

## Module 2 - Materials for Polymer Composites

### Introduction

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. 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. 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 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.

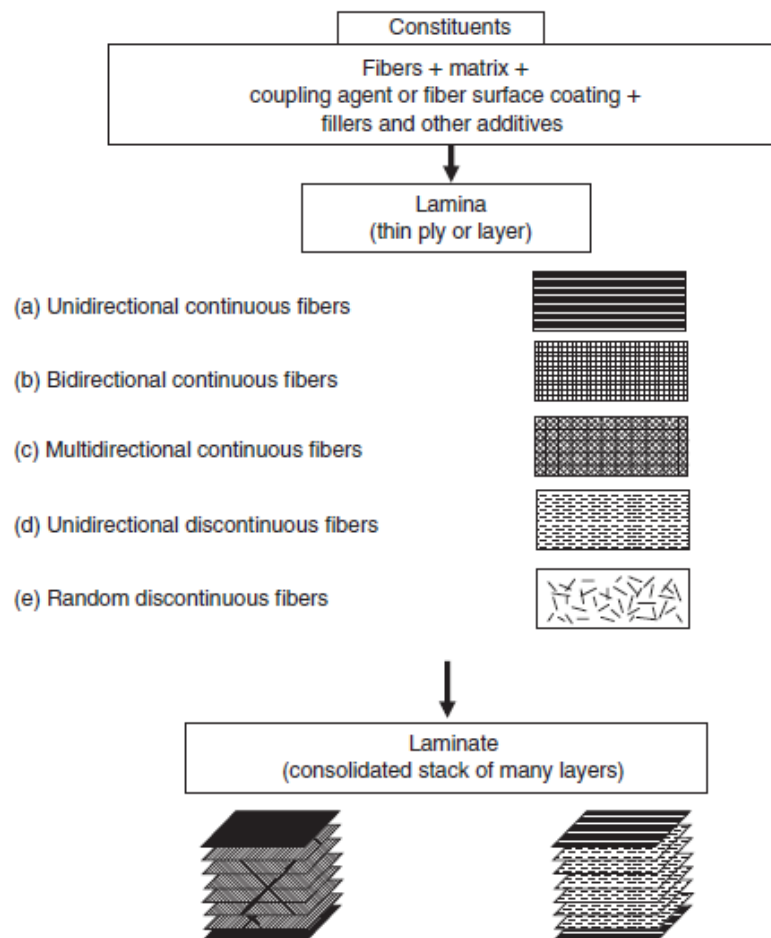


FIGURE 2.1 Basic building blocks in fiber-reinforced composites.

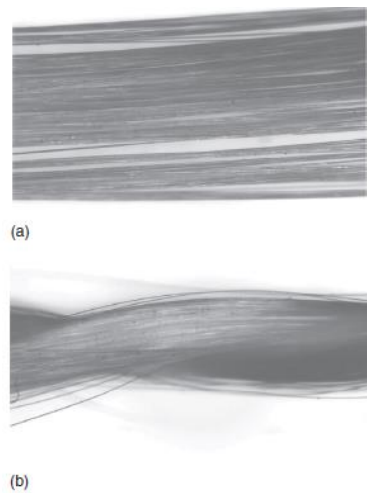
## FIBERS

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

The filament diameters for the fibers are extremely small. 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).



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

### GLASS FIBERS

Glass fibers are the most common of all reinforcing fibers for polymeric matrix composites (PMC).

The principal advantages of glass fibers are,

1. low cost,
2. high tensile strength,
3. high chemical resistance, and
4. excellent insulating properties.

The disadvantages are,

1. relatively low tensile modulus and high density (among the commercial fibers),
2. sensitivity to abrasion during handling (which frequently decreases its tensile strength),

3. relatively low fatigue resistance, and high hardness (which causes excessive wear on molding dies and cutting tools).

The 3 types of glass fibers commonly used in the fiber-reinforced plastics (FRP) industry are

1. E-glass
2. S-glass
3. C-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.

C-glass, is used in chemical applications requiring greater corrosion resistance to acids than is provided by E-glass.

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.

As in common soda-lime glass (window and container glasses), the principal ingredient in all glass fibers is silica ( $\text{SiO}_2$ ). Other oxides, such as  $\text{B}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$ , are added to modify the network structure of  $\text{SiO}_2$  as well as to improve its workability. Unlike soda-lime glass, the  $\text{Na}_2\text{O}$  and  $\text{K}_2\text{O}$  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).

