4
Polymeric Matrix Materials

4.1 Introduction

The matrix, as discussed in the Chapter 1, serves the following functions: 1) transfers load into and out from the fibers, 2) separates the fibers to prevent failure of adjacent fibers when one fails, 3) protects the fiber from environmental damage, supports the fibers in the shape of the component.

The mechanical properties of the composite that are significantly affected by the properties of the polymeric matrix (and fiber/matrix bond strength) include 1) longitudinal compression strength, 2) transverse tensile strength, and 3) interlaminar shear strength. These are generally called *matrix-dominated properties*.

To be suitable as matrices, polymers must also have resistance to aircraft solvents such as fuel, hydraulic fluid, and paint stripper and to service temperatures typically up to around 80°C for civil and 150°C for military applications; however, a capability to over 200°C may be required in some applications.

In the production of advanced composites suitable for aerospace applications, it is important that the method of matrix incorporation does not damage the reinforcement fibers or inadvertently change their orientation. One suitable method is to infiltrate an aligned fiber bed with a low-viscosity liquid that is then converted, by chemical reaction or simply by cooling, to form a continuous solid matrix with the desired properties.

4.1.1 Background on Polymeric Materials

Polymers consist of very long chain molecules,[1] generally with a backbone consisting of covalently bonded carbon atoms. In the simplest type of polymer, each carbon atom is joined to two others to form a linear polymer. The other two available bonds not used in the chain are linked to side groups (Fig. 4.1). If, however, the carbon atoms link with carbon atoms that are not in simple groups, then a three-dimensional network or cross-linked polymer results.

Figure 4.2 is a highly simplified schematic[2] comparing the polymer backbones of linear and cross-linked polymer chain configurations. There are, however, several intermediate forms, including branched and ladder polymers, shown in

$$\begin{array}{c}
\quad\ \ CH_3\ \ H\quad\ CH_3\ \ H \\
\quad\ \ |\qquad|\qquad|\qquad| \\
-C-C-C-C- \\
\quad\ \ |\qquad|\qquad|\qquad| \\
\quad\ \ CH_3\ \ H\quad\ CH_3\ \ H
\end{array}$$
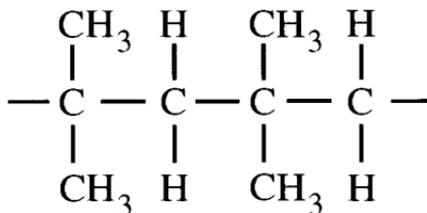
Fig. 4.1   Example of the polymer chain arrangement of a simple linear polymer.

Figure 4.2. Polymer branching can occur with linear or cross-linked polymers; ladder polymers are made of two linear polymers joined by regular linkages. As may be expected, ladder polymers are more rigid than simple linear polymers.

Linear molecules can be characterized in terms of the molecular weight, which is an indication of the average length of the molecular chain; however, this has no meaning for cross-linked polymers because these do not form as discrete molecules. The formula for a linear polymer is $(M)_n$ where M is the repeating unit and n the degree of polymerization. For example, in a sample of the polymer with an average n of 5000, the range will typically be in the range 1000–10,000.

If there is only one type of repeating unit, the polymer is called a homopolymer. When, however, there are two types of repeating unit based on two types of monomer, the resulting polymer is called a copolymer. In a block copolymer, each repeating unit has a regular distribution of long sequences. If, however, the sequence is random, the resulting polymer is called a regular or random copolymer. If there is a chain of one type of polymer with branches of another type, the resulting polymer is called a graft copolymer.

a)

b)

c)

d)
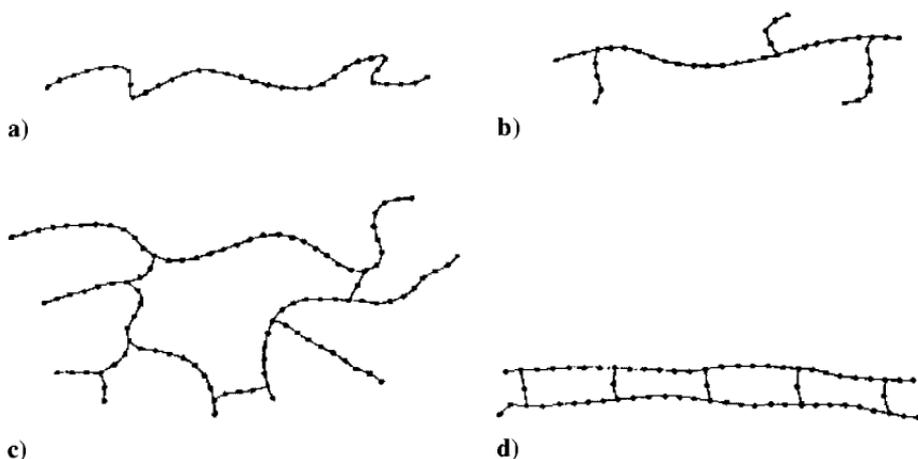
Fig. 4.2   Schematic illustration of the molecular configuration of a) linear, b) branched, c) cross-linked, and d) ladder polymers.

The process of polymerization generally involves the linking of carbon atoms in short-chain organic compounds called monomers, through reaction or by catalysis. The two principal types of polymerization are called condensation polymerization and addition polymerization.

