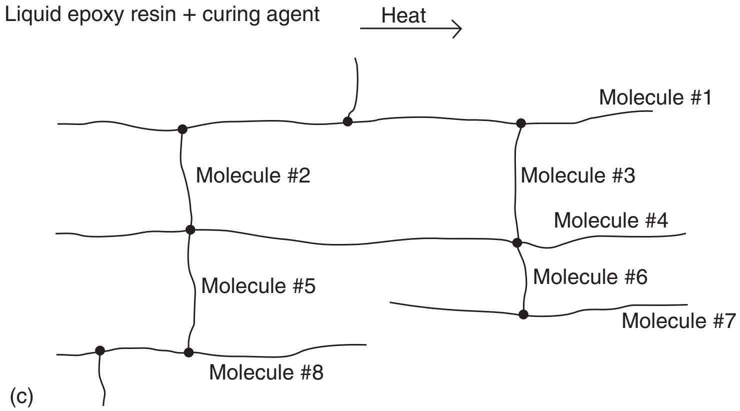


FIGURE 2.28 (continued) (c) three-dimensional network structure of solid epoxy.

If the curing reaction is slowed by external means (e.g., by lowering the reaction temperature) before all the molecules are cross-linked, the resin would exist in B-stage form. At this stage, cross-links have formed at widely spaced points in the reactive mass. Hardness, tackiness, and the solvent reactivity of the B-staged resin depend on the cure advancement or the degree of cure at the end of B-staging. The B-staged resin can be transformed into a hard, insoluble mass by completing the cure at a later time.

Curing time (also called pot life) and temperature to complete the polymerization reaction depend on the type and amount of curing agent. With some curing agents, the reaction initiates and proceeds at room temperature; but with others, elevated temperatures are required. Accelerators are sometimes added to the liquid mix to speed up a slow reaction and shorten the curing time.

The properties of a cured epoxy resin depend principally on the cross-link density (spacing between successive cross-link sites). In general, the tensile modulus, glass transition temperature, and thermal stability as well as chemical resistance are improved with increasing cross-link density, but the strain-to-failure and fracture toughness are reduced. Factors that control the cross-link density are the chemical structure of the starting liquid resin (e.g., number of epoxide groups per molecule and spacing between epoxide groups), functionality of the curing agent (e.g., number of active hydrogen atoms in DETA), and the reaction conditions, such as temperature and time.

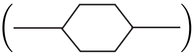
The continuous use temperature for DGEBA-based epoxies is 150°C or less. Higher heat resistance can be obtained with epoxies based on novolac and cycloaliphatics, for example, which have a continuous use temperature ranging up to 250°C. In general, the heat resistance of an epoxy is improved if it contains more aromatic () rings in its basic molecular chain.

TABLE 2.8
Typical Properties of Cast Epoxy Resin (at 23°C)

Density (g/cm^3)	1.2–1.3
Tensile strength, MPa (psi)	55–130 (8,000–19,000)
Tensile modulus, GPa (10^6 psi)	2.75–4.10 (0.4–0.595)
Poisson's ratio	0.2–0.33
Coefficient of thermal expansion, 10^{-6} m/m per °C (10^{-6} in./in. per °F)	50–80 (28–44)
Cure shrinkage, %	1–5

Epoxy matrix, as a class, has the following advantages over other thermoset matrices:

1. Wide variety of properties, since a large number of starting materials, curing agents, and modifiers are available
2. Absence of volatile matters during cure
3. Low shrinkage during cure
4. Excellent resistance to chemicals and solvents
5. Excellent adhesion to a wide variety of fillers, fibers, and other substrates

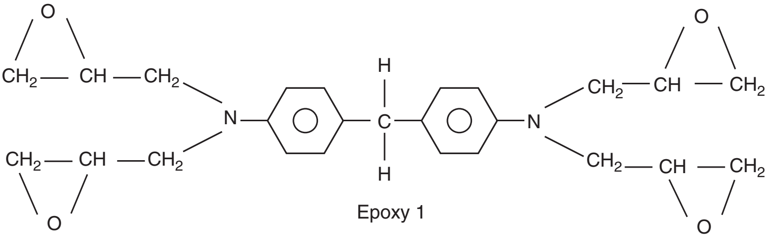
The principal disadvantages are its relatively high cost and long cure time. Typical properties of cast epoxy resins are given in Table 2.8.

One of the epoxy resins used in the aerospace industry is based on tetraglycidal diaminodiphenyl methane (TGDDM). It is cured with diaminodiphenyl sulfone (DDS) with or without an accelerator. The TGDDM–DDS system is used due to its relatively high glass transition temperature (240°C–260°C, compared with 180°C–190°C for DGEBA systems) and good strength retention even after prolonged exposure to elevated temperatures. Prepregs made with this system can be stored for a longer time period due to relatively low curing reactivity of DDS in the "B-staged" resin. Limitations of the TGDDM system are their poor hot–wet performance, low strain-to-failure, and high level of atmospheric moisture absorption (due to its highly polar molecules). High moisture absorption reduces its glass transition temperature as well as its modulus and other mechanical properties.

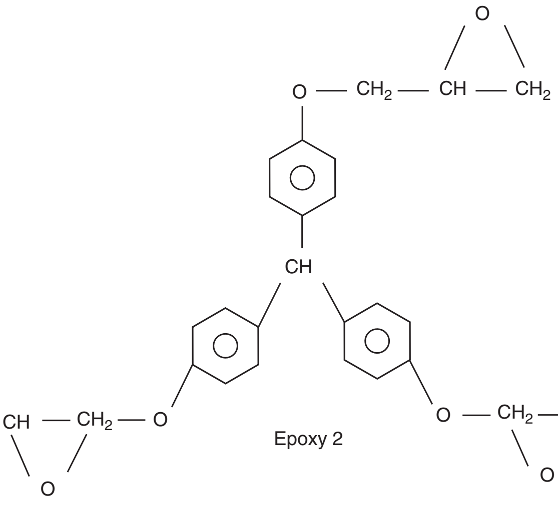
Although the problems of moisture absorption and hot–wet performance can be reduced by changing the resin chemistry (Table 2.9), brittleness or low strain-to-failure is an inherent problem of any highly cross-linked resin. Improvement in the matrix strain-to-failure and fracture toughness is considered essential for damage-tolerant composite laminates. For epoxy resins, this can be accomplished by adding a small amount of highly reactive carboxyl-terminated butadiene–acrylonitrile (CTBN) liquid elastomer, which forms a

TABLE 2.9
Mechanical Properties of High-Performance Epoxy Resins[a,b]

Property	Epoxy 1	Epoxy 2 (Epon HPT 1072, Shell Chemical)	Epoxy 3 (Tactix 742, Dow Chemical)
T_g, °C	262	261	334
Flexural properties (at room temperature)			
Strength, MPa (ksi)	140.7 (20.4)	111.7 (16.2)	124.1 (18)
Modulus, GPa (Msi)	3.854 (0.559)	3.378 (0.490)	2.965 (0.430)
Flexural properties (hot–wet)[c]			
Strength (% retained)	55	65	—
Modulus (% retained)	64.5	87.3	—
Fracture energy, G_{Ic}, kJ/m^2 (in. lb/in.^{2})	0.09 (0.51)	0.68 (3.87)	0.09 (0.51)
Moisture gain, %	5.7	2.6	—



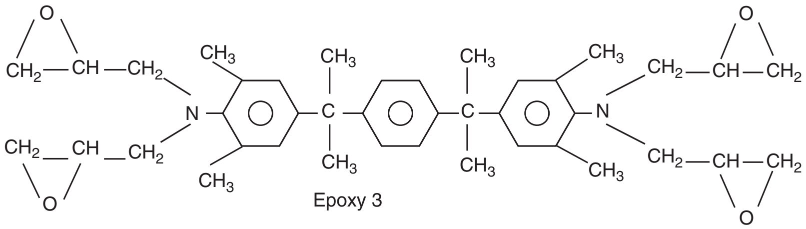
Epoxy 1



Epoxy 2

(*continued*)

TABLE 2.9 (continued)
Mechanical Properties of High-Performance Epoxy Resins[a,b]



[a] All epoxies were cured with DDS.

[b] Molecular structures for Epoxies 1–3 are given in the accompanying figures.

[c] Percent retained with room temperature and dry properties when tested in water at 93°C after 2 week immersion at 93°C.

second phase in the cured matrix and impedes its microcracking. Although the resin is toughened, its glass transition temperature, modulus, and tensile strength as well as solvent resistance are reduced (Table 2.10). This problem is overcome by blending epoxy with a tough thermoplastic resin, such as polyethersulfone, but the toughness improvement depends on properly matching the epoxy and thermoplastic resin functionalities, their molecular weights, and so on [17].

2.3.2 POLYESTER

The starting material for a thermoset polyester matrix is an unsaturated polyester resin that contains a number of C=C double bonds. It is prepared by the

TABLE 2.10
Effect of CTBN Addition on the Properties of Cast Epoxy Resin

CTBN parts per 100 parts of epoxy[a]	0	5	10	15
Tensile strength, MPa	65.8	62.8	58.4	51.4
Tensile modulus, GPa	2.8	2.5	2.3	2.1
Elongation at break (%)	4.8	4.6	6.2	8.9
Fracture energy, G_{Ic}, kJ/m^2	1.75	26.3	33.3	47.3
HDT, °C (at 1.82 MPa)	80	76	74	71

Source: Adapted from Riew, C.K., Rowe, E.H., and Siebert, A.R., *Toughness and Brittleness of Plastics*, R.D. Deanin and A.M. Crugnola, eds., American Chemical Society, Washington, D.C., 1976.

[a] DGEBA epoxy (Epon 828, Shell) cured with five parts of piperidine at 120°C for 16 h.

reaction of maleic anhydride and ethylene glycol or propylene glycol (Figure 2.29a). Saturated acids, such as isophthalic acid or orthophthalic acid, are also added to modify the chemical structure between the cross-linking sites; however, these acids do not contain any C═C double bonds. The resulting polymeric liquid is dissolved in a reactive (polymerizable) diluent, such as styrene (Figure 2.29b), which reduces its viscosity and makes it easier to handle. The diluent also contains C═C double bonds and acts as a cross-linking agent by bridging the adjacent polyester molecules at their unsaturation points. Trace amounts of an inhibitor, such as hydroquinone or benzoquinone, are added to the liquid mix to prevent premature polymerization during storage.

The curing reaction for polyester resins is initiated by adding small quantities of a catalyst, such as an organic peroxide or an aliphatic azo compound (Figure 2.29c), to the liquid mix. With the application of heat (in the temperature range

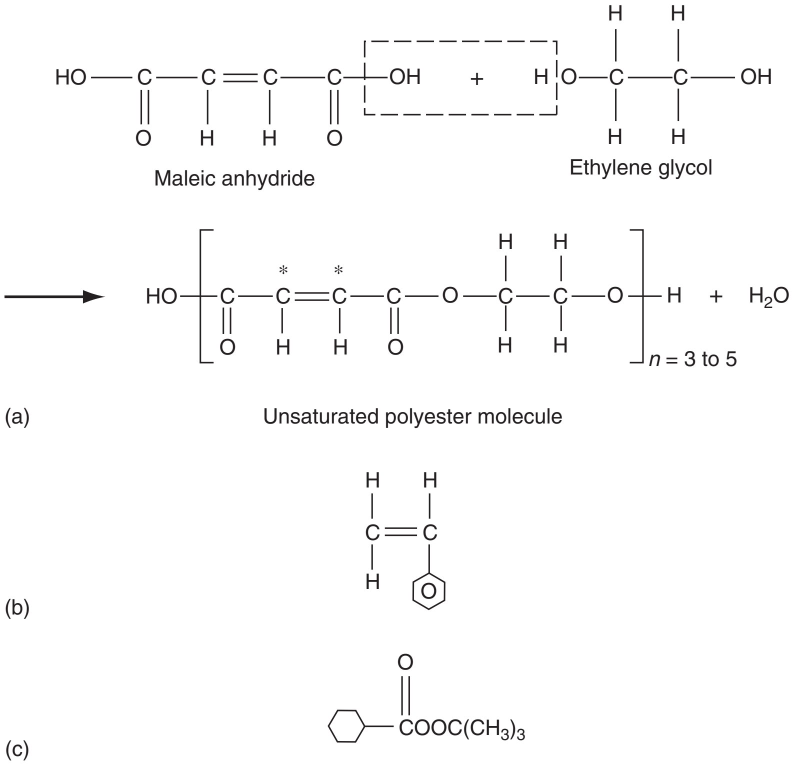


FIGURE 2.29 Principal ingredients in the preparation of a thermoset polyester matrix. (a) Unsaturated polyester molecule. The asterisk denotes unsaturation points (reactive sites) in the unsaturated polyester molecule; (b) styrene molecule; and (c) *t*-butyl perbenzoate molecule (tBPB).