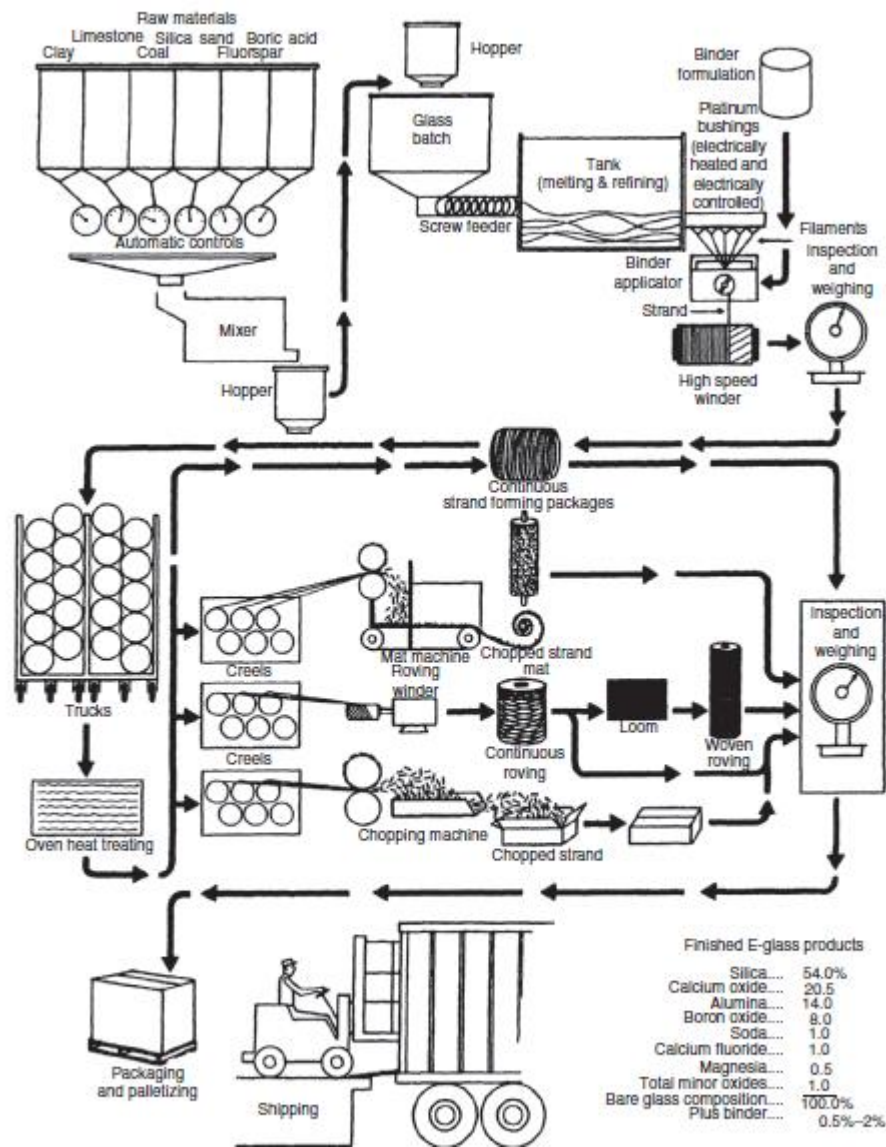


FIGURE 2.9 Flow diagram in glass fiber manufacturing. (Courtesy of PPG Industries. With permission.)

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 through a number of orifices contained in a platinum bushing and rapidly drawn into filaments of ~10 mm 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.

### Forms of glass fibers

The basic commercial form of continuous glass fibers is a **strand**, which is a collection of parallel filaments numbering 204 or more. 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 prepregnated 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 are used in injection-molding operations. Longer strands, up to 50.8 mm 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. 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. 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. However, surface damage (flaws) produced by abrasion, either by rubbing against each other or by contact with the processing equipment, tends to reduce it to values that are in the range of 1.72–2.07 GPa.

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 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.

### **CARBON FIBERS**

Carbon fibers are commercially available with a variety of tensile modulus values ranging from 207 GPa on the low side to 1035 GPa 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.

#### **Advantages of carbon fibers**

1. Exceptionally high tensile strength–weight ratios as well as tensile modulus–weight ratios,
2. Very low coefficient of linear thermal expansion (which provides dimensional stability in such applications as space antennas),
3. High fatigue strengths and high thermal conductivity (which is even higher than that of copper).

#### **Disadvantages**

1. Low strain-to-failure,
2. Low impact resistance, and
3. High electrical conductivity, which may cause “shorting” in unprotected electrical machinery.
4. 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 inter connecting regular hexagons (Figure 2.12) .