In condensation polymerization, the monomers link together (or cure) producing water or other small molecules as a by-product, while in addition polymerization, the monomers link without producing any by-product. The production of small volatile molecules during matrix formation is highly undesirable, as it can lead to extensive voiding. However, voiding can be minimized in these systems if polymerization occurs under high-pressure conditions.

Polymers with a three-dimensional network structure are called thermosetting polymers, and the process of network formation is called curing. The precursor materials used to form the network are monomer or oligomer (several monomers joined together) mixtures called resins. These, depending on formulation and temperature, can range in viscosity from free-flowing liquids, similar to a light oil (< 1000 centipoise) or highly viscous semi-solids ($> 100,000$ centipoise). Curing is brought about by the reaction of the resin with a curing agent (which may be another resin) or a catalyst, often at elevated temperature. Thermosets, once cured, become solids that cannot be melted and reformed. Thermoplastics are higher molecular weight linear polymers that undergo no permanent chemical change on heating (below the decomposition temperature). They flow upon heating so that they can be reformed.

Finally, a common chemical theme among polymeric materials used for aerospace matrices is that they contain rigid rings (aromatic rings) in their structure. This provides the required chemical resistance and mechanical properties at elevated temperature.

4.1.2 Structure and Mechanical Properties

Thermosetting and thermoplastic polymers differ in many respects. One important difference is that some degree of crystallinity is possible with thermoplastics, whereas thermosets are amorphous. The degree of crystallinity in thermoplastic polymers depends on many parameters, particularly those that allow or inhibit easy alignment of the polymer chains, for example the size and regularity of the side groups. Depending on the temperature, the molecular chains are in a constant state of motion relative to one another. At modest temperatures, depending on the polymer chain, islands of crystallinity exist in an amorphous matrix.

The crystalline regions consist of regions of aligned chains, generally produced by folding of a single chain (Fig. 4.3). In some cases, order is further increased by groups of crystals forming ordered regions known as spherulites because of their spherical geometry. The important point is that the density of the polymer is much higher in the crystalline regions, but its random molecular
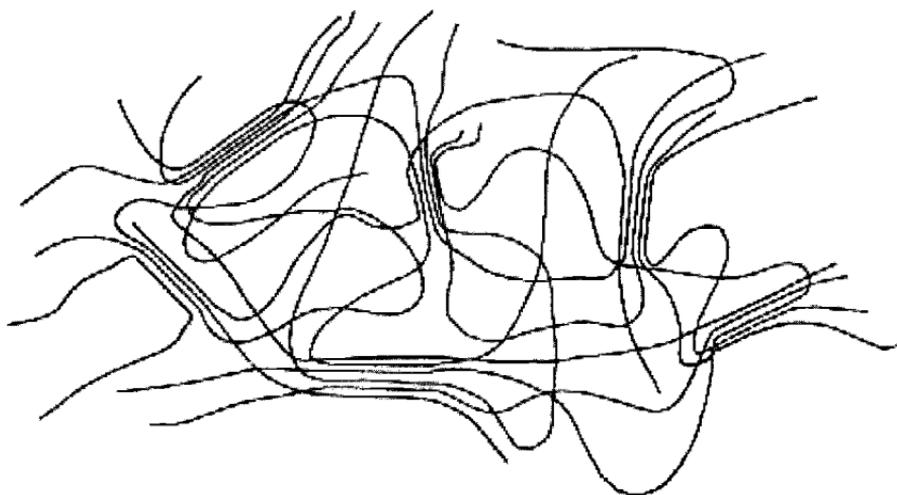
Fig. 4.3   Schematic representation of a linear polymer showing amorphous and local areas of crystallization where the polymer chains are aligned.

motion is reduced, resulting in increases in mechanical properties such as stiffness and chemical properties such as solvent resistance. This degree of order is changed at elevated temperature as the crystalline order is reduced, resulting in a marked but gradual change in, for example, stiffness. Unlike simple solids where a definite transition from a crystal to a liquid occurs at a specific temperature T_m, in polymers T_m is a range and melting results in an amorphous semi-solid material (Fig. 4.4). In contrast, since there are no regions of crystallinity, thermosets and amorphous thermoplastics show no sharp melting point, but a gradual reduction in stiffness over a range of temperatures.

At low temperatures, thermoplastics form a solid that may be partially crystalline and partially amorphous. The degree of crystallinity depends on the polymer structure and the cooling rate. With rapid cooling or with polymers having bulky side chains, the structure could be largely amorphous.

Below a certain temperature called the glass-transition temperature T_g, the random molecular motion drops to a very low level, which is particularly marked in the amorphous regions. The chains thus become set in their random patterns, and the material becomes rigid and glass-like. Above T_g, polymers exhibit a low stiffness and rubbery behavior. This behavior above and below T_g also occurs for similar reasons in thermosets, but is not so marked as the movement of the polymer chains is restricted by the cross-links.