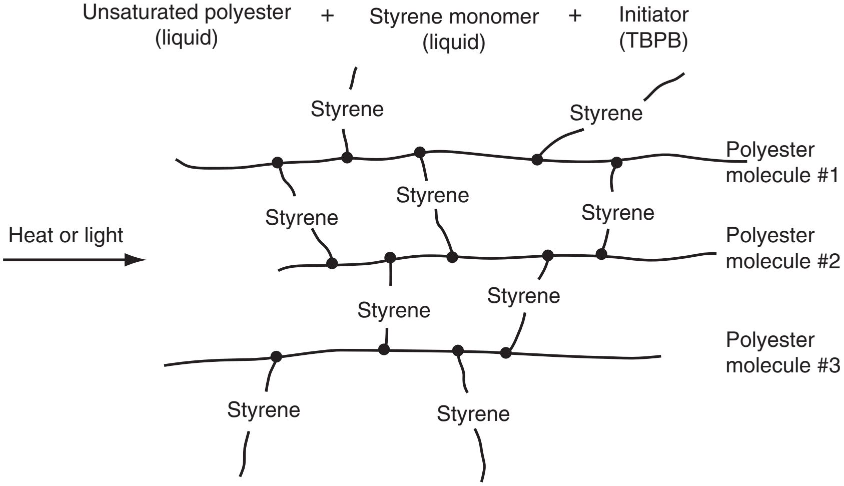


FIGURE 2.30 Schematic representation of a cross-linked polyester resin.

of 107°C–163°C), the catalyst decomposes rapidly into free radicals, which react (mostly) with the styrene molecules and break their C=C bonds. Styrene radicals, in turn, join with the polyester molecules at their unsaturation points and eventually form cross-links between them (Figure 2.30). The resulting material is a solid polyester resin.

The curing time for polyester resins depends on the decomposition rate of the catalyst, which can be increased by increasing the curing temperature. However, for a given resin–catalyst system, there is an optimum temperature at which all of the free radicals generated from the catalyst are used in curing the resin. Above this optimum temperature, free radicals are formed so rapidly that wasteful side reactions occur and deterioration of the curing reaction is observed. At temperatures below the optimum, the curing reaction is very slow. The decomposition rate of a catalyst is increased by adding small quantities of an accelerator, such as cobalt naphthanate (which essentially acts as a catalyst for the primary catalyst).

As in the case of epoxy resins, the properties of polyester resins depend strongly on the cross-link density. The modulus, glass transition temperature, and thermal stability of cured polyester resins are improved by increasing the cross-link density, but the strain-to-failure and impact energy are reduced. The major factor influencing the cross-link density is the number of unsaturation points in an uncured polyester molecule. The simplest way of controlling the frequency of unsaturation points is to vary the weight ratio of various ingredients used for making unsaturated polyesters. For example, the frequency of unsaturation in an isophthalic polyester resin decreases as the weight ratio

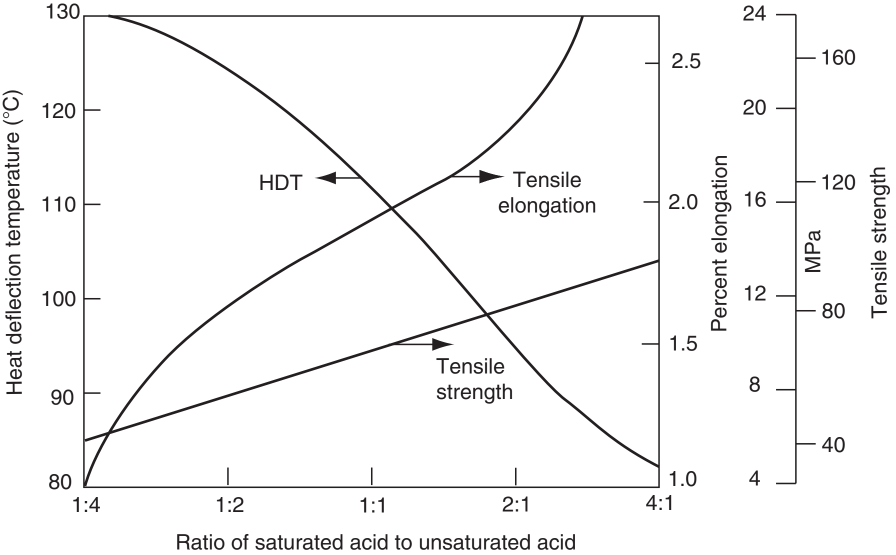


FIGURE 2.31 Effect of unsaturation level on the properties of a thermoset polyester resin. (After How ingredients influence unsaturated polyester properties, Amoco Chemicals Corporation, Bulletin IP-70, 1980.)

of isophthalic acid to maleic anhydride is increased. The effect of such weight ratio variation on various properties of a cured isophthalic polyester resin is shown in Figure 2.31. The type of ingredients also influences the properties and processing characteristics of polyester resins. For example, terephthalic acid generally provides a higher HDT than either isophthalic or orthophthalic acid, but it has the slowest reactivity of the three phthalic acids. Adipic acid, if used instead of any of the phthalic acids, lowers the stiffness of polyester molecules, since it does not contain an aromatic ring in its backbone. Thus, it can be used as a flexibilizer for polyester resins. Another ingredient that can also lower the stiffness is diethylene glycol. Propylene glycol, on the other hand, makes the polyester resin more rigid, since the pendant methyl groups in its structure restrict the rotation of polyester molecules.

The amount and type of diluent are also important factors in controlling the properties and processing characteristics of polyester resins. Styrene is the most widely used diluent because it has low viscosity, high solvency, and low cost. Its drawbacks are flammability and potential (carcinogenic) health hazard due to excessive emissions. Increasing the amount of styrene reduces the modulus of the cured polyester resin, since it increases the space between polyester molecules. Because styrene also contributes unsaturation points, higher styrene content in the resin solution increases the total amount of unsaturation and, consequently, the curing time is increased. An excessive amount of styrene tends to promote self-polymerization (i.e., formation of

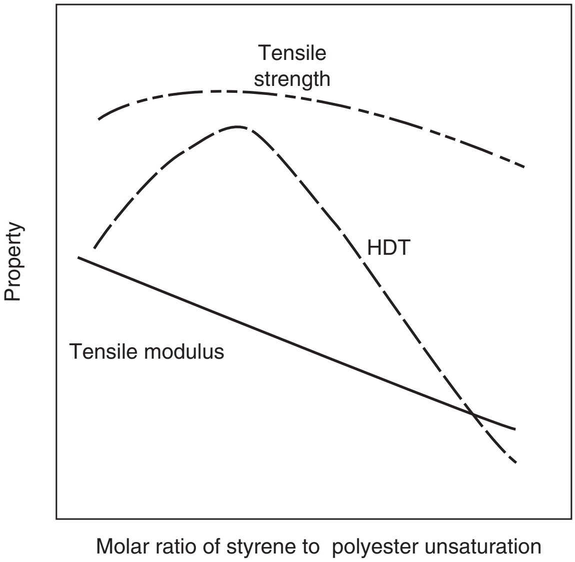


FIGURE 2.32 Effect of increasing styrene content on the properties of a thermoset polyester resin.

polystyrene) and causes polystyrene-like properties to dominate the cured polyester resin (Figure 2.32).

Polyester resins can be formulated in a variety of properties ranging from hard and brittle to soft and flexible. Its advantages are low viscosity, fast cure time, and low cost. Its properties (Table 2.11) are generally lower than those for epoxies. The principal disadvantage of polyesters over epoxies is their high volumetric shrinkage. Although this allows easier release of parts from the mold, the difference in shrinkage between the resin and fibers results in uneven depressions (called *sink marks*) on the molded surface. The sink marks are undesirable for exterior surfaces requiring high gloss and good appearance

TABLE 2.11
Typical Properties of Cast Thermoset Polyester Resins (at 23°C)

Density (g/cm^3)	1.1–1.43
Tensile strength, MPa (psi)	34.5–103.5 (5,000–15,000)
Tensile modulus, GPa (10^6 psi)	2.1–3.45 (0.3–0.5)
Elongation, %	1–5
HDT, °C (°F)	60–205 (140–400)
Cure shrinkage, %	5–12

(e.g., Class A surface quality in automotive body panels, such as hoods). One way of reducing these surface defects is to use low-shrinkage (also called low-profile) polyester resins that contain a thermoplastic component (such as polystyrene or PMMA). As curing proceeds, phase changes in the thermoplastic component allow the formation of microvoids that compensate for the normal shrinkage of the polyester resin.

2.3.3 VINYL ESTER

The starting material for a vinyl ester matrix is an unsaturated vinyl ester resin produced by the reaction of an unsaturated carboxylic acid, such as methacrylic or acrylic acid, and an epoxy (Figure 2.33). The C=C double bonds (unsaturation points) occur only at the ends of a vinyl ester molecule, and therefore, cross-linking can take place only at the ends, as shown schematically in Figure 2.34. Because of fewer cross-links, a cured vinyl ester resin is more flexible and has higher fracture toughness than a cured polyester resin. Another unique characteristic of a vinyl ester molecule is that it contains a number of OH (hydroxyl) groups along its length. These OH groups can form hydrogen bonds with similar groups on a glass fiber surface resulting in excellent wet-out and good adhesion with glass fibers.

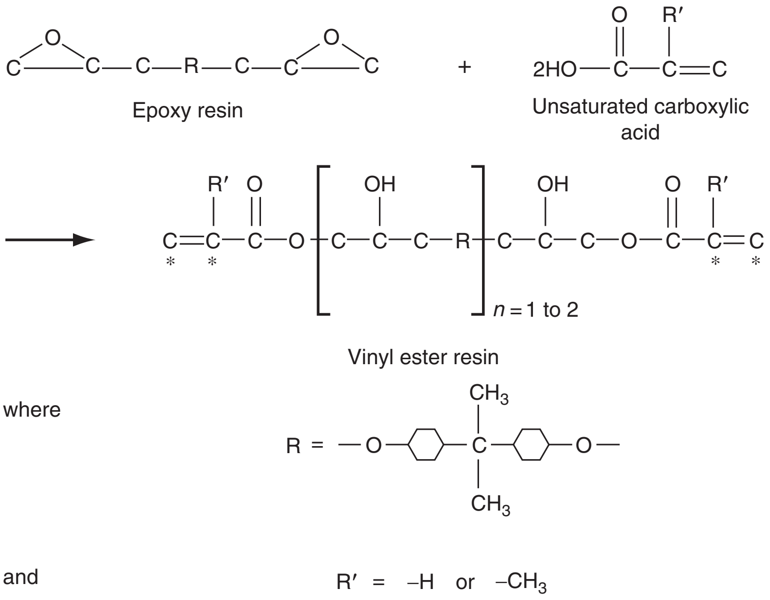


FIGURE 2.33 Chemistry of a vinyl ester resin. The asterisk denotes unsaturation points (reactive sites).

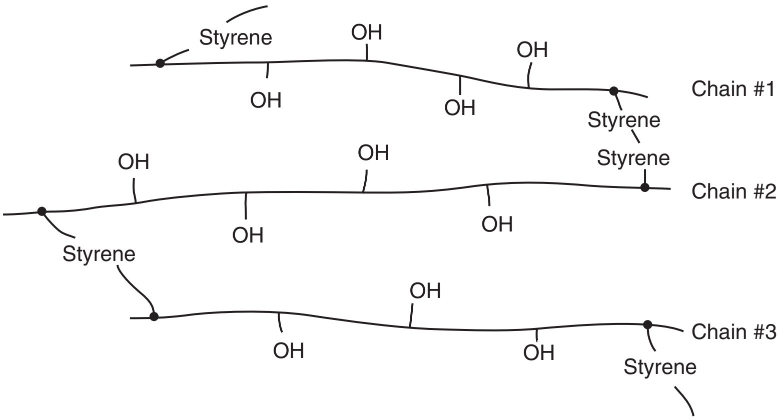


FIGURE 2.34 Schematic representation of a cross-linked vinyl ester resin.

Vinyl ester resins, like unsaturated polyester resins, are dissolved in styrene monomer, which reduces their viscosity. During polymerization, styrene coreacts with the vinyl ester resin to form cross-links between the unsaturation points in adjacent vinyl ester molecules. The curing reaction for vinyl ester resins is similar to that for unsaturated polyesters.

Vinyl ester resins possess good characteristics of epoxy resins, such as excellent chemical resistance and tensile strength, and of unsaturated polyester resins, such as low viscosity and fast curing. However, the volumetric shrinkage of vinyl ester resins is in the range of 5%–10%, which is higher than that of the parent epoxy resins (Table 2.12). They also exhibit only moderate adhesive strengths compared with epoxy resins. The tensile and flexural properties of cured vinyl ester resins do not vary appreciably with the molecular weight and type of epoxy resin or other coreactants. However, the HDT and thermal stability can be improved by using heat-resistant epoxy resins, such as phenolic-novolac types.