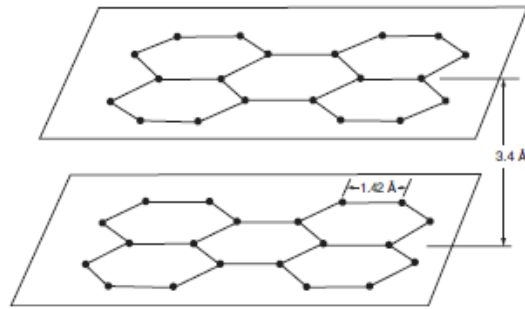


FIGURE 2.12 Arrangement of carbon atoms in a graphite crystal.

The distance between the planes ( $3.4 \text{ \AA}$ ) is larger than that between the adjacent atoms in each plane ( $1.42 \text{ \AA}$ ). 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 ( $\alpha$ ), in the radial ( $r$ ) and circumferential ( $\theta$ ) 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 arrangement in the skin and either radial or random arrangement in the core is commonly observed.

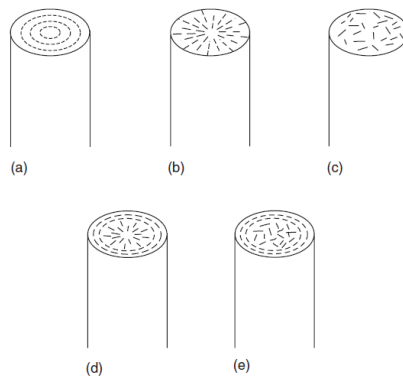


FIGURE 2.13 Arrangement of graphite crystals in a direction transverse to the fiber axis: (a) circumferential, (b) radial, (c) random, (d) radial-circumferential, and (e) random-circumferential.

## Manufacture



Carbon fibers are manufactured from two types of precursors (starting materials), namely,

1. textile precursors and
2. pitch precursors.

The manufacturing process from both precursors is outlined in Figure 2.14.

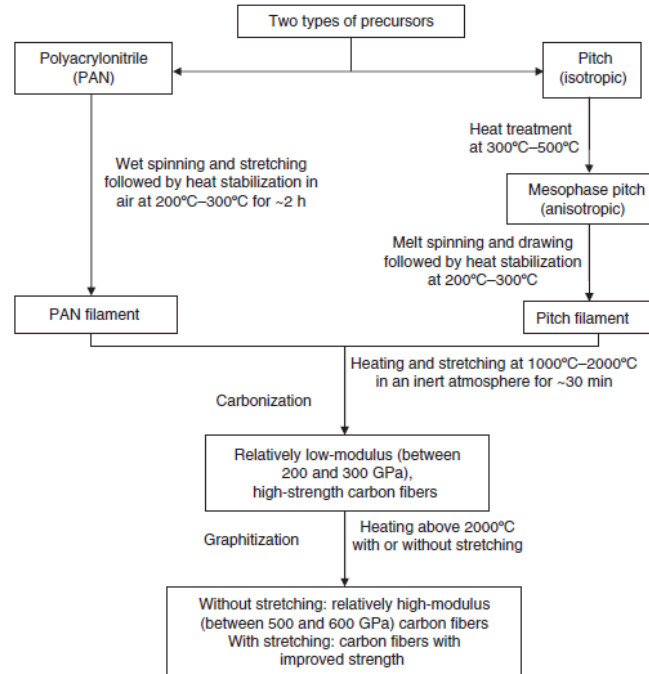


FIGURE 2.14 Flow diagram in carbon fiber manufacturing.

### PAN Process

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.

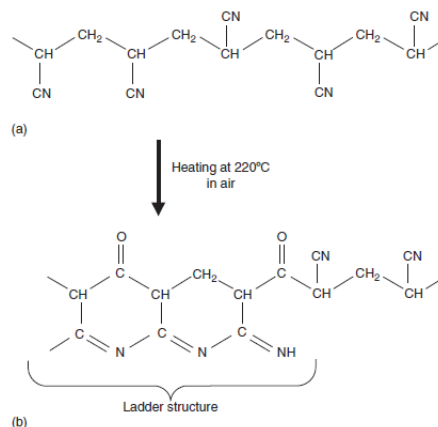


FIGURE 2.15 Ladder structure in an oxidized PAN molecule. (a) Molecular structure of PAN and (b) rigid ladder structure.

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<sub>2</sub> 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, 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. 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.

### **Pitch process**

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 sheet like 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).

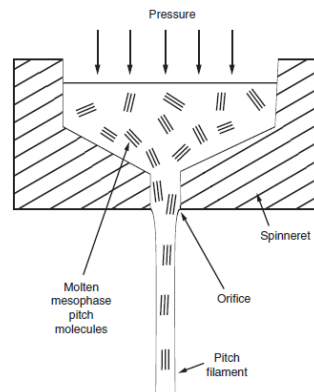


FIGURE 2.17 Alignment of mesophase pitch into a pitch filament. (After *Commercial Opportunities for Advanced Composites*, ASTM STP, 704, 1980.)