Figure 4.5 schematically illustrates this behavior for 1) a crystalline thermoplastic, 2) an amorphous thermoplastic, 3) a thermoset, and 4) a rubber. Because the crystalline regions inhibit slippage of the polymer chains even above T_g, the drop in stiffness is dramatic when crystalline melting occurs.
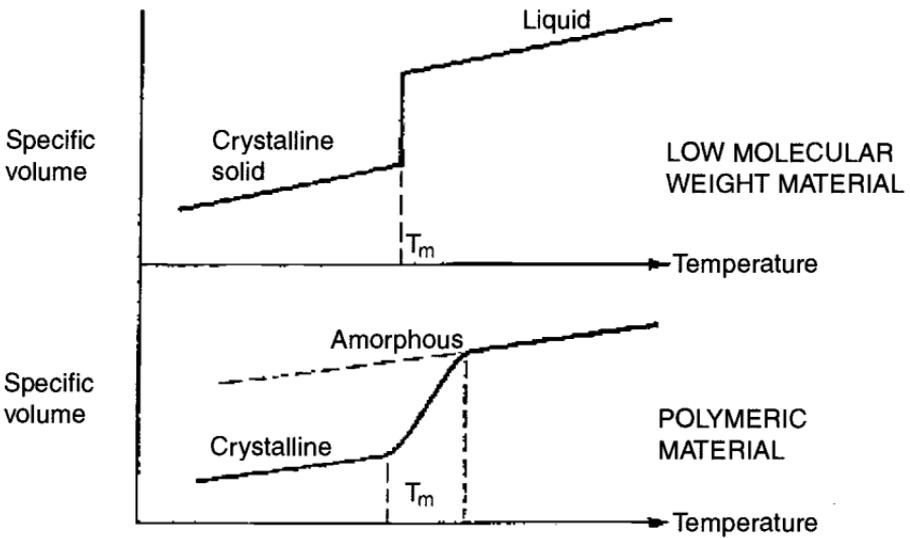
Fig. 4.4 Schematic plot of the variation of specific volume with temperature for a low molecular weight material, such as a metal, and for a linear polymeric material.

The temperature determined for T_g is generally a function of the method of measurement. Most practical determinations of T_g involve stressing the sample and determining the effect of temperature. The speed of application of the stress and the rate of change of temperature has a pronounced effect on the observed temperature of the glass transition. Modern dynamic mechanical (thermal) analysis equipment is able to simultaneously carry out such stress testing at a
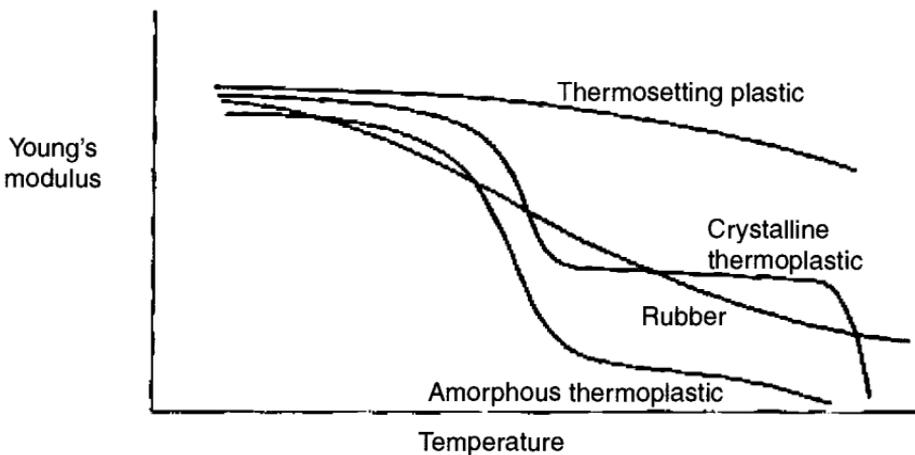
Fig. 4.5 Schematic plot of variation of Young's modulus with temperature for various types of polymer.

range of frequencies. The mechanical failure mode of particular composite items made with these resins could therefore be different at different temperatures as well as under different testing regimens. Many rubbery materials will fail in a "glassy manner" if tested at a high enough speed.

4.2   Thermoset and Thermoplastic Polymer Matrix Materials

As discussed earlier, polymers fall into the two major categories: thermosetting and thermoplastic. Thermosets have the great advantage that they allow fabrication of composites at relatively low temperatures and pressures because they go through a low-viscosity stage (sometimes very low) before polymerization and cross-linking.

Based on Ref. 3, the relative properties of thermosets and thermoplastics, and their advantages and disadvantages, are summarized in Table 4.1.

Table 4.1   Thermoset Matrices and Thermoplastic Matrices

Thermoset	Thermoplastic
Main Characteristics	
• Undergoes chemical change when cured	• Non-reacting, no cure required
• Low strain to failure	• High strain to failure
• Low fracture energy	• High fracture energy
• Processing is irreversible	• Very high viscosity
• Very low viscosity possible	• Processing is reversible
• Absorbs moisture	• Absorbs little moisture
• Highly resistant to solvents	• Limited resistance to organic solvents, in some cases
Advantages	
• Relatively low processing temperature	• Short processing times possible
• Good fiber wetting	• Reusable scrap
• Formable into complex shapes	• Post-formable can be reprocessed
• Liquid-resin manufacturing feasible	• Rapid processing
• Resistant to creep	• Unlimited shelf life without refrigeration
	• High delamination resistance
Disadvantages	
• Long processing time	• Lower resistance to solvents
• Long (∼1–2 h) cure	• Requires high temperature (300–400° C) and pressure processing
• Restricted storage life (requires refrigeration)	• Can be prone to creep
	• Very poor drapability and tack

Of all thermosetting resins, epoxy resins are the most widely used in aircraft structures. Epoxies have excellent chemical and mechanical properties, have low shrinkage, and adhere adequately to most types of fiber. Importantly, they go through a low-viscosity stage during cure and so allow for the use of liquid resin-forming techniques such as resin-transfer molding (RTM). In general, the glass transition temperature T_g of epoxy resins increases with increasing temperature of cure. Thereby, epoxy systems cured at 120 °C and 180 °C have upper (dry) service temperatures of 100–130 °C and 150 °C, respectively (note a significant margin on T_g is mandated in designs; see Chapter 12). It is important to note that T_g is reduced significantly by absorbed moisture, as discussed later.