TABLE 2.12
Typical Properties of Cast Vinyl Ester Resins (at 23°C)

Density (g/cm^3)	1.12–1.32
Tensile strength, MPa (psi)	73–81 (10,500–11,750)
Tensile modulus, GPa (10^6 psi)	3–3.5 (0.44–0.51)
Elongation, %	3.5–5.5
HDT, °C (°F)	93–135 (200–275)
Cure shrinkage, %	5.4–10.3

2.3.4 BISMALEIMIDES AND OTHER THERMOSET POLYIMIDES

Bismaleimide (BMI), PMR-15 (for polymerization of monomer reactants), and acetylene-terminated polyimide (ACTP) are examples of thermoset polyimides (Table 2.13). Among these, BMIs are suitable for applications requiring a service temperature of 127°C–232°C. PMR and ACTP can be used up to 288°C and 316°C, respectively. PMR and ACTP also have exceptional thermo-oxidative stability and show only 20% weight loss over a period of 1000 h at 316°C in flowing air [18].

Thermoset polyimides are obtained by addition polymerization of liquid monomeric or oligomeric imides to form a cross-linked infusible structure. They are available either in solution form or in hot-melt liquid form. Fibers can be coated with the liquid imides or their solutions before the cross-linking reaction. On curing, they not only offer high temperature resistance, but also high chemical and solvent resistance. However, these materials are inherently very brittle due to their densely cross-linked molecular structure. As a result, their composites are prone to excessive microcracking. One useful method of reducing their brittleness without affecting their heat resistance is to combine them with one or more tough thermoplastic polyimides. The combination produces a semi-interpenetrating network (semi-IPN) polymer [19], which retains the easy processability of a thermoset and exhibits the good toughness of a thermoplastic. Although the reaction time is increased, this helps in broadening the processing window, which otherwise is very narrow for some

TABLE 2.13
Properties of Thermoset Polyimide Resins (at 23°C)

Property	Bismaleimide[a] Without Modifier	Bismaleimide[a] With[b] Modifier	PMR-15[c]	ACTP[d]
Density (g/cm^3)	—	1.28	1.32	1.34
Tensile strength, MPa (ksi)	—	—	38.6 (5.6)	82.7 (12)
Tensile modulus, GPa (Msi)	—	—	3.9 (0.57)	4.1 (0.60)
Strain-to-failure (%)	—	—	1.5	1.5
Flexural strength, MPa (ksi)	60 (8.7)	126.2 (18.3)	176 (25.5)	145 (21)
Flexural modulus, GPa (Msi)	5.5 (0.8)	3.7 (0.54)	4 (0.58)	4.5 (0.66)
Fracture energy, G_{Ic}, J/m^2 (in. lb/in.^{2})	24.5 (0.14)	348 (1.99)	275 (1.57)	—

[a] Compimide 353 (Shell Chemical Co.).

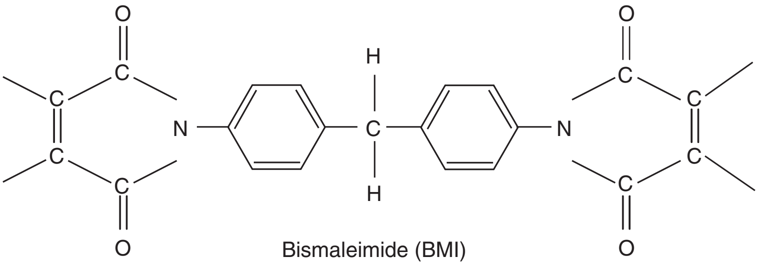
[b] Compimide 353 melt blended with a bis-allylphenyl compound (TM 121), which acts as a toughening modifier (Shell Chemical Co.).

[c] From Ref. [18].

[d] Thermid 600 (National Starch and Chemical Corporation).

of these polyimides and causes problems in manufacturing large or complex composite parts.

BMIs are the most widely used thermoset polyimides in the advanced composite industry. BMI monomers (prepolymers) are prepared by the reaction of maleic anhydride with a diamine. A variety of BMI monomers can be prepared by changing the diamine. One commercially available BMI monomer has the following chemical formula:



Bismaleimide (BMI)

BMI monomers are mixed with reactive diluents to reduce their viscosity and other comonomers, such as vinyl, acrylic, and epoxy, to improve the toughness of cured BMI. The handling and processing techniques for BMI resins are similar to those for epoxy resins. The curing of BMI occurs through addition-type homopolymerization or copolymerization that can be thermally induced at 170°C–190°C.

2.3.5 CYANATE ESTER

Cyanate ester resin has a high glass transition temperature ($T_g = 265°C$), lower moisture absorption than epoxies, good chemical resistance, and good dimensional stability [20]. Its mechanical properties are similar to those of epoxies. The curing reaction of cyanate ester involves the formation of thermally stable triazine rings, which is the reason for its high temperature resistance. The curing shrinkage of cyanate ester is also relatively small. For all these reasons, cyanate ester is considered a good replacement for epoxy in some aerospace applications. Cyanate ester is also considered for printed circuit boards, encapsulants, and other electronic components because of its low dielectric constant and high dielectric breakdown strength, two very important characteristics for many electronic applications.

Cyanate ester is commonly used in blended form with other polymers. For example, it is sometimes blended with epoxy to reduce cost. Blending it with BMI has shown to improve its T_g. Like many other thermoset polymers, cyanate ester has low fracture toughness. Blending it with thermoplastics, such as polyarylsulfone and polyethersulfone, has shown to improve its fracture toughness.

2.4 THERMOPLASTIC MATRIX

Table 2.14 lists the mechanical properties of selected thermoplastic polymers that are considered suitable for high-performance composite applications. The molecules in these polymers contain rigid aromatic rings that give them a relatively high glass transition temperature and an excellent dimensional stability at elevated temperatures. The actual value of T_g depends on the size and flexibility of other chemical groups or linkages in the chain.

2.4.1 POLYETHER ETHER KETONE

Polyether ether ketone (PEEK) is a linear aromatic thermoplastic based on the following repeating unit in its molecules:

TABLE 2.14
Properties of Selected Thermoplastic Matrix Resins (at 23°C)

Property	**PEEK**[a]	**PPS**[b]	**PSUL**[c]	**PEI**[d]	**PAI**[e]	**K-III**[f]	**LARC-TPI**[g]
Density (g/cm^3)	1.30–1.32	1.36	1.24	1.27	1.40	1.31	1.37
Yield (Y) or tensile (T) strength, MPa (ksi)	100 (14.5) (Y)	82.7 (12) (T)	70.3 (10.2) (Y)	105 (15.2) (Y)	185.5 (26.9) (T)	102 (14.8) (T)	138 (20) (T)
Tensile modulus, GPa (Msi)	3.24 (0.47)	3.3 (0.48)	2.48 (0.36)	3 (0.43)	3.03 (0.44)	3.76 (0.545)	3.45 (0.5)
Elongation-at-break (%)	50	4	75	60	12	14	5
Poisson's ratio	0.4	—	0.37	—	—	0.365	0.36
Flexural strength, MPa (ksi)	170 (24.65)	152 (22)	106.2 (15.4)	150 (21.75)	212 (30.7)	— —	— —
Flexural modulus, GPa (Msi)	4.1 (0.594)	3.45 (0.5)	2.69 (0.39)	3.3 (0.48)	4.55 (0.66)	— —	— —
Fracture energy (G_{Ic}), kJ/m^2	6.6	—	3.4	3.7	3.9	1.9	—
HDT, °C (at 1.82 MPa)	160	135	174	200	274	—	—
CLTE, 10^{-5}/°C	4.7	4.9	5.6	5.6	3.6	—	3.5

[a] Victrex.

[b] Ryton.

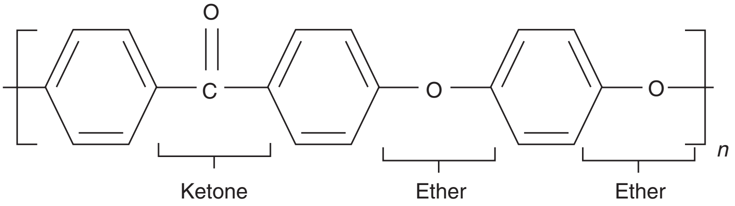
[c] Udel.

[d] Ultem.

[e] Torlon.

[f] Avimid.

[g] Durimid.



Polyetherether ketone (PEEK)

Continuous carbon fiber-reinforced PEEK composites are known in the industry as aromatic polymer composite or APC.

PEEK is a semicrystalline polymer with a maximum achievable crystallinity of 48% when it is cooled slowly from its melt. Amorphous PEEK is produced if the melt is quenched. At normal cooling rates, the crystallinity is between 30% and 35%. The presence of fibers in PEEK composites tends to increase the crystallinity to a higher level, since the fibers act as nucleation sites for crystal formation [21]. Increasing the crystallinity increases both modulus and yield strength of PEEK, but reduces its strain-to-failure (Figure 2.35).

PEEK has a glass transition temperature of 143°C and a crystalline melting point of 335°C. Melt processing of PEEK requires a temperature range of 370°C–400°C. The maximum continuous use temperature is 250°C.

The outstanding property of PEEK is its high fracture toughness, which is 50–100 times higher than that of epoxies. Another important advantage of PEEK is its low water absorption, which is less than 0.5% at 23°C compared with 4%–5% for conventional aerospace epoxies. As it is semicrystalline, it does not dissolve in common solvents. However, it may absorb some of these

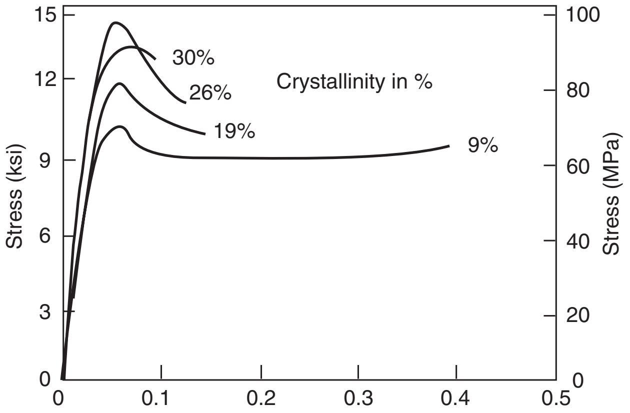
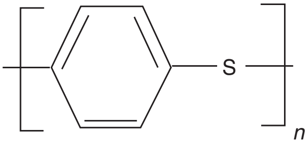


FIGURE 2.35 Tensile stress–strain diagram of PEEK at different crystallinities. (Adapted from Seferis, J.C., *Polym. Compos.*, 71, 58, 1986.)

solvents, most notably methylene chloride. The amount of solvent absorption decreases with increasing crystallinity.

2.4.2 POLYPHENYLENE SULFIDE

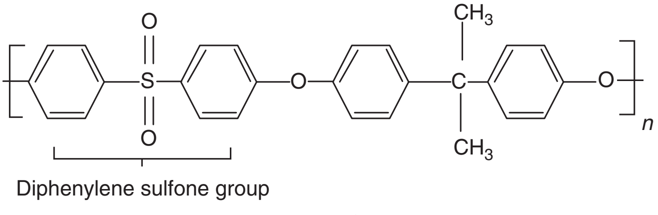
Polyphenylene sulfide (PPS) is a semicrystalline polymer with the following repeating unit in its molecules:



PPS is normally 65% crystalline. It has a glass transition temperature of 85°C and a crystalline melting point of 285°C. The relatively low T_g of PPS is due to the flexible sulfide linkage between the aromatic rings. Its relatively high crystallinity is attributed to the chain flexibility and structural regularity of its molecules. Melt processing of PPS requires heating the polymer in the temperature range of 300°C–345°C. The continuous use temperature is 240°C. It has excellent chemical resistance.

2.4.3 POLYSULFONE

Polysulfone is an amorphous thermoplastic with the repeating unit shown as follows:



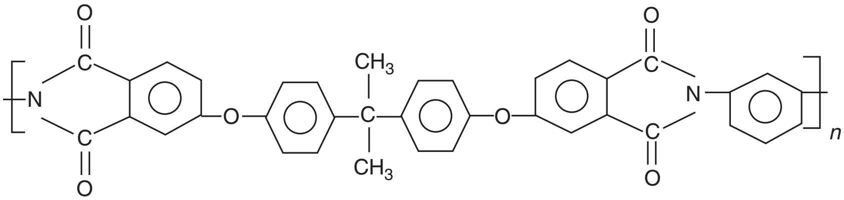
Polysulfone

Polysulfone has a glass transition temperature of 185°C and a continuous use temperature of 160°C. The melt processing temperature is between 310°C and 410°C. It has a high tensile strain-to-failure (50%–100%) and an excellent hydrolytic stability under hot–wet conditions (e.g., in steam). Although polysulfone has good resistance to mineral acids, alkalis, and salt solutions, it will swell, stress-crack, or dissolve in polar organic solvents such as ketones, chlorinated hydrocarbons, and aromatic hydrocarbons.