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.

### Classification of carbon fibers

PAN carbon fibers are generally categorized into

1. high tensile strength (HT),
2. high modulus (HM), and
3. ultrahigh modulus (UHM) types.

### Properties of carbon fibers

The high tensile strength PAN carbon fibers, such as T-300 and AS-4 have the 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 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. The PAN carbon fibers have lower thermal conductivity and electrical conductivity than pitch carbon fibers. 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.

### **Forms of carbon fibers**

Carbon fibers are commercially available in three basic forms, namely,

1. long and continuous tow,
2. chopped (6–50 mm long), and
3. milled (30–3000 mm 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. Hybrid fabrics containing commingled or co-weaved 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.

### **Fabrics**

There are two major types of fabrics available in composites industry:

1. woven fabrics and
2. nonwoven (noncrimp) fabrics.

### **Woven Fabrics**

Woven fabrics are used in trailers, containers, barge covers, and water tower blades, and in other marine wet lay-up applications. These fabrics are woven yarns, rovings,

or tows in mat form in a single layer. Common weave styles are shown in Figure 2.6. Figure 2.7 shows carbon fabrics in a variety of weave styles. The amount of fiber in different directions is controlled by the weave pattern. For example, in unidirectional woven fabrics, fibers are woven in such a way that the fibers in  $0^\circ$  are up to 95% of the total weight of the fabric. In a plain-weave pattern, fibers in  $0^\circ$  and  $90^\circ$  directions are equally distributed. Hybrid fabrics in various combinations, such as glass/carbon and aramid/carbon, are also available. For lightning strike purposes, conductive wires are woven into fabric forms to distribute the energy imparted by lightning, thus minimizing damage to the structure. Woven fabrics are also used to make prepregs, as well as in RTM and SRIM processes as feedstock. Woven fabrics have the advantage of being inexpensive.

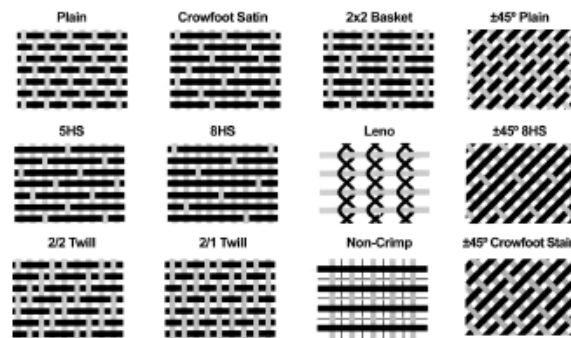



FIGURE 2.6 Various weave styles for fabrics. (Courtesy of Cytec Fiberite.)

### Noncrimp Fabrics

In noncrimp fabrics, yarns are placed parallel to each other as shown in Figure 2.8 and then stitched together using polyester thread. Warp unidirectional fabric is used when fibers are needed in one direction only, for example, in stiffness-critical applications such as water ski applications where the fabric is laid along the length of the ski to improve resistance to bending. In warp fabrics, reinforcements are laid at  $0^\circ$  (or warp direction) only as shown in Figure 2.9; whereas in weft unidirectional fabrics, reinforcements are laid at  $90^\circ$  (or weft direction) only as shown in Figure 2.10. Weft fabrics are typically used in filament wound tubes and pipes and also pultruded components where reinforcement in the weft direction is necessary. Warp triaxial ( $0^\circ, \pm 45^\circ$ ) fabric is used to increase longitudinal stiffness and torsional rigidity, whereas weft triaxial ( $90^\circ, \pm 45^\circ$ ) fabric is used to increase transverse stiffness and torsional rigidity. Quadraxial fabrics are quasi-isotropic, providing strength in all four fiber axial directions. Fabrics typically come in the weight range of 9 to 200 oz/yd<sup>2</sup>. Noncrimp fabrics offer greater flexibility compared to woven fabrics. For