Bismaleimide resins (BMIs) have similar excellent processability and comparable mechanical properties to epoxies. Importantly, they can operate at higher temperatures; however, as with epoxies, T_g is markedly reduced by absorbed moisture. Generally, BMI resins cured at around 200 °C have upper service temperatures above 180 °C. The higher cost of BMI resins limits their use to applications where the operating temperatures exceed the capability of epoxies.

If even higher operating temperatures are required, composites based on polyimide resin matrices may be the only option. These high-temperature thermosetting resins typically cure around 270 °C and allow operating temperatures of up to 300 °C. However, there are penalties of a higher cost than BMIs and much more difficult processing.

Thermosetting resins have relatively low fracture strains and fracture toughness as inelastic deformation is limited by the highly cross-linked structure. This translates into poor fracture resistance in the composite. These systems also absorb atmospheric moisture, in some cases over 3%, resulting in reduced matrix-dominated properties in the composite, such as elevated temperature shear and compressive strength.

Thermoplastics suitable for use as matrices for high-performance composites include polymers such as polyetheretherketone (PEEK), for applications up to approximately 120 °C; polyetherketone (PEK) for up to 145 °C; and polyimide (thermoplastic type) for up to 270 °C. Fabrication of thermoplastic composites involves melting and forming steps.[4] Because these materials are already fully polymerized, their viscosity, even when melted, is generally much higher than that of most thermosetting resins. They are thus not well suited to conventional liquid resin techniques such as RTM. Fabrication techniques based on resin-film infusion (RFI) or pre-preging (pre-coating the fibers by dissolving the polymer in an appropriate solvent) and then hot-pressing are more appropriate (See Chapter 5).

An advantage of thermoplastic composites is their higher retained hot/wet properties as they absorb less moisture (typically around 0.2%) than thermosetting resin composites. These polymers also have a much higher strain to failure because they can undergo plastic deformation, resulting in significantly improved impact resistance.

Aerospace-grade thermoplastics are generally more expensive than thermosets and are more costly to fabricate, due to the high temperatures and pressures involved. In addition, with continual research and development improvements in thermosets, even the toughness advantage of thermoplastic composites is being eroded. There is little doubt that thermoplastics will be used extensively in the future—especially in niche areas in which high resistance to impact or edge damage (for example, in the case of doors) justifies the higher cost.

The comparative physical properties of the standard matrix resins are discussed in Ref. 5 and 6, and Ref. 7 provides a good overview of the chemistry of the various systems.

The following sections provide more details on the various polymer matrix materials.

4.3   Thermosetting Resin Systems

Table 4.2 and 4.3 list some of the relevant attributes of some of the thermosetting thermoplastic matrices, and Table 4.4 provides details on some of the important properties, including fracture energy.

4.3.1   Epoxy Resins

Epoxy resins[8] are a class of compounds containing two or more epoxide groups per molecule. Figure 4.6 depicts the structures of the major epoxy systems used in aerospace composite matrices. The epoxide is the three-membered ring formed by the oxygen and the two carbons. It is also called an oxirane ring, or the glycidyl group.

Epoxies are formed by reacting polyphenols or other active hydrogen compounds with epichlorohydrin under basic conditions. The most common phenol used is bisphenol A (Diphenylolpropane). It provides the basis of a whole family of aerospace epoxy resins having the general structure shown in Figure 4.6a. These are usually complex mixtures of molecules with various values of n. The lower the value of n or the more complex the mixture, the lower the resin viscosity but the more brittle the final cured resin. Trade names of these resins include such materials as Epikote or Epon 828, Dow DER 331, and Araldite F.

There are many other epoxy resins manufactured for special purposes, but of particular importance in advanced aerospace materials are the tetraglycidyl derivative of diaminodiphenylmethane (TGDDM) (Fig. 4.6b) and the triglycidyl derivative of p-aminophenol (TGAP) (Fig. 4.6c). The high functionality of these materials makes for higher resin reactivity and greater cross-linking, which translates into higher composite stiffness and glass transition temperatures. In contrast, use is often made of small amounts of reactive diluent epoxy resins such as the bis epoxy from butane diol (Fig. 4.6d) to improve the flow