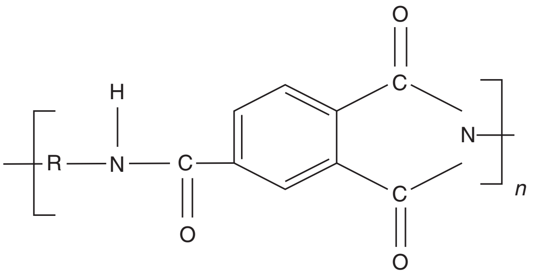
2.4.4 THERMOPLASTIC POLYIMIDES

Thermoplastic polyimides are linear polymers derived by condensation polymerization of a polyamic acid and an alcohol. Depending on the types of the polyamic acid and alcohol, various thermoplastic polyimides can be produced. The polymerization reaction takes place in the presence of a solvent and produces water as its by-product. The resulting polymer has a high melt viscosity and must be processed at relatively high temperatures. Unlike thermosetting polyimides, they can be reprocessed by the application of heat and pressure.

Polyetherimide (PEI) and polyamide-imide (PAI) are melt-processable thermoplastic polyimides. Their chemical structures are shown as follows.



Polyetherimide (PEI)

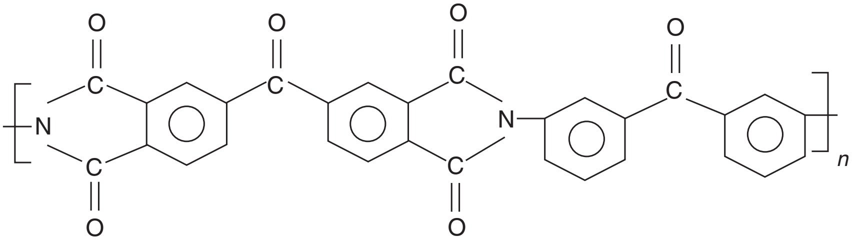


Polyamide-imide (PAI)

Both are amorphous polymers with high glass transition temperatures, 217°C for PEI and 280°C for PAI. The processing temperature is 350°C or above.

Two other thermoplastic polyimides, known as K polymers and Langley Research Center Thermoplastic Imide (LARC-TPI), are generally available as prepolymers dissolved in suitable solvents. In this form, they have low viscosities so that the fibers can be coated with their prepolymers to produce flexible prepregs. Polymerization, which for these polymers means imidization or imide ring formation, requires heating up to 300°C or above.

The glass transition temperatures of K polymers and LARC-TPI are 250°C and 265°C, respectively. Both are amorphous polymers, and offer excellent heat and solvent resistance. Since their molecules are not cross-linked, they are not as brittle as thermoset polymers. They are processed with fibers from low-viscosity solutions much like the thermoset resins; yet after imidization, they can be made to flow and be shape-formed like conventional thermoplastics by heating them over their T_g. This latter characteristic is due to the presence of flexible chemical groups between the stiff, fused-ring imide groups in their backbones. In LARC-TPI, for example, the sources of flexibility are the carbonyl groups and the *meta*-substitution of the phenyl rings in the diamine-derived portion of the chain. The *meta*-substitution, in contrast to *para*-substitution, allows the polymer molecules to bend and flow.



LARC-TPI

2.5 FIBER SURFACE TREATMENTS

The primary function of a fiber surface treatment is to improve the fiber surface wettability with the matrix and to create a strong bond at the fiber–matrix interface. Both are essential for effective stress transfer from the matrix to the fiber and vice versa. Surface treatments for glass, carbon, and Kevlar fibers for their use in polymeric matrices are described in this section.*

2.5.1 GLASS FIBERS

Chemical coupling agents are used with glass fibers to (1) improve the fiber–matrix interfacial strength through physical and chemical bonds and (2) protect the fiber surface from moisture and reactive fluids.

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* Several investigators [27] have suggested that there is a thin but distinct interphase between the fibers and the matrix. The interphase surrounds the fiber and has properties that are different from the bulk of the matrix. It may be created by local variation of the matrix microstructure close to the fiber surface. For example, there may be a variation in cross-link density in the case of a thermosetting matrix, or a variation of crystallinity in the case of a semicrystalline thermoplastic matrix, both of which are influenced by the presence of fibers as well as the fiber surface chemistry. The interphase may also contain microvoids (resulting from poor fiber surface wetting by the matrix or air entrapment) and unreacted solvents or curing agents that tend to migrate toward the fiber surface.

Common coupling agents used with glass fibers are organofunctional silicon compounds, known as silanes. Their chemical structure is represented by R'-$Si(OR)_3$, in which the functional group R' must be compatible with the matrix resin in order for it to be an effective coupling agent. Some representative commercial silane coupling agents are listed in Table 2.15.

The glass fiber surface is treated with silanes in aqueous solution. When a silane is added to water, it is hydrolyzed to form R'-$Si(OH)_3$:

$$\underset{\text{Silane}}{R' - Si(OR)_3} + \underset{\text{Water}}{3H_2O} \rightarrow R' - Si(OH)_3 + 3HOR.$$

Before treating glass fiber with a coupling agent, its surface must be cleaned from the size applied at the time of forming. The size is burned away by heating the fiber in an air-circulating oven at 340°C for 15–20 h. As the heat-cleaned fibers are immersed into the aqueous solution of a silane, chemical bonds (Si–O–Si) as well as physical bonds (hydrogen bonds) are established between the (OH) groups on the glass fiber surface (which is hydroscopic owing to alkaline content) and $R' - Si(OH)_3$ molecules.

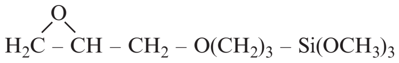
TABLE 2.15
Recommended Silane Coupling Agents for Glass Fiber-Reinforced Thermoset Polymers

With epoxy matrix:

1. γ-Aminopropyltriethoxysilane

   $H_2N - (CH_2)_3 - Si(OC_2H_5)_3$

2. γ-Glycidyloxypropyltrimethoxysilane

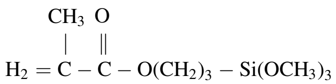
   $H_2C - CH - CH_2 - O(CH_2)_3 - Si(OCH_3)_3$

3. *N*-β-Aminoethyl-γ-aminopropyltrimethoxysilane

   $H_2N - CH_2 - CH_2 - NH - (CH_2)_3 - Si(OCH_3)_3$

With polyester and vinyl ester matrix:

1. γ-Methacryloxypropyltrimethoxysilane

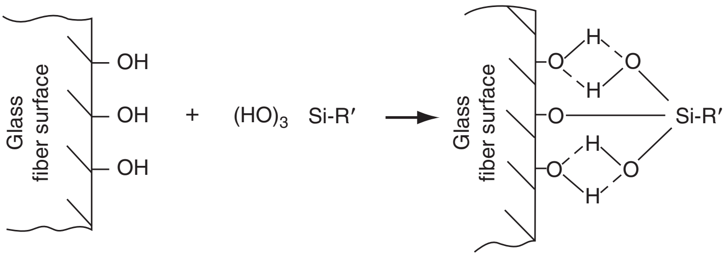
   $H_2 = \overset{CH_3}{\overset{|}{C}} - \overset{O}{\overset{\|}{C}} - O(CH_2)_3 - Si(OCH_3)_3$

2. Vinyl triethoxysilane

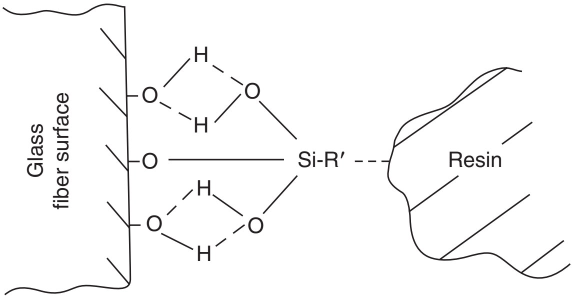
   $H_2C = CH - Si(OC_2H_5)_3$

3. Vinyl tris(β-methoxyethoxy)silane

   $H_2C = CH - Si(OCH_2 - CH_2 - O - CH_3)_3$



When treated glass fibers are incorporated into a resin matrix, the functional group R′ in the silane film reacts with the resin to form chemical coupling between fibers and matrix.



Without a coupling agent, stress transfer between the fibers and the polymer matrix is possible owing to a mechanical interlocking that arises because of higher thermal contraction of the matrix relative to the fibers. Since the coefficient of thermal expansion (and contraction) of the polymer matrix is nearly 10 times higher than that of the fibers, the matrix shrinks considerably more than the fibers as both cool down from the high processing temperature. In addition, polymerization shrinkage in the case of a thermoset polymer and crystallization shrinkage in the case of a semicrystalline polymer contribute to mechanical interlocking. Residual stresses are generated in the fiber as well as the matrix surrounding the fiber as a result of mechanical interlocking. However, at elevated service temperatures or at high applied loads, the difference in expansion of fibers and matrix may relieve this mechanical interlocking and residual stresses. Under extreme circumstances, a microcrack may be formed at the interface, resulting in reduced mechanical properties for the composite. Furthermore, moisture or other reactive fluids that may diffuse through the resin can accumulate at the interface and cause deterioration in fiber properties.

Evidence of fiber–matrix coupling effect can be observed in Figure 2.36, in which fracture surfaces of uncoupled and coupled fiber-reinforced epoxies are compared. In the uncoupled system (Figure 2.36a), the interfacial failure

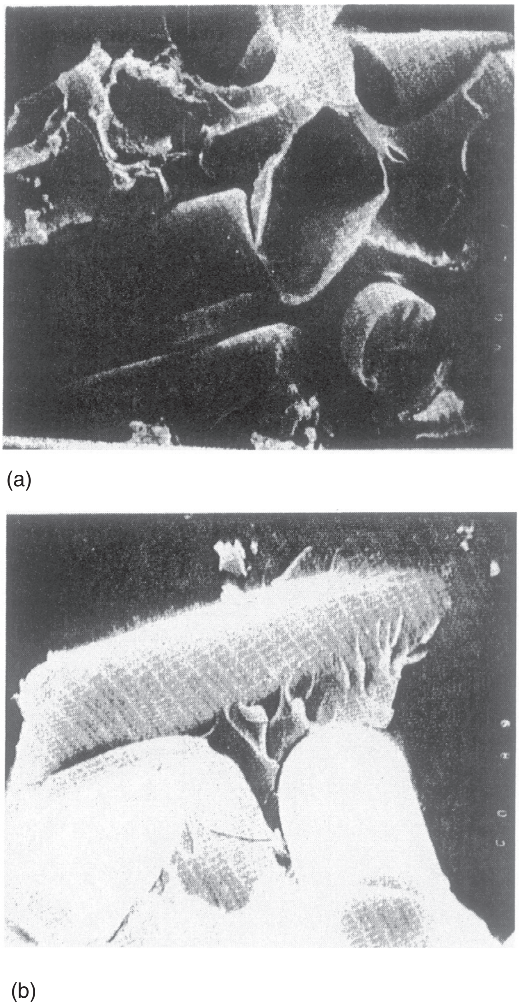


FIGURE 2.36 Photomicrographs of fracture surfaces of E-glass–epoxy composites demonstrating (a) poor adhesion with an incompatible silane coupling agent and (b) good adhesion with a compatible silane coupling agent.

is characterized by clean fiber surfaces, thin cracks (debonding) between fibers and matrix, and clear impressions in the matrix from which the fibers have pulled out or separated. In the coupled system (Figure 2.36b), strong interfacial strength is characterized by fiber surfaces coated with thin layers of matrix and the absence of fiber–matrix debonding as well as absence of clear fiber surface impressions in the matrix. In the former, debonding occurs at

TABLE 2.16
Effect of Silane Coupling Agent on the Strength of E-Glass Fiber-Reinforced Polyester Rods

	Strength (MPa)	
Treatment	**Dry**	**Wet**[a]
No silane	916	240
Vinyl silane	740	285
Glycidyl silane	990	380
Methacryl silane	1100	720

[a] After boiling in water at 100°C for 72 h.

the fiber–matrix interface, but in the latter, cohesive failure occurs in the matrix.

The interfacial bond created by silanes or other coupling agents allows a better load stress transfer between fibers and matrix, which in turn improves the tensile strength as well as the interlaminar shear strength of the composite. However, the extent of strength improvement depends on the compatibility of the coupling agent with the matrix resin. Furthermore, it has been observed that although a strong interface produces higher strength, a relatively weaker interface may contribute to higher energy dissipation through debonding at the fiber–matrix interface, which may be beneficial for attaining higher fracture toughness.