example, fibers can be laid at almost any angle from  $0^\circ$  to  $90^\circ$ , including  $45^\circ$ ,  $90^\circ$ ,  $30^\circ$ ,  $60^\circ$ , and  $22^\circ$ , and then stitched to make multiaxial stitched plies, whereas woven fabrics are made from rovings mostly on the  $0^\circ$  and  $90^\circ$  axes. Noncrimp fabrics offer greater strength because fibers remain straight; whereas in woven fabrics, fibers bend over each other. Noncrimp fabrics are available in a thick layer and thus an entire laminate could be achieved in a single-layer fabric. This is useful in making thicker laminates such as boat hulls and reduces the number of fabrication steps. To make noncrimp glass fabrics, input rovings are selected by yield numbers in combinations of 113, 218, 450, 675, 1200, and 1800 yd/lb. A larger yield number denotes a finer roving and, therefore, more yards are required to achieve a given weight. The selection of yield number is determined by the physical, mechanical, and aesthetic requirements of the laminate. The finer filaments mean higher fiber content and less resin. This improves strength and can reduce weight. To meet the market need for heavier fabrics, stitched fabrics with various combinations of plies are produced. Figure 2.11 shows a bi-ply fabric in which woven fabrics and a chopped strand mat are stitched together to form the fabric. Figure 2.12 shows a mat made using continuous fibers or random cut fibers 5 to 10 cm in length.

### **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.

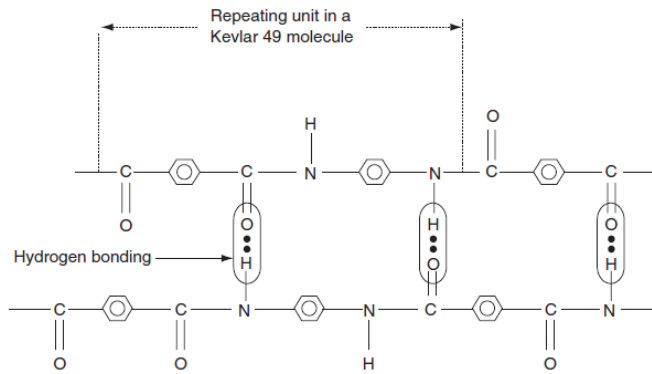


FIGURE 2.18 Molecular structure of Kevlar 49 fiber.

Kevlar 49 filaments are manufactured by extruding an acidic solution of a proprietary precursor (a polycondensation product of terephthaloyl 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. 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.

**TABLE 2.1**  
Properties of Fibers and Conventional Bulk Materials

Material	Diameter ( $\mu\text{m}$ )	Density ( $\rho$ ) ( $\text{g}/\text{cm}^3$ )	Tensile Modulus (E) (GPa)	Tensile Strength ( $\sigma$ ) (GPa)	Specific Modulus (E/ $\rho$ )	Specific Strength	Melting Point (°C)	% Elongation at Break	Relative Cost
Fibers									
E-glass	7	2.54	70	3.45	27	1.35	1540+	4.8	Low
S-glass	15	2.50	86	4.50	34.5	1.8	1540+	5.7	Moderate
Graphite, high modulus	7.5	1.9	400	1.8	200	0.9	>3500	1.5	High
Graphite, high strength	7.5	1.7	240	2.6	140	1.5	>3500	0.8	High
Boron	130	2.6	400	3.5	155	1.3	2300	—	High
Kevlar 29	12	1.45	80	2.8	55.5	1.9	500(D)	3.5	Moderate
Kevlar 49	12	1.45	130	2.8	89.5	1.9	500(D)	2.5	Moderate
Bulk materials									
Steel		7.8	208	0.34–2.1	27	0.04–0.27	1480	5–25	<Low
Aluminum alloys		2.7	69	0.14–0.62	26	0.05–0.23	600	8–16	Low

## MATRIX

The roles of the matrix in a fiber -reinforced compo site 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

1. compressive,
2. inter laminar shear as well as
3. 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 composite sites, the processing characteristics include the liquid viscosity, the curing temperature, and the curing time.

Among the matrix resin system, 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.

### **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 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
3. Low strain-to-failure, which also contributes to their low impact strengths

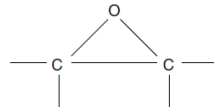
The most important advantage of thermoplastic polymers over thermoset polymers is their high impact strength and fracture resistance, which in turn impart an excellent damage tolerance characteristic to the composite material. In general, thermoplastic polymers have higher strain-to-failure (Figure 2.25)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

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

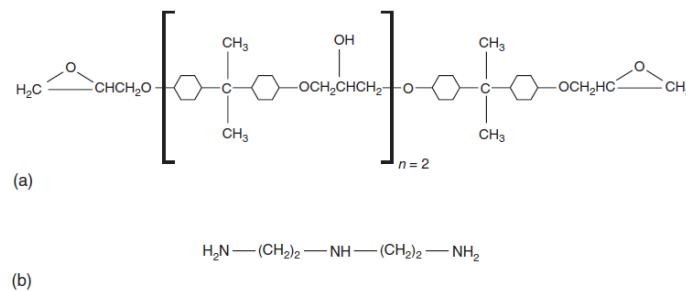
## THERMOSET MATRIX

### 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 ( $\text{NH}_2$ ) 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.