Matrix	Examples	~Cure °C/KPa	Max (wet) Capability °C	Comments on Performance as Matrix
Epoxy	Hexcel 920	120/700	80+	Best properties all around.
Epoxy	Hercules 3501–6 Fiberite 934 Narmco 5208	180/700	100+	Excellent adhesion to fibers. Easy to process, wide viscosity range, good wetting, and large process window. Not prone to voiding, low volatile emission. Excellent water and other chemical resistance. Large database for aerospace application. Fairly low toughness, composites sensitive to impact damage. Limited temperature capability. Absorbs moisture, reducing elevated temperature. Mechanical properties. Sensitive to UV exposure.
Epoxy Toughened	Hercules 3502 Fiberite 977–2	180/700	100+	All of the above, plus: Improved tolerance to damage. Increased moisture sensitivity.
BMI	Hexcel F560	180/700 + postcure 200	230	Exceeds epoxy temperature capability. Relatively easy to process. Even less tough than epoxies. Undergoes shrinkage during cure. Prone to microcrack with thermal cycling.
BMI Toughened	Cytec 5250–4	180/700	180	All of the characteristics listed for BMI, plus: More damage resistant. Lower temperature capability than untoughened.
Polyimide Condensation	PMR-15	300/4100	320	Resistant to oxidation. Similar properties to epoxy—matrix composites possible but overextended temperature range. Low toughness. Prone to severe voiding. Difficult to process.

Table 4.3 Some Details on Selected Thermoplastic Matrix Materials Used in Aerospace Composites (continued)

Polymer	Examples	Process Temp~°C	T_g°C	Comments on Performance as a Matrix
PEEK, Polyether-etherketone	Victrex	400	145	Excellent mechanical properties, including toughness. For application at temperatures up to 120°C. Highly resistant to damage by aircraft fluid. Excellent fire resistance. Most widely used for high-performance composites.
PPS, Polyphenylene-sulfide	Ryton	340	90	Good strength, stiffness, and temperature capability. Some grades have low viscosity, aiding composite manufacture. Resistant to most aircraft fluids, but attacked by some solvents, including paint stripper. Good fire resistance. Low impact resistance.
PSF, Polysulfone	Udel	400	190	
PAS, Polyarylsulfone	Radel	400	220	
PES, Polyether-sulfone	Vitrex	400	230	
PI, Polyimide	Kapton	390	320	Selected for highest-temperature applications. Highly viscous. Difficult to process.
PEI, Polyetherimide	Ultem	370	215	Selected for high-temperature applications. Lower cost than PI.

Table 4.4   Approximate Properties of Selected Polymer Matrix Materials

Matrix Material Details	G_{1C} (J/m^2)	E (GPa)	ε (%)	T_g (°C) Dry	Wet ~
920 Hexcel	541	3.8	8.4	107	85
RTM6 Resin transfer molding resin	168	2.9	3.4	183	167
F584 First generation pre-preg epoxy	175	4.1	1.8	171	121
914 First generation pre-preg epoxy	103	3.9	1.5	190	N/A
F593 Pre-preg epoxy	420	3.0	2	172	131
977-3 Pre-preg epoxy	217	N/A	N/A	218	178
977-2 Toughened version of 977-3	478	3.5	N/A	212	N/A
6376 Toughened pre-preg epoxy	432	3.0	3.1	N/A	N/A
8552 Toughened pre-preg epoxy	N/A	4.0	4	195	154
524C Modified BMI resin	67	3.3	2.9	220	–
PMR 15 Polyimide	280	4.0	1.1	340	–
Udel Polysulfone	3200	2.7	50	190	–
Radel Polyarylsulfone	5500	2.8	60	220	–
PES Polyether sulfone	2600	2.9	40	220	–
Ultem Polyetherimide	3700	4.0	60	220	–
Torlon Polyamideimide	3400	4.9	15	275	–
PEEK Polyetheretherketone	4400	3.6	30	145	–
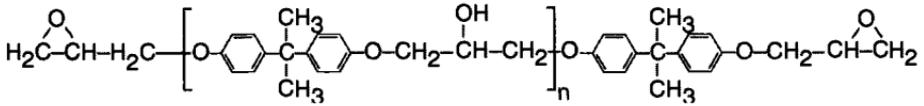
a)
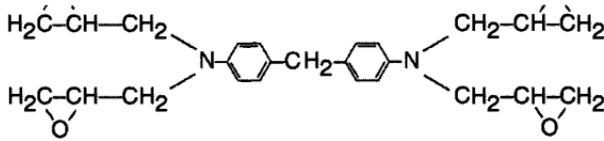
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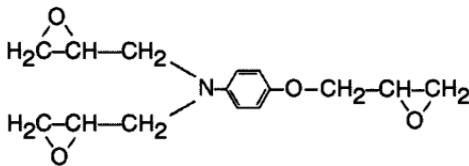
c)
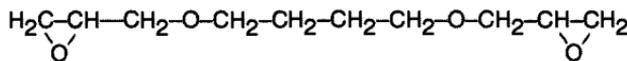
d)

Fig. 4.6   Major epoxy resins used in aerospace composite matrices: *a*) bisphenol A-epichorohydrin (DGEBA) resins; *b*) tetraglycidyl derivative of diamino diphenyl methane (TGGM); *c*) triglycidyl derivative of p-aminophenol (TGAP); *d*) reactive diluent epoxy resin such as the bis epoxy from butane diol.

characteristics of epoxy formulations before cure. This does, however, result in some loss in final high-temperature properties.