The data in Table 2.16 show the improvement in strength achieved by using different silane coupling agents on the glass fiber surface of a glass fiber–polyester composite. The wet strength of the composite, measured after boiling in water for 72 h, is lower than the dry strength; however, by adding the silane coupling agent and creating a stronger interfacial bond between the fibers and the matrix, the wet strength is significantly improved.

2.5.2 CARBON FIBERS

Carbon fiber surfaces are chemically inactive and must be treated to form surface functional groups that promote good chemical bonding with the polymer matrix. Surface treatments also increase the surface area by creating micropores or surface pits on already porous carbon fiber surface. Increase in surface area provides a larger number of contact points for fiber–matrix bonding.

Commercial surface treatments for carbon fibers are of two types, oxidative or nonoxidative [4,5]:

1. Oxidative surface treatments produce acidic functional groups, such as carboxylic, phenolic, and hydroxylic, on the carbon fiber surface. They may be carried out either in an oxygen-containing gas (air, oxygen, carbon dioxide, ozone, etc.) or in a liquid (nitric acid, sodium hypochloride, etc.).

   The gas-phase oxidation is conducted at 250°C or above and often in the presence of a catalyst. Oxidation at very high temperatures causes excessive pitting on the carbon fiber surface and reduces the fiber strength.

   Nitric acid is the most common liquid used for the liquid-phase oxidation. The effectiveness of treatment in improving the surface properties depends on the acid concentration, treatment time, and temperature, as well as the fiber type.
2. Several nonoxidative surface treatments have been developed for carbon fibers. In one of these treatments, the carbon fiber surface is coated with an organic polymer that has functional groups capable of reacting with the resin matrix. Examples of polymer coatings are styrene–maleic anhydride copolymers, methyl acrylate–acrylonitrile copolymer, and polyamides. The preferred method of coating the fiber surface is electropolymerization, in which carbon fibers are used as one of the electrodes in an acidic solution of monomers or monomer mixtures [22]. Improved results are obtained if the carbon fiber surface is oxidized before the coating process.

2.5.3 KEVLAR FIBERS

Similar to carbon fibers, Kevlar 49 fibers also suffer from weak interfacial adhesion with most matrix resins. Two methods have been successful in improving the interfacial adhesion of Kevlar 49 with epoxy resin [7]:

1. Filament surface oxidation or plasma etching, which reduces the fiber tensile strength but tends to improve the off-axis strength of the composite, which depends on better fiber–matrix interfacial strength.
2. Formation of reactive groups, such as amines ($-NH_2$), on the fiber surface. These reactive groups form covalent bonds with the epoxide groups across the interface.

2.6 FILLERS AND OTHER ADDITIVES

Fillers are added to a polymer matrix for one or more of the following reasons:

1. Reduce cost (since most fillers are much less expensive than the matrix resin)
2. Increase modulus

TABLE 2.17
Properties of Calcium Carbonate-Filled Polyester Resin

Property	Unfilled Polyester	Polyester Filled with 30 phr $CaCO_3$
Density, g/cm^3	1.30	1.48
HDT, °C (°F)	79 (174)	83 (181)
Flexural strength, MPa (psi)	121 (17,600)	62 (9,000)
Flexural modulus, GPa (10^6 psi)	4.34 (0.63)	7.1 (1.03)

3. Reduce mold shrinkage
4. Control viscosity
5. Produce smoother surface

The most common filler for polyester and vinyl ester resins is calcium carbonate ($CaCO_3$), which is used to reduce cost as well as mold shrinkage. Examples of other fillers are clay, mica, and glass microspheres (solid as well as hollow). Although fillers increase the modulus of an unreinforced matrix, they tend to reduce its strength and impact resistance. Typical properties obtained with calcium carbonate-filled polyester matrix are shown in Table 2.17.

Impact strength and crack resistance of brittle thermosetting polymers can be improved by mixing them with small amounts of a liquid elastomeric toughener, such as carboxyl-terminated polybutadiene acrylonitrile (CTBN) [23]. In addition to fillers and tougheners, colorants, flame retardants, and ultraviolet (UV) absorbers may also be added to the matrix resin [24].

2.7 INCORPORATION OF FIBERS INTO MATRIX

Processes for incorporating fibers into a polymer matrix can be divided into two categories. In one category, fibers and matrix are processed directly into the finished product or structure. Examples of such processes are filament winding and pultrusion. In the second category, fibers are incorporated into the matrix to prepare ready-to-mold sheets that can be stored and later processed to form laminated structures by autoclave molding or compression molding. In this section, we briefly describe the processes used in preparing these ready-to-mold sheets. Knowledge of these processes will be helpful in understanding the performance of various composite laminates. Methods for manufacturing composite structures by filament winding, pultrusion, autoclave molding, compression molding, and others are described in Chapter 5.

Ready-to-mold fiber-reinforced polymer sheets are available in two basic forms, prepregs and sheet-molding compounds.

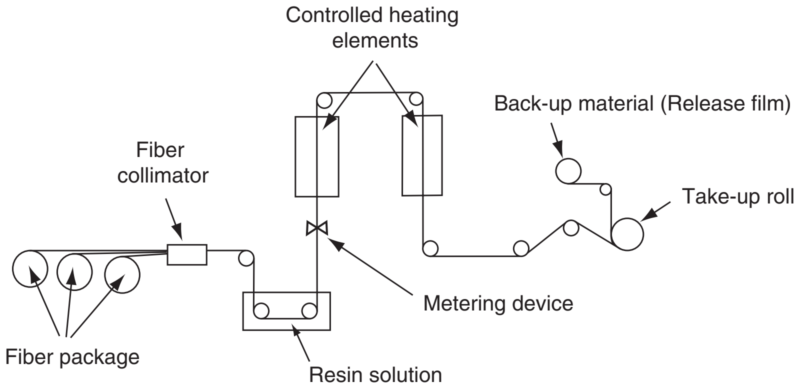


FIGURE 2.37 Schematic of prepreg manufacturing.

2.7.1 PREPREGS

These are thin sheets of fibers impregnated with predetermined amounts of uniformly distributed polymer matrix. Fibers may be in the form of continuous rovings, mat, or woven fabric. Epoxy is the primary matrix material in prepreg sheets, although other thermoset and thermoplastic polymers have also been used. The width of prepreg sheets may vary from less than 25 mm (1 in.) to over 457 mm (18 in.). Sheets wider than 457 mm are called broadgoods. The thickness of a ply cured from prepreg sheets is normally in the range of 0.13–0.25 mm (0.005–0.01 in.). Resin content in commercially available prepregs is between 30% and 45% by weight.

Unidirectional fiber-reinforced epoxy prepregs are manufactured by pulling a row of uniformly spaced (collimated) fibers through a resin bath containing catalyzed epoxy resin dissolved in an appropriate solvent (Figure 2.37). The solvent is used to control the viscosity of the liquid resin. Fibers preimpregnated with liquid resin are then passed through a chamber in which heat is applied in a controlled manner to advance the curing reaction to the B-stage. At the end of B-staging, the prepreg sheet is backed up with a release film or waxed paper and wound around a take-up roll. The backup material is separated from the prepreg sheet just before it is placed in the mold to manufacture the composite part. The normal shelf life (storage time before molding) for epoxy prepregs is 6–8 days at 23°C; however, it can be prolonged up to 6 months or more if stored at –18°C.

2.7.2 SHEET-MOLDING COMPOUNDS

Sheet-molding compounds (SMC) are thin sheets of fibers precompounded with a thermoset resin and are used primarily in compression molding process [25]. Common thermoset resins for SMC sheets are polyesters and vinyl esters. The longer cure time for epoxies has limited their use in SMC.

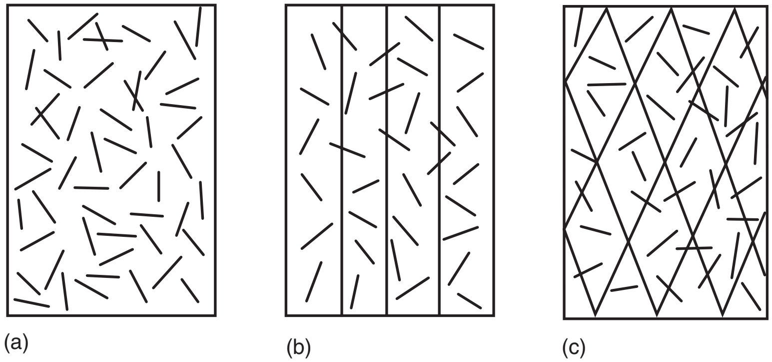


FIGURE 2.38 Various types of sheet-molding compounds (SMC): (a) SMC-R, (b) SMC-CR, and (c) XMC.

The various types of sheet-molding compounds in current use (Figure 2.38) are as follows:

1. SMC-R, containing randomly oriented discontinuous fibers. The nominal fiber content (by weight percent) is usually indicated by two-digit numbers after the letter R. For example, the nominal fiber content in SMC-R30 is 30% by weight.
2. SMC-CR, containing a layer of unidirectional continuous fibers on top of a layer of randomly oriented discontinuous fibers. The nominal fiber contents are usually indicated by two-digit numbers after the letters C and R. For example, the nominal fiber contents in SMC-C40R30 are 40% by weight of unidirectional continuous fibers and 30% by weight of randomly oriented discontinuous fibers.
3. XMC (trademark of PPG Industries), containing continuous fibers arranged in an X pattern, where the angle between the interlaced fibers is between 5° and 7°. Additionally, it may also contain randomly oriented discontinuous fibers interspersed with the continuous fibers.

A typical formulation for sheet-molding compound SMC-R30 is presented in Table 2.18. In this formulation, the unsaturated polyester and styrene are polymerized together to form the polyester matrix. The role of the low shrink additive, which is a thermoplastic polymer powder, is to reduce the polymerization shrinkage. The function of the catalyst (also called the initiator) is to initiate the polymerization reaction, but only at an elevated temperature. The function of the inhibitor is to prevent premature curing (gelation) of the resin that may start by the action of the catalyst while the ingredients are blended together. The mold release agent acts as an internal lubricant, and helps in releasing the molded part from the die. Fillers assist in reducing shrinkage of

TABLE 2.18
Typical Formulation of SMC-R30

Material	**Weight (%)**	
Resin paste		70%
Unsaturated polyester	10.50	
Low shrink additive	3.45	
Styrene monomer	13.40	
Filler ($CaCO_3$)	40.70	
Thickener (MgO)	0.70	
Catalyst (TBPB)	0.25	
Mold release agent (zinc stearate)	1.00	
Inhibitor (benzoquinone)	<0.005 g	
Glass fiber (25.4 mm, chopped)		30%
Total		100%

the molded part, promote better fiber distribution during molding, and reduce the overall cost of the compound. Typical filler–resin weight ratios are 1.5:1 for SMC-R30, 0.5:1 for SMC-R50, and nearly 0:1 for SMC-R65. The *thickener* is an important component in an SMC formulation since it increases the viscosity of the compound without permanently curing the resin and thereby makes it easier to handle an SMC sheet before molding. However, the thickening reaction should be sufficiently slow to allow proper wet-out and impregnation of fibers with the resin. At the end of the thickening reaction, the compound becomes dry, nontacky, and easy to cut and shape. With the application of heat in the mold, the thickening reaction is reversed and the resin paste becomes sufficiently liquid-like to flow in the mold. Common thickeners used in SMC formulations are oxides and hydroxides of magnesium and calcium, such as MgO, $Mg(OH)_2$, CaO, and $Ca(OH)_2$. Another method of thickening is known as the interpenetrating thickening process (ITP), in which a proprietary polyurethane rubber is used to form a temporary three-dimensional network structure with the polyester or vinyl ester resin.

SMC-R and SMC-CR sheets are manufactured on a sheet-molding compound machine (Figure 2.39). The resin paste is prepared by mechanically blending the various components listed in Table 2.18. It is placed on two moving polyethylene carrier films behind the metering blades. The thickness of the resin paste on each carrier film is determined by the vertical adjustment of the metering blades. Continuous rovings are fed into the chopper arbor, which is commonly set to provide 25.4 mm long discontinuous fibers. Chopped fibers are deposited randomly on the bottom resin paste. For SMC-CR sheets, parallel lines of continuous strand rovings are fed on top of the chopped fiber layer. After covering the fibers with the top resin paste, the carrier films are

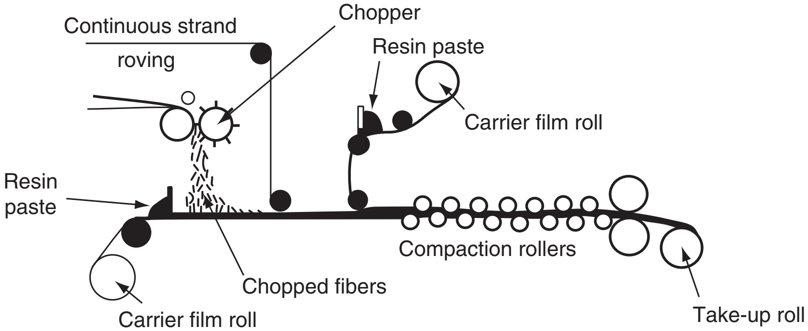


FIGURE 2.39 Schematic of a sheet molding compounding operation.

pulled through a number of compaction rolls to form a sheet that is then wound around a take-up roll. Wetting of fibers with the resin paste takes place at the compaction stage.