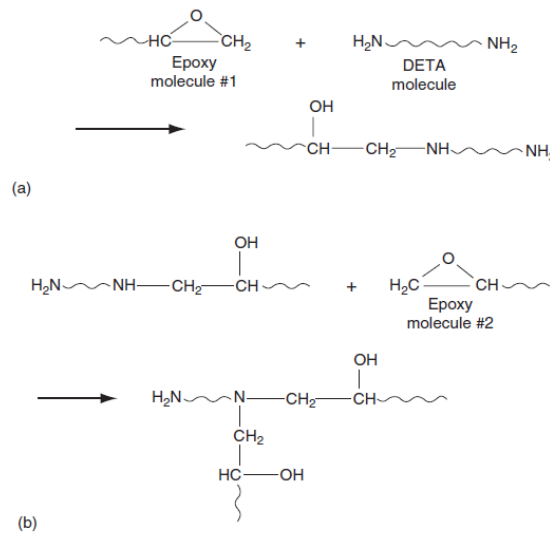


FIGURE 2.28 Schematic representation of a cross-linked epoxy resin. (a) Reaction of epoxide group with DETA molecule; (b) formation of cross-links; and

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 crosslink 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  $(\text{---}\text{C}_6\text{H}_4\text{---})$  in its basic molecular chain.

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
6. The principal disadvantages are its relatively high cost and long cure time.

Typical properties of cast epoxy resins are given in Table 2.8.

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

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

## 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 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.

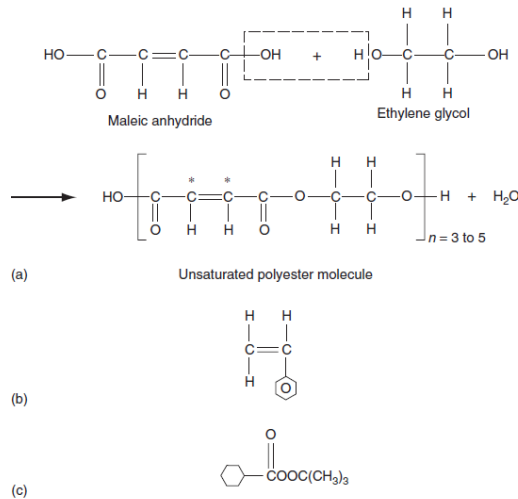


FIGURE 2.29 Principal ingredients in the preparation of a thermoset polyester matrix. (a) Unsaturated polyester molecule. The asterisk denotes unsaturation points (reactive sites) in the unsaturated polyester molecule; (b) styrene molecule; and (c) *t*-butyl perbenzoate molecule (tBPB).

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 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).

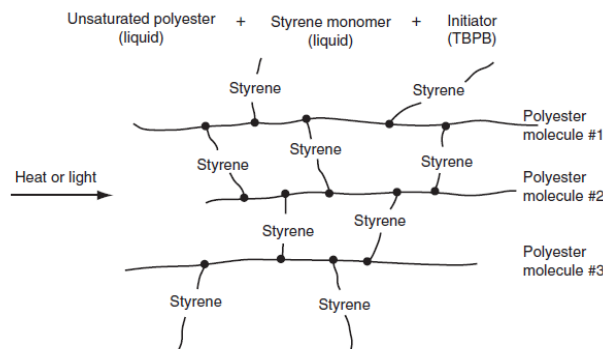


FIGURE 2.30 Schematic representation of a cross-linked polyester resin.

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 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.

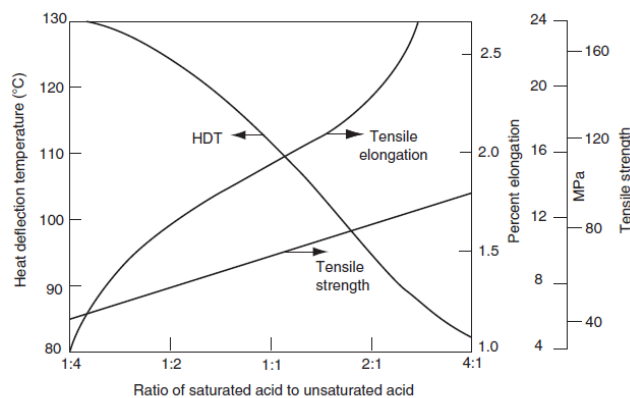


FIGURE 2.31 Effect of unsaturation level on the properties of a thermoset polyester resin. (After How ingredients influence unsaturated polyester properties, Amoco Chemicals Corporation, Bulletin IP-70, 1980.)