4.3.1.1 Curing of Epoxy Resins.   The epoxide group has unfavorable bonding angles, which makes it chemically reactive with a variety of substances that can easily open the ring to form a highly cross-linked structure. The cross linking may occur through the epoxy groups or the resulting hydroxy groups.

While epoxy resins can be self-polymerized using suitable catalysts, the majority of applications make use of curing agents—often called hardeners. The major classes of curing agents include aliphatic amines, which give cold-curing systems and aromatic amines and polyanhydrides, which give heat-curing

systems. Aromatic amines form the bulk of the curing agents in the advanced aerospace composites as they produce matrix materials and hence composites with high glass-transition temperatures.

An epoxy resin cure is the result of a complex series of individual chemical reactions that have different rates, even at the same temperature. An example is the reaction of an amino group in a hardener with an epoxy group in the resin, as shown in Figure 4.7. Reaction *1* is usually much faster than *2*, which is in turn faster than *3* (epoxy self-polymerization), but this sequence can change with different catalysts and as the viscosity changes. The last reaction is often the major type of reaction that can occur at high viscosities, after gelation or in highly cross-linked systems. Because of this reaction rate difference, it is very important to follow an exact cure profile in making a composite part: the incorrect cure cycle gives different molecular architecture and hence different, possibly inferior, mechanical and chemical properties. What is also important about this sequence of individual reactions to form the solid matrix (called a step growth mechanism of polymerization) is that it requires the correct "stoichiometry," or ratio of functional groups, and each step required takes time. This contrasts with the polyester mechanism, described later. Another important point to be considered with an epoxy resin is that it goes through a number of physical states as it cures. An initial low-viscosity state is important to get the resin to flow into and wet-out all the fine crevasses between the fibers in a composite part. The viscosity reaches a minimum, caused by outside heat or the heat of reaction of the functional groups, and then increases rapidly due to molecular chain extension. The next step in the reaction is gelation—when the chains start to cross-link, the resin no longer flows and most individual reaction rates decrease markedly. The final step at high cross-linking is called vitrification, at which point-chain motion stops.

a) $R-NH_2 + H_2C-CH-E \longrightarrow R-\overset{H}{\underset{}{N}}-CH_2-\underset{OH}{CH}-E$

b) $R-\underset{R'}{NH} + H_2C-CH-E \longrightarrow R-\underset{R'}{N}-CH_2-\underset{OH}{CH}-E$

c) $-\underset{OH}{CH}- + H_2C-CH-E \longrightarrow -CH- \underset{O-CH_2-CH-E}{}$
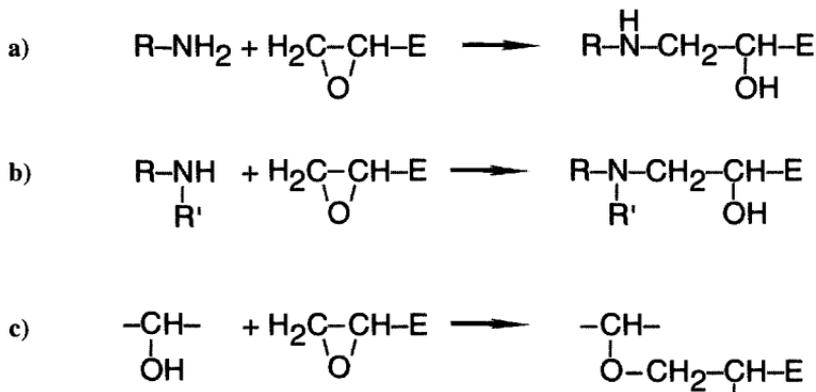
Fig. 4.7   Epoxy cure reactions: *a*) primary amine-epoxy reaction, *b*) secondary amine-epoxy reaction, *c*) hydroxyl group reaction (etherification). R is a general amine backbone, E is a general epoxy backbone.

Diffusion of the reacting groups in this glassy phase is very slow, and the normal cure reactions effectively stop at this point.

As mentioned above, the cure of an epoxy resin can be accelerated by the use of suitable catalysts (such as dicyanimide or BF_3-monoethylamine) or heat, but the maximum rate is normally much slower than for polyesters. This is partly because the epoxy/hardener group reaction is strongly exothermic (generates heat), so the use of excessive quantities of catalyst or inappropriately high cure temperatures will result in thermal degradation of the matrix, especially in thick composite sections. In particularly bad cases or where there are large quantities of resin, uncontrollable exothermic decomposition can occur. Use of catalysts also allows the development of resin systems with long pot lives; this is very important for manufacturing processes such as filament winding.

4.3.1.2 Epoxy Matrix Properties. The occurrence of rubber (gelled) and glassy states is characteristic of amorphous polymers such as epoxy resins. Such polymers become glassy at relatively low temperatures, and at high temperatures they usually become rubbery again. As the normal polymerization mechanism of an epoxy resin stops in the glassy state, it is very difficult to design a system that will be capable of operation at much over the maximum temperature in the cure cycle. Systems cured at room temperature, using aliphatic polyamine curing agents, are not suitable for use at temperatures much higher than 50°C. Systems cured with aromatic polyamines or anhydrides are usually cured at temperatures around 120–180°C and can often be postcured at 150–220°C. These can have maximum operating temperatures in the range of 100–250°C.