XMC sheets are manufactured by the filament winding process (see Chapter 5) in which continuous strand rovings are pulled through a tank of resin paste and wound under tension around a large rotating cylindrical drum. Chopped fibers, usually 25.4 mm long, are deposited on the continuous fiber layer during the time of winding. After the desired thickness is obtained, the built-up material is cut by a knife along a longitudinal slit on the drum to form the XMC sheet.

At the end of manufacturing, SMC sheets are allowed to "mature" (thicken or increase in viscosity) at about 30°C for 1–7 days. The matured sheet can be either compression molded immediately or stored at -18°C for future use.

2.7.3 INCORPORATION OF FIBERS INTO THERMOPLASTIC RESINS

Incorporating fibers into high-viscosity thermoplastic resins and achieving a good fiber wet-out are much harder than those in low-viscosity thermoset resins. Nevertheless, several fiber incorporation techniques in thermoplastic resins have been developed, and many of them are now commercially used to produce thermoplastic prepregs. These prepregs can be stored for unlimited time without any special storage facility and, whenever required, stacked and consolidated into laminates by the application of heat and pressure.

1. *Hot-melt impregnation* is used mainly for semicrystalline thermoplastics, such as PEEK and PPS, for which there are no suitable solvents available for solution impregnation. Amorphous polymers are also used for hot-melt impregnation.

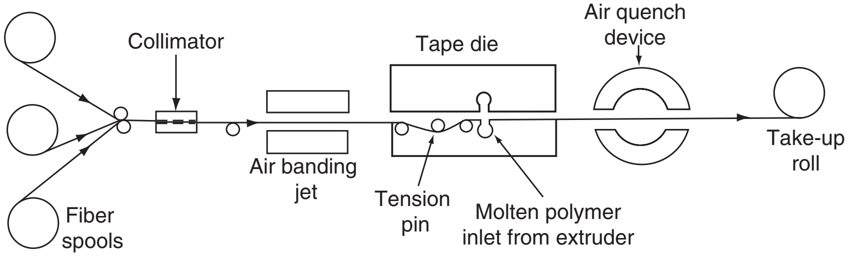


FIGURE 2.40 Hot-melt impregnation of thermoplastic prepregs. (Adapted from Muzzy, J.D., *The Manufacturing Science of Composites*, T.G. Gutowski, ed., ASME, New York, 1988.)

In this process, collimated fiber tows are pulled through a die attached at the end of an extruder, which delivers a fine sheet of hot polymer melt under high pressure to the die. To expose the filaments to the polymer melt, the fiber tows are spread by an air jet before they enter the die (Figure 2.40). The hot prepreg exiting from the die is rapidly cooled by a cold air jet and wound around a take-up roll.

For good and uniform polymer coating on filaments, the resin melt viscosity should be as low as possible. Although the viscosity can be reduced by increasing the melt temperature, there may be polymer degradation at very high temperatures. Hot-melt-impregnated prepregs tend to be stiff, boardy, and tack-free (no stickiness). This may cause problems in draping the mold surface and sticking the prepreg layers to each other as they are stacked before consolidation.

2. *Solution impregnation* is used for polymers that can be dissolved in a suitable solvent, which usually means an amorphous polymer, such as polysulfone and PEI. The choice of solvent depends primarily on the polymer solubility, and therefore, on the chemical structure of the polymer and its molecular weight. The solvent temperature also affects the polymer solubility. In general, a low-boiling-point solvent is preferred, since it is often difficult to remove high-boiling-point solvents from the prepreg.

   Solution impregnation produces drapable and tacky prepregs. However, solvent removal from the prepreg is a critical issue. If the solvent is entrapped, it may create a high void content in the consolidated laminate and seriously affect its properties.
3. *Liquid impregnation* uses low-molecular-weight monomers or prepolymers (precursors) to coat the fibers. This process is commonly used for LARC-TPI and a few other thermoplastic polyimides. In this case, the precursor is dissolved in a solvent to lower its viscosity.

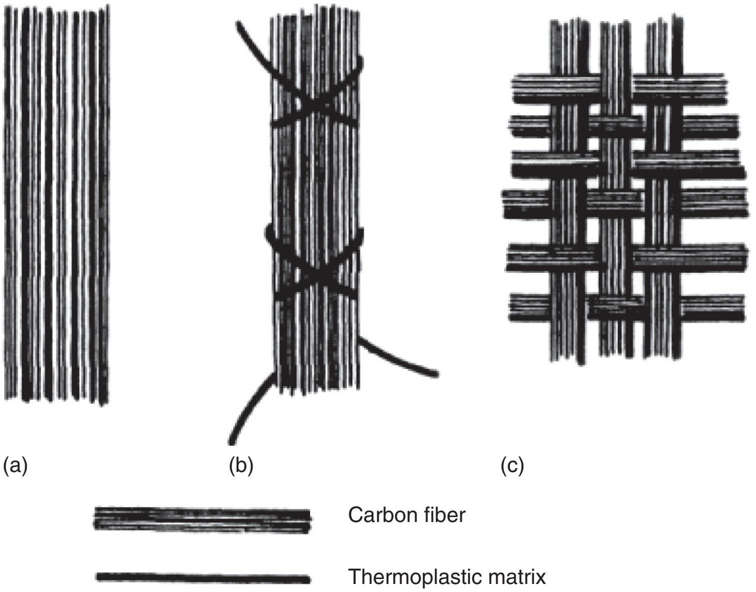


FIGURE 2.41 (a) Commingled, (b) wrapped, and (c) coweaved fiber arrangements.

Liquid-impregnated prepregs are drapable and tacky. However, the removal of residual solvents and reaction by-products from the prepreg during the consolidation stage can be difficult.

4. *Film stacking* is primarily used with woven fabrics or random fiber mats, which are interleaved between unreinforced thermoplastic polymer sheets. The layup is then heated and pressed to force the thermoplastic into the reinforcement layers and thus form a prepregged sheet.
5. *Fiber mixing* is a process of intimately mixing thermoplastic fibers with reinforcement fibers by *commingling*, *wrapping*, or *coweaving* (Figure 2.41). Commingled and wrapped fibers can be woven, knitted, or braided into two- or three-dimensional hybrid fabrics. The thermoplastic fibers in these fabrics can be melted and spread to wet the reinforcement fibers at the consolidation stage during molding.

The principal advantage of using hybrid fabrics is that they are highly flexible and can be draped over a contoured mold, whereas the other thermoplastic prepregs are best suited for relatively flat surfaces. However, fiber mixing is possible only if the thermoplastic polymer is available in filamentary form. Such is the case for PEEK and PPS that are spun into monofilaments with diameters in the range of 16–18 μm. Polypropylene (PP) and polyethylene terephthalate (PET) fibers are also used in making commingled rovings and fabrics.

6. *Dry powder coating* [26] uses charged and fluidized thermoplastic powders to coat the reinforcement fibers. After passing through the fluidized bed, the fibers enter a heated oven, where the polymer coating is melted on the fiber surface.

2.8 FIBER CONTENT, DENSITY, AND VOID CONTENT

Theoretical calculations for strength, modulus, and other properties of a fiber-reinforced composite are based on the fiber volume fraction in the material.

Experimentally, it is easier to determine the fiber weight fraction w_f, from which the fiber volume fraction v_f and composite density ρ_c can be calculated:

$$v_f = \frac{w_f/\rho_f}{(w_f/\rho_f) + (w_m/\rho_m)}, \tag{2.7}$$

$$\rho_c = \frac{1}{(w_f/\rho_f) + (w_m/\rho_m)}, \tag{2.8}$$

where

w_f = fiber weight fraction (same as the fiber mass fraction)
w_m = matrix weight fraction (same as the matrix mass fraction) and is equal to $(1-w_f)$
ρ_f = fiber density
ρ_m = matrix density

In terms of volume fractions, the composite density ρ_c can be written as

$$\rho_c = \rho_f v_f + \rho_m v_m, \tag{2.9}$$

where v_f is the fiber volume fraction and v_m is the matrix volume fraction. Note that v_m is equal to $(1-v_f)$.

The fiber weight fraction can be experimentally determined by either the ignition loss method (ASTM D2854) or the matrix digestion method (ASTM D3171). The ignition loss method is used for PMC-containing fibers that do not lose weight at high temperatures, such as glass fibers. In this method, the cured resin is burned off from a small test sample at 500°C–600°C in a muffle furnace. In the matrix digestion method, the matrix (either polymeric or metallic) is dissolved away in a suitable liquid medium, such as concentrated nitric acid. In both cases, the fiber weight fraction is determined by comparing the weights of the test sample before and after the removal of the matrix. For unidirectional composites containing electrically conductive fibers (such as carbon) in a nonconductive matrix, the fiber volume fraction can be determined directly by comparing the electrical resistivity of the composite with that of fibers (ASTM D3355).

During the incorporation of fibers into the matrix or during the manufacturing of laminates, air or other volatiles may be trapped in the material. The trapped air or volatiles exist in the laminate as microvoids, which may significantly affect some of its mechanical properties. A high void content (over 2% by volume) usually leads to lower fatigue resistance, greater susceptibility to water diffusion, and increased variation (scatter) in mechanical properties. The void content in a composite laminate can be estimated by comparing the theoretical density with its actual density:

$$\mathrm{v_v} = \frac{\rho_c - \rho}{\rho_c}, \tag{2.10}$$

where

$\mathrm{v_v}$ = volume fraction of voids
ρ_c = theoretical density, calculated from Equation 2.8 or 2.9
ρ = actual density, measured experimentally on composite specimens (which is less than ρ_c due to the presence of voids)

EXAMPLE 2.1

Calculate $\mathrm{v_f}$ and ρ_c for a composite laminate containing 30 wt% of E-glass fibers in a polyester resin. Assume $\rho_f = 2.54$ g/cm^3 and $\rho_m = 1.1$ g/cm^3.

SOLUTION

Assume a small composite sample of mass 1 g and calculate its volume.

	Fiber	**Matrix**
Mass (g)	0.3	1 − 0.3 = 0.7
Density (g/cm^3)	2.54	1.1
Volume (cm^3)	$\frac{0.3}{2.54} = 0.118$	$\frac{0.7}{1.1} = 0.636$

Therefore, volume of 1 g of composite is (0.118 + 0.636) or 0.754 cm^3. Now, we calculate

$$\text{Fiber volume fraction } \mathrm{v_f} = \frac{0.118}{0.754} = 0.156 \text{ or } 15.6\%$$

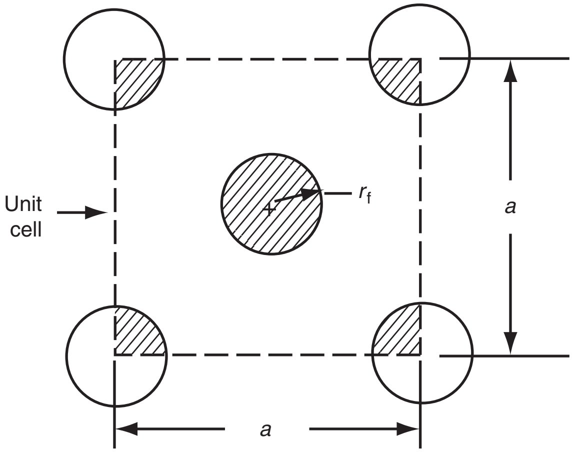
$$\text{Matrix volume fraction } \mathrm{v_m} = 1 - \mathrm{v_f} = 1 - 0.156 = 0.844 \text{ or } 84.4\%$$

Composite density $\rho_c = \frac{1 \text{ g}}{0.754 \text{ cm}^3} = 1.326 \text{ g/cm}^3$

Note: These values can also be obtained using Equations 2.7 and 2.8.

EXAMPLE 2.2

Assume that the fibers in a composite lamina are arranged in a square array as shown in the figure. Determine the maximum fiber volume fraction that can be packed in this arrangement.



SOLUTION

Number of fibers in the unit cell = 1 + (4) (1/4) = 2
Fiber cross-sectional area in the unit cell = (2) (πr_f^2)
Unit cell area = a^2
Therefore,
Fiber volume fraction $(v_f) = \frac{2\pi r_f^2}{a^2}$
from which, we can write

$$a = \frac{\sqrt{2\pi}}{v_f^{1/2}} r_f.$$

Interfiber spacing (R) between the central fiber and each corner fiber is given by

$$R = \frac{a}{\sqrt{2}} - 2r_f = r_f \left[\left(\frac{\pi}{v_f} \right)^{1/2} - 2 \right].$$

For maximum volume fraction, $R = 0$, which gives

$$v_{f_{max}} = 0.785 \text{ or } 78.5\%.$$

2.9 FIBER ARCHITECTURE

Fiber architecture is defined as the arrangement of fibers in a composite, which not only influences the properties of the composite, but also its processing. The characteristics of fiber architecture that influence the mechanical properties include fiber continuity, fiber orientation, fiber crimping, and fiber interlocking. During processing, matrix flow through the fiber architecture determines the void content, fiber wetting, fiber distribution, dry area and others in the final composite, which in turn, also affect its properties and performance.