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

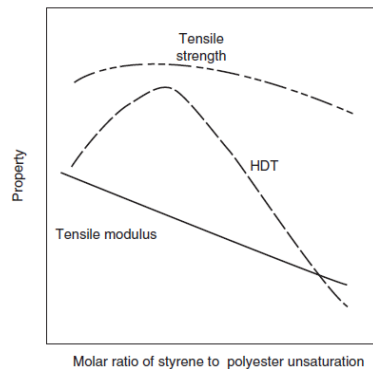


FIGURE 2.32 Effect of increasing styrene content on the properties of a thermoset polyester resin.

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.

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

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

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 (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 micro voids that compensate for the normal shrinkage of the polyester resin.



## 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, crosslinking 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.

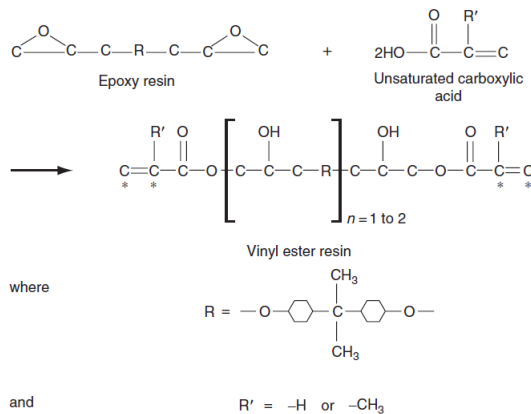


FIGURE 2.33 Chemistry of a vinyl ester resin. The asterisk denotes unsaturation points (reactive sites).

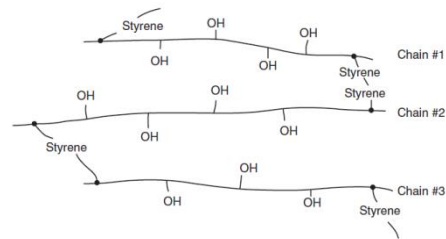


FIGURE 2.34 Schematic representation of a cross-linked vinyl ester resin.

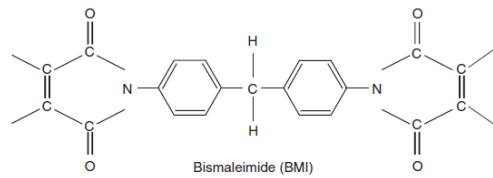
Vinyl ester resins, like unsaturated polyester resins, are dissolved in styrene monomer, which reduces their viscosity. During polymerization, styrene co reacts with the vinyl ester resin to form cross-links between the unsaturation points in adjacent vinyl ester molecules. The curing reaction for vinyl 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 co reactants. 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 <sup>3</sup> )	1.12–1.32
Tensile strength, MPa (psi)	73–81 (10,500–11,750)
Tensile modulus, GPa (10 <sup>6</sup> 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

## BISMALEIMIDES AND OTHER THERMOSET POLYIMIDES

Bismaleimide (BMI), PMR-15 (for polymerization of monomer reactants), and acetylene-terminated polyimide (ACTP) are examples of thermoset polyimides. 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. 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, 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 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:



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.

#### Properties of Thermoset Polyimide Resins (at 23°C)

Property	Bismaleimide <sup>a</sup>		PMR-15 <sup>c</sup>	ACTP <sup>d</sup>
	Without Modifier	With <sup>b</sup> Modifier		
Density (g/cm <sup>3</sup> )	—	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 <sup>2</sup> (in. lb/in. <sup>2</sup> )	24.5 (0.14)	348 (1.99)	275 (1.57)	—

<sup>a</sup> Compimide 353 (Shell Chemical Co.).

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

<sup>c</sup> From Ref. [18].

<sup>d</sup> Thermid 600 (National Starch and Chemical Corporation).

#### CYANATE ESTER

Cyanate ester resin has a high glass transition temperature ( $T_g=265^\circ\text{C}$ ), lower moisture absorption than epoxies, good chemical resistance, and good dimensional stability. 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.

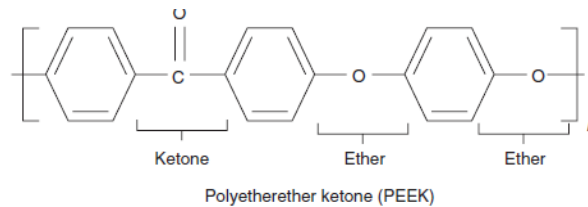
Blending it with thermoplastics, such as polyarylsulfone and polyethersulfone, has shown to improve its fracture toughness.

### 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<sub>g</sub> depends on the size and flexibility of other chemical groups or linkages in the chain.

### POLYETHER ETHER KETONE

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



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. Increasing the crystallinity increases both modulus and yield strength of PEEK, but reduces its strain-to-failure (Figure 2.35).