Gillham[9] devised a very helpful diagrammatic representation of the cure properties of various matrix resins (especially epoxy materials). Such a generalized time-temperature-transformation diagram is shown in Figure 4.8.

4.3.1.3 Formulating With Epoxy Resins. The properties of the final cured matrix are partially defined by the choice of resin and curing agent but may be further modified by a range of additives. As always, the choice of starting materials for a particular purpose depends on a whole series of compromises, not the least of which are cost and availability. For example, the DGEBA materials of structure Figure 4.6a provided the bulk of the epoxy resins previously used in the aerospace industry; more recent formulations have substituted the multifunctional resins TGDDM (Fig. 4.6b) and TGAP (Fig. 4.6c). These improve the thermal stability properties and modulus, with some loss in toughness and an increase in costs.
The choice of resin curing agents or hardeners often includes a compromise on safety, with some of the more active amine hardeners being relatively toxic or unpleasant.

The various additives that can be used to modify resin properties include:

(1) Diluents are added to reduce the viscosity before cure to aid in handling, wet-out, etc. (usually these cause decreases in the maximum operating temperatures, except for low-viscosity aromatic resins like TGAP).
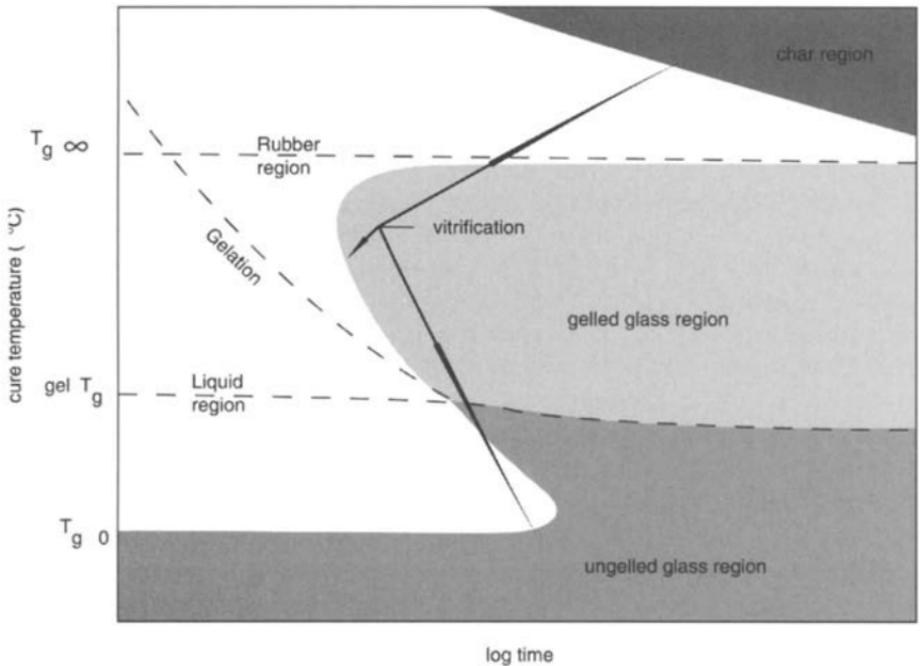
Fig. 4.8   Time-temperature-transformation (phase diagram).

(2) Flexibilizers are added to reduce the elastic modulus and increase the elongation to failure.

(3) Toughening agents that precipitate from the reacting matrix during cure as fine particles, designed to modify the crack propagation properties in a cured matrix. In the past, most of these were reactive rubbers, but much more interest is now centered on engineering thermoplastic additives because they have fewer detrimental effects on the high-temperature properties of a matrix resin. Toughening mechanisms are discussed in the following section.

(4) Inert fillers, including hollow spheres, are added to alter density, resin flow, cost, and effective modulus.

4.3.1.4 Toughening Epoxy Resins.   Epoxies, though they generally have relatively high strength and stiffness and many other desirable properties, are too brittle to be used in their unmodified form as structural adhesives. Thus, various approaches are used to provide toughening, including the formation of a solid solution with a more ductile polymer, precipitation of a elastomeric second phase, and development of interpenetrating polymer networks.

By far, the most explored and practically exploited approach to the toughening of epoxy resins is the formation of a finely distributed elastomeric second phase. There are two ways of achieving this microstructure. The main way is by the addition of an elastomer in the unreacted form to the base resin. It is important

that the elastomer molecules employed react with the resin matrix (by copolymerization) and that they then precipitate out by phase separation to form a dispersed second phase, without leaving excessive amounts of the elastomer completely dissolved in the matrix. Significant amounts of dissolved elastomer would result in an unacceptable reduction in T_g. The main elastomer used is a carboxy-terminated butadiene nitrile rubber (CTBN) that can be used in concentrations of up to about 18% in the uncured epoxy. Figure 4.9 shows a typical relationship between CTBN and measured fracture toughness.

Another approach is to add the elastomer as a very fine powder to form a dispersion. However, this is generally used in addition to the precipitation approach to increase the total amount of dispersed phase.

A number of processes result in the toughening observed with elastomer modification.[10] Firstly, it is thought that the hydrostatic tensile stresses at the crack tip are relieved by dilation and fracture of the elastomer particles, allowing increased ductility at the crack tip. Secondly, the local stress concentrations associated with the elastomeric particles are considered to encourage shear yielding of the epoxy matrix around the crack tip, which is both more extensive and at more sites. Thirdly (and probably least important), some rubber particles actually bridge the growing crack, increasing the fracture energy by the work required to elongate and rupture them; for this mechanism to operate, a strong bond between the elastomer particles and the matrix is essential.