If continuous fibers are used, the fiber architecture can be one-dimensional, two-dimensional, or three-dimensional. The one-dimensional architecture can be produced by the prepregging technique described earlier or by other manufacturing methods, such as pultrusion. The two- and three-dimensional architectures are produced by textile manufacturing processes and are used with liquid composite molding processes, such as resin transfer molding, in which a liquid polymer is injected into the dry fiber preform containing two- or three-dimensional fiber architecture. Each fiber architecture type has its unique characteristics, and if properly used, can provide an opportunity not only to tailor the structural performance of the composite, but also to produce a variety of structural shapes and forms.

In the one-dimensional architecture, fiber strands (or yarns) are oriented all in one direction. The unidirectional orientation of continuous fibers in the composite produces the highest strength and modulus in the fiber direction, but much lower strength and modulus in the transverse to the fiber direction. A multilayered composite laminate can be built using the one-dimensional architecture in which each layer may contain unidirectional continuous fibers, but the angle of orientation from layer to layer can be varied. With proper orientation of fibers in various layers, the difference in strength and modulus values in different directions can be reduced. However, one major problem with many multilayered laminates is that their interlaminar properties can be low and they can be prone to early failure by delamination, in which cracks originated at the interface between the layers due to high interlaminar tensile and shear stresses cause separation of layers.

The two-dimensional architecture with continuous fibers can be either bidirectional or multidirectional. In a bidirectional architecture, fiber yarns (or strands) are either woven or interlaced together in two mutually perpendicular directions (Figure 2.42a). These two directions are called warp and fill directions, and represent 0° and 90° orientations, respectively. The fiber yarns are crimped or undulated as they move up and down to form the interlaced

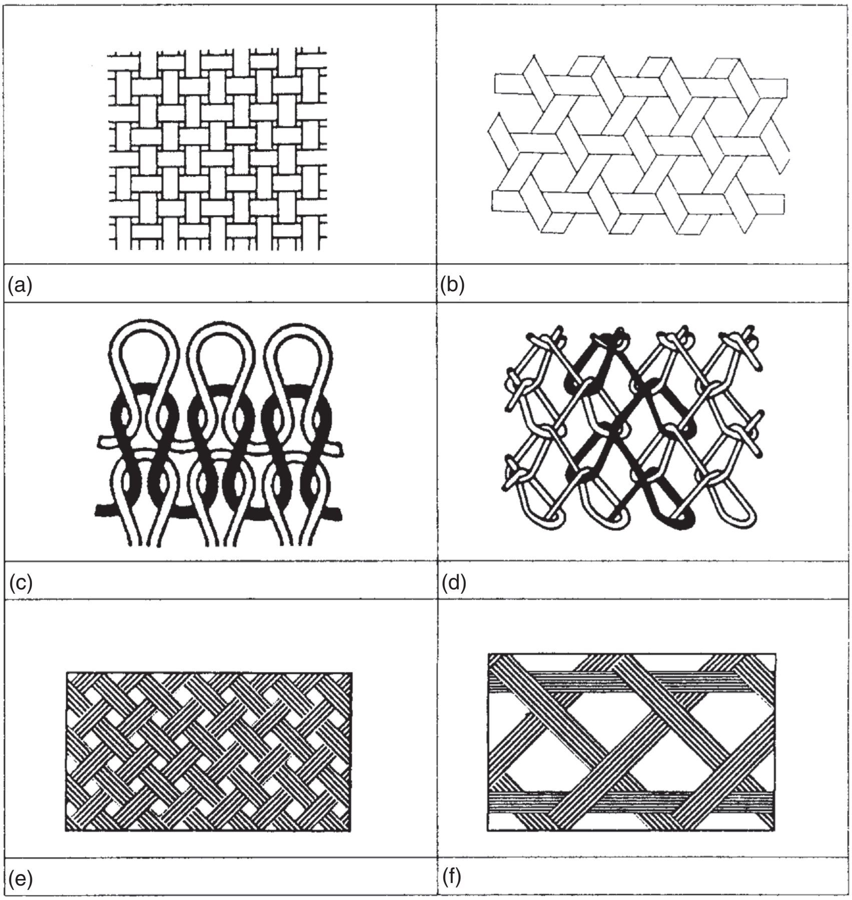


FIGURE 2.42 Two-dimensional fiber architectures with continuous fibers. (a) Bidirectional fabric, (b) Multidirectional fabric, (c) Weft-knitted fabric, (d) Warp-knitted fabric, (e) Biaxial braided fabric, and (f) Triaxial braided fabric.

structure. The nomenclature used for woven fabric architecture is given in Appendix A.1. By changing the number of fiber yarns per unit width in the warp and fill directions, a variety of properties can be obtained in these two directions. If the number of fiber yarns is the same in both warp and fill directions, then the properties are the same in these two directions and the fabric is balanced. However, the properties in other directions are still low. In order to improve the properties in the other directions, fiber yarns can be interlaced in the other directions to produce multidirectional fabrics (Figure 2.42b), such as $0/\pm\theta$ or $0/90/\pm\theta$ fabric. The angle $\pm\theta$ refers to $+\theta$ and $-\theta$ orientation of the bias yarns relative to the warp or 0° direction.

Knitting and braiding are two other textile processes used for making two-dimensional fiber architecture. In a knitted fabric, the fiber yarns are interlooped instead of interlaced (Figure 2.42c and d). If the knitting yarn runs in the cross-machine direction, the fabric is called the weft knit, and if it runs in the machine direction, it is called the warp knit. Knitted fabrics are produced on industrial knitting machines in which a set of closely spaced needles pull the yarns and form the loops. Knitted fabrics are more flexible than woven fabrics and are more suitable for making shapes with tight corners. Biaxial braided fabrics are produced by intertwining two sets of continuous yarns, one in the $+\theta$ direction and the other in the $-\theta$ direction relative to the braiding axis (Figure 2.42e). The angle θ is called the braid angle or the bias angle. Triaxial braids contain a third set of yarns oriented along the braiding axis (Figure 2.42f). Braided construction is most suitable for tubular structures, although it is also used for flat form.

A two-dimensional architecture can also be created using randomly oriented fibers, either with continuous lengths or with discontinuous lengths (Figure 2.43). The former is called the continuous fiber mat (CFM), while the latter is called the chopped strand mat (CSM). In a CFM, the continuous yarns can be either straight or oriented in a random swirl pattern. In a CSM, the fiber yarns are discontinuous (chopped) and randomly oriented. In both mats, the fibers are held in place using a thermoplastic binder. Because of the random orientation of fibers, the composite made from either CFM or CSM displays equal or nearly equal properties in all directions in the plane of the composite and thus, can be considered planar isotropic.

Composites made with one- and two-dimensional fiber architectures are weak in the z-direction (thickness direction) and often fail by delamination. To improve the interlaminar properties, fibers are added in the thickness direction, creating a three-dimensional architecture (Figure 2.44). The simplest form of

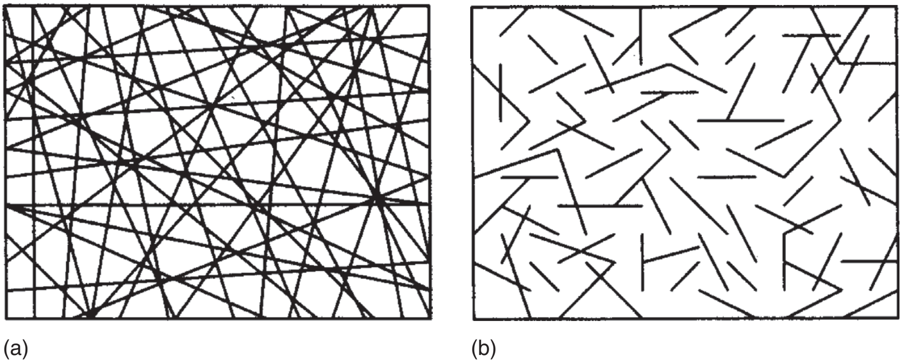


FIGURE 2.43 Two-dimensional fiber architecture with random fibers. (a) Continuous fiber mat (CFM) and (b) Chopped strand mat (CSM).

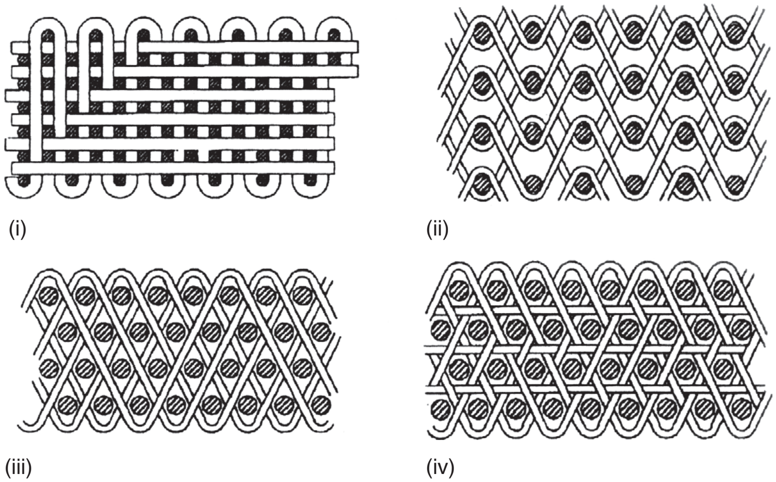


FIGURE 2.44 Examples of three-dimensional fiber architecture. (i) 3D, (ii) 2D or angle interlock, (iii) 3X, and (iv) 3X with warp stuffer yarns. (From Wilson, S., Wenger, W., Simpson, D. and Addis, S., "SPARC" 5 Axis, 3D Woven, Low Crimp Performs, Resin Transfer Molding, *SAMPE Monograph 3, SAMPE*, 1999. With permission.)

three-dimensional architecture can be created by stitching a stack of woven fabrics with stitching threads. The three-dimensional architecture can also be produced by weaving or braiding.

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PROBLEMS

P2.1. The linear density of a dry carbon fiber tow is 0.198 g/m. The density of the carbon fiber is 1.76 g/cm^3 and the average filament diameter is 7 μm. Determine the number of filaments in the tow.

P2.2. Glass fiber rovings are commonly designated by the term *yield*, which is the length of the roving per unit weight (e.g., 1275 yd/lb). Estimate the yield for a glass fiber roving that contains 20 ends (strands) per roving. Each strand in the roving is made of 204 filaments, and the average filament diameter is 40×10^{-5} in.

P2.3. The strength of brittle fibers is expressed by the well-known Griffith's formula:

$$\sigma_{\text{fu}} = \left(\frac{2E_{\text{f}}\gamma_{\text{f}}}{\pi c} \right)^{1/2},$$

where
σ_{fu} = fiber tensile strength
E_{f} = fiber tensile modulus
γ_{f} = surface energy
c = critical flaw size

1. The average tensile strength of as-drawn E-glass fibers is 3.45 GPa, and that of commercially available E-glass fibers is 1.724 GPa. Using Griffith's formula, compare the critical flaw sizes in these two types of fibers. Suggest a few reasons for the difference.
2. Assuming that the critical flaw size in the as-drawn E-glass fiber is 10^{-4} cm, estimate the surface energy of E-glass fibers.

P2.4. Scanning electron microscope study of fracture surfaces of carbon fibers broken in tension shows that they fail either at the surface flaws (pits) or at the internal voids. The surface energy of graphite is 4.2 J/m^2. Assuming this as the surface energy of carbon fibers, estimate the range of critical flaw size in these fibers if the observed strength values vary between 1.3 and 4.3 GPa. The fiber modulus in tension is 230 GPa. Use Griffith's formula in Problem P2.3.

P2.5. The filament strength distribution of a carbon fiber is represented by the Weibull distribution function given by Equation 2.4. The following Weibull parameters are known for this particular carbon fiber: $\alpha = 6.58$ and $\sigma_{\text{o}} = 2.56$ GPa at $L_{\text{f}} = 200$ mm. Determine the filament strength at which 99% of the filaments are expected to fail if the filament length is (a) 20 mm, (b) 100 mm, (c) 200 mm, and (d) 500 mm.