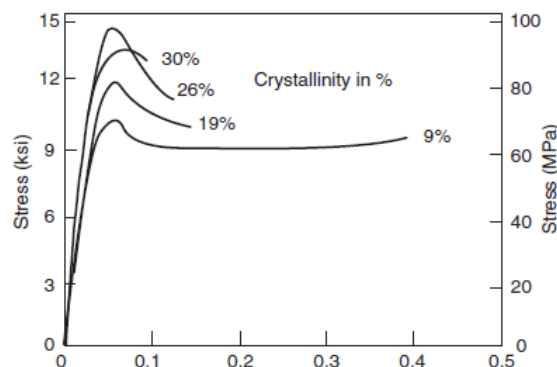
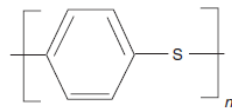


FIGURE 2.35 Tensile stress-strain diagram of PEEK at different crystallinities. (Adapted from Seferis, J.C., *Polym. Compos.*, 71, 58, 1986.)

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

### POLYPHENYLENE SULFIDE

Polyphenylene sulfide (PPS) is a semicrystalline polymer with the following

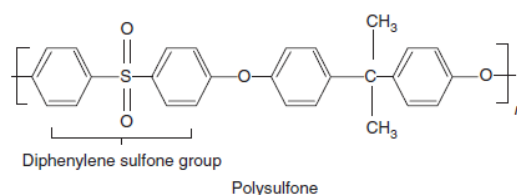


repeating unit in its molecules:

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<sub>g</sub> 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.

### POLYSULFONE

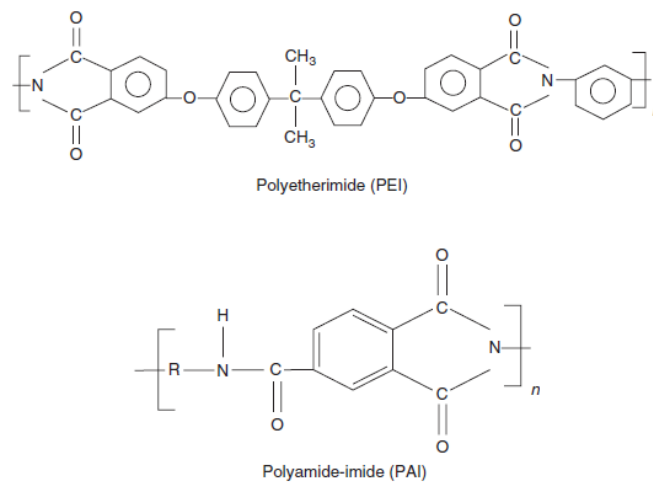
Polysulfone is an amorphous thermoplastic with the repeating unit shown as follows:



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.

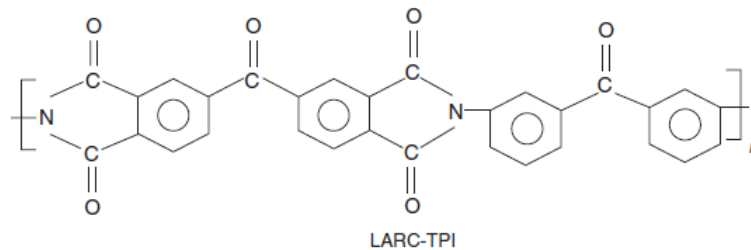
## THERMOPLASTIC POLYIMIDES

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.



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<sub>g</sub>. 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.



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

Property	PEEK <sup>a</sup>	PPS <sup>b</sup>	PSUL <sup>c</sup>	PEI <sup>d</sup>	PAI <sup>e</sup>	K-III <sup>f</sup>	LARC-TPI <sup>g</sup>
Density (g/cm <sup>3</sup> )	1.30–1.32	1.36	1.24	1.27	1.40	1.31	1.37
Yield ( <i>Y</i> ) or tensile ( <i>T</i> ) strength, MPa (ksi)	100 (14.5)	82.7 (12)	70.3 (10.2)	105 (15.2)	185.5 (26.9)	102 (14.8)	138 (20)
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 ( <i>G<sub>IC</sub></i> ), kJ/m <sup>2</sup>	6.6	—	3.4	3.7	3.9	1.9	—
HDT, °C (at 1.82 MPa)	160	135	174	200	274	—	—
CLTE, 10 <sup>-5</sup> /°C	4.7	4.9	5.6	5.6	3.6	—	3.5

<sup>a</sup> Victrex.

<sup>b</sup> Ryton.

<sup>c</sup> Udel.

<sup>d</sup> Ultem.

<sup>e</sup> Torlon.

<sup>f</sup> Avimid.

<sup>g</sup> Durimid.

## References:

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