P2.6. A carbon fiber bundle containing 2000 parallel filaments is being tested in tension. The filament length is 100 mm. The strength distribution of individual filaments is described in Problem P2.5. Compare the mean filament strength and the mean fiber bundle strength. Schematically show the tensile stress–strain diagram of the carbon fiber bundle and compare it with that of the carbon filament. (*Note*: For $\alpha = 6.58$, $\Gamma\left(1 + \frac{1}{\alpha}\right) \cong 0.93$.)

P2.7. The Weibull parameters for the filament strength distribution of an E-glass fiber are $\alpha = 11.32$ and $\sigma_o = 4.18$ GPa at $L_f = 50$ mm. Assume that the filament stress–strain relationship obeys Hooke's law, that is, $\sigma_f = E_f\varepsilon_f$, where $E_f =$ fiber modulus $= 69$ GPa, and the tensile load applied on the bundle in a fiber bundle test is distributed uniformly among the filaments, develop the tensile load–strain diagram of the fiber bundle. State any assumption you may make to determine the load–strain diagram.

P2.8. It has been observed that the strength of a matrix-impregnated fiber bundle is significantly higher than that of a dry fiber bundle (i.e., without matrix impregnation). Explain.

P2.9. The strength of glass fibers is known to be affected by the time of exposure at a given stress level. This phenomenon, known as the static fatigue, can be modeled by the following equation:

$$\sigma = A - B \, \log(t + 1),$$

where A and B are constants and t is the time of exposure (in minutes) under stress. For an as-drawn E-glass fiber, $A = 450{,}000$ psi and $B = 20{,}000$ psi.

Determine the tensile strength of an as-drawn E-glass fiber after 1000 h of continuous tensile loading at 23°C. Using the results of Problem P2.3, determine the rate of increase of the critical flaw size in this fiber at 1, 10, and 1000 h.

P2.10. Kevlar 49 fiber strands are used in many high strength cable applications where its outstanding strength–weight ratio leads to a considerable weight saving over steel cables.

1. Compare the breaking loads and weights of Kevlar 49 and steel cables, each with a 6.4 mm diameter
2. Compare the maximum stresses and elongations in 1000 m long Kevlar 49 and steel cables due to their own weights

P2.11. The smallest radius to which a fiber can be bent or knotted without fracturing is an indication of how easily it can be handled in a manufacturing operation. The handling characteristic of a fiber is particularly important in continuous manufacturing operations, such as filament winding or pultrusion, in which continuous strand rovings are pulled through a number of guides or eyelets with sharp corners. Frequent breakage of fibers at these locations is undesirable since it slows down the production rate.

Using the following relationship between the bending radius r_b and the maximum tensile strain in the fiber,

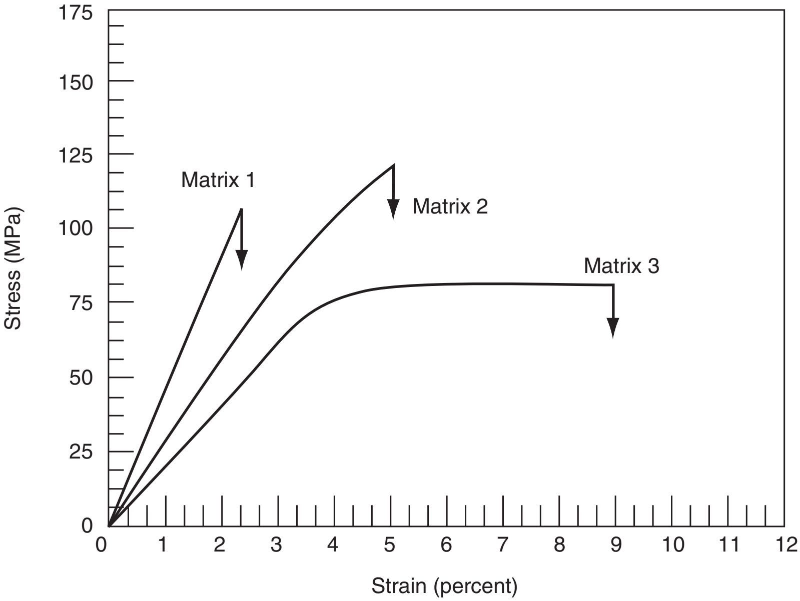
$$r_b = \frac{d_f}{2\varepsilon_{\max}},$$

compare the smallest radii to which various glass, carbon, and Kevlar fibers in Table 2.1 can be bent without fracturing.

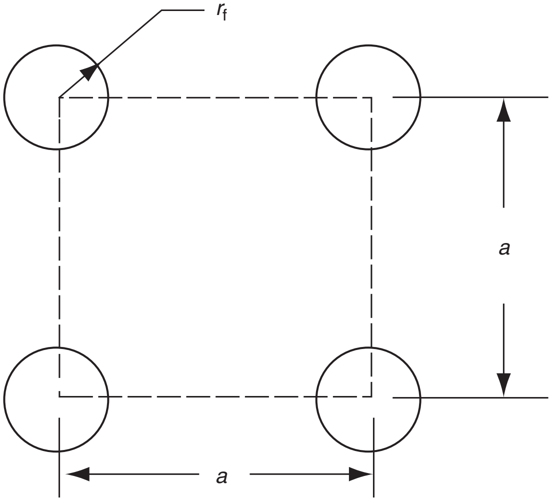
P2.12. During a filament winding operation, T-300 carbon fiber tows containing 6000 filaments per tow are pulled over a set of guide rollers 6 mm in diameter. The mean tensile strength of the filaments is 3000 MPa, and the standard deviation is 865 MPa (assuming a standard normal distribution for filament strength). Determine the percentage of filaments that may snap as the tows are pulled over the rollers. The fiber modulus is 345 GPa, and the filament diameter is 7 μm.

P2.13. The energy required to snap (break) a brittle fiber is equal to the strain energy stored (which is equal to the area under the stress–strain diagram) in the fiber at the time of its failure. Compare the strain energies of E-glass, T-300, IM-7, GY-70, Kevlar 49, and Spectra 900 fibers.

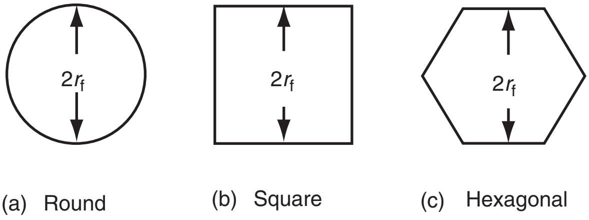
P2.14. Assume that the area under the stress–strain diagram of a material is a measure of its toughness. Using the stress–strain diagrams shown in the following figure, compare the toughness values of the three matrix resins considered.



P2.15. Assuming that the unidirectional continuous fibers of round cross section are arranged in a simple square array as shown in the accompanying figure, calculate the theoretical fiber volume fraction in the composite lamina. What is the maximum fiber volume fraction that can be arranged in this fashion?

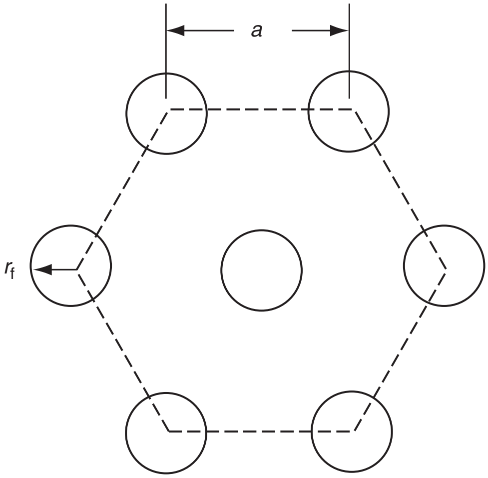


P2.16. Using the simple square arrangement in the earlier figure , show that fibers with square or hexagonal cross sections can be packed to higher fiber volume fractions than fibers with round cross sections. Compare the fiber surface area per unit volume fraction for each cross section. What is the significance of the surface area calculation?



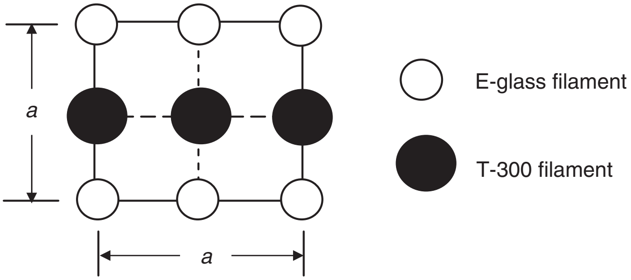
P2.17. Assuming that the fibers in a bundle are arranged in a simple square array, calculate the interfiber spacings in terms of the fiber radius r_f for a fiber volume fraction of 0.6.

P2.18. Assuming that the fibers in a unidirectional continuous fiber composite are arranged in a hexagonal packing as shown in the accompanying figure, show that the fiber volume fraction is given by 3.626 $(r_f/a)^2$. Calculate the maximum volume fraction of fibers that can be packed in this fashion.



P2.19. Assume that the unit cell of a composite containing commingled filaments of E-glass and T-300 carbon fibers can be represented by a square array shown in the following figure. The diameters of the E-glass filaments and T-300 filaments are 7×10^{-6} m and 10×10^{-6} m, respectively.

1. Determine the unit cell dimension if the fiber volume fraction is 60%
2. Determine the theoretical density of the composite



P2.20. The following data were obtained in a resin burn-off test of an E-glass–polyester sample:

Weight of an empty crucible = 10.1528 g
Weight of crucible + sample before burn-off = 10.5219 g
Weight of crucible + sample after burn-off = 10.3221 g

Calculate the fiber weight fraction, the fiber volume fraction, and the density of the composite sample. Assume $\rho_f = 2.54$ g/cm^3 and $\rho_m = 1.25$ g/cm^3. Do you expect the calculated value to be higher or lower than the actual value?

P2.21. An interply hybrid composite contains 30 wt% AS-4 carbon fibers, 30 wt% Kevlar 49 fibers, and 40 wt% epoxy resin. Assume that the density of the epoxy resin is 1.2 g/cm^3. Calculate the density of the composite.

P2.22. The fiber content in an E-glass fiber-reinforced polypropylene is 30% by volume.

1. How many kilograms of E-glass fibers are in the composite for every 100 kg of polypropylene? The density of polypropylene is 0.9 g/cm^3.
2. Assume that half of the E-glass fibers (by weight) in part (1) is replaced with T-300 carbon fibers. How will the density of the new composite compare with the density of the original composite?

P2.23. The density, ρ_m, of a semicrystalline polymer matrix, such as PEEK, can be expressed as

$$\rho_m = \rho_{mc}v_{mc} + \rho_{ma}v_{ma},$$

where ρ_{mc} and ρ_{ma} are the densities of the crystalline phase and the amorphous phase in the matrix, respectively, and, v_{mc} and v_{ma} are the corresponding volume fractions.

The density of an AS-4 carbon fiber-reinforced PEEK is reported as 1.6 g/cm^3. Knowing that the fiber volume fraction is 0.6, determine the volume and weight fractions of the crystalline phase in the matrix. For PEEK, $\rho_{mc} = 1.401$ g/cm^3 and $\rho_{ma} = 1.263$ g/cm^3.

P2.24. A carbon fiber–epoxy plate of thickness t was prepared by curing N prepeg plies of equal thickness. The number of fiber yarns per unit prepreg width is n, and the yarn weight per unit length is W_y. Show that the fiber volume fraction in the plate is

$$v_f = \frac{W_y n N}{t \rho_f g},$$

where
ρ_f is the fiber density
g is the acceleration due to gravity

P2.25. Determine the weight and cost of prepreg required to produce a hollow composite tube (outside diameter = 50 mm, wall thickness = 5 mm, and length = 4 m) if it contains 60 vol% AS-4 carbon fibers (at \$60/kg) in an epoxy matrix (at \$8/kg). The tube is manufactured by wrapping the prepreg around a mandrel, and the cost of prepregging is \$70/kg.

P2.26. The material in a composite beam is AS-1 carbon fiber-reinforced epoxy ($v_f = 0.60$). In order to save cost, carbon fibers are being replaced by equal volume percent of E-glass fibers. To compensate for the lower modulus of E-glass fibers, the thickness of the beam is increased threefold. Assuming that the costs of carbon fibers, E-glass fibers, and epoxy are \$40/kg, \$4/kg, and \$6/kg, respectively, determine the percent material cost saved. The density of epoxy is 1.25 g/cm^3.

P2.27. Calculate the average density of an interply hybrid beam containing m layers of T-300 carbon fiber–epoxy and n layers of E-glass fiber–epoxy. The thickness of each carbon fiber layer is t_c and that of each glass layer is t_g. The fiber volume fractions in carbon and glass layers are v_c and v_g, respectively.

P2.28. An interply hybrid laminate contains 24 layers of GY-70 carbon fiber–epoxy and 15 layers of Kevlar 49 fiber–epoxy. The fiber weight fraction in both carbon and Kevlar 49 layers is 60%. Determine

1. Overall volume fraction of carbon fibers in the laminate
2. Volume fraction of layers containing carbon fibers