4.3.1.5 Moisture Sensitivity in Epoxy Resins and Other Thermosets. Each type of epoxy matrix has a moisture sensitivity that depends largely on the polarity
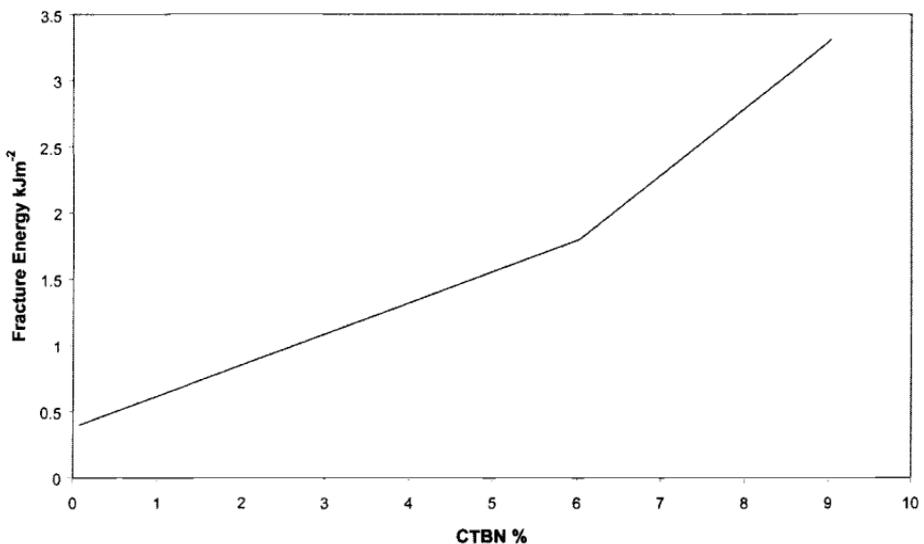
Fig. 4.9   Fracture energy of epoxy resin system as a function of the carboxyl-terminated butadiene acrylonitrile (CTBN) content.

of the molecular structure. For example, for the relatively non-polar but high-shrinkage polyester and vinylester resins, the moisture absorption problems tend to be between the fiber surface and the resin. However, for the highly polar epoxy resins, which have been most heavily studied, the major moisture problems occur because of changes to the bulk resin.

Depending on their individual molecular structures as well as their degree of cure, epoxy resins have a tendency to absorb considerable amounts of moisture, especially in very humid environments. A typical aerospace TGDDM cured resin may absorb between 4.5% and 7% by weight of water at equilibrium, and this may reduce the glass transition temperature by 70–100°C, which will have a major effect on composite properties. The sorption of water may also cause irreversible damage to the material as a result of the formation of microcracks through repeated absorption/desorption cycles. Of course the rate of absorption of water in an epoxy matrix composite will depend on the thickness of the composite and the type and architecture of the fiber. However, there is usually a fast early absorption peak followed by a long, slow absorption plateau before equilibrium is reached.

To explain some of the anomalies in the behavior of epoxy resins, it has been postulated that the absorbed water is made up of at least two different species. One species forms a molecular solution, hydrogen bonded to polar groups in the molecule (such as the hydroxyl or amine groups), and another species is confined to areas of abnormally large free volume often called holes or microvoids. There has been considerable spectroscopic evidence obtained from Fourier transform infrared spectra (FTIR) mainly mid IR and near IR as well as nuclear magnetic resonance (NMR), supporting this view, but not everyone agrees. The absorbed moisture that is present in the polymer matrix is believed to act as a plasticizer, especially at elevated temperatures. However, as only the bound water should have this effect, it is important to understand the ratio of bound to unbound water. The environmental effects that appear to be especially damaging are sudden large temperature changes, referred to as "thermal spikes," and these are encountered, for example, by aircraft flying at supersonic speeds. There is considerable experimental evidence that these thermal spikes can significantly and permanently alter both the moisture absorption levels and the mechanical properties of a composite material over time. Both long-term ageing studies (with commercially important materials) and attempts at theoretical predictions from fundamental chemical structures have been carried out (and are ongoing) to try to quantify the problems that these moisture effects cause in aircraft composite parts.

4.3.1.6 Improved Flame and Thermal Resistance. The flame resistance[6] of epoxy and other themoset polymers, such as polyesters, can be improved by using flame retardants such as aluminum oxide trihydrate, halogenated compounds in combination with antimony oxide, and phosphorous and phosphorous-halogen compounds. Although the use of aromatic bromine

compounds with antimony oxide has wide commercial applications, when charring, these systems produce highly toxic and corrosive compounds during combustion. Finally, epoxy resins incorporating cyclic phosphine oxide and tetra-oxirane ring in the polymer backbone have good thermal stability and high char yield.

4.3.1.7 Advantages and Disadvantages of Epoxy Resins.

The main advantages of epoxy resins are 1) the ability to formulate for optimum properties for a particular application; 2) the control of fracture toughness; 3) the convenience and safety of use due to low volatiles. Other advantages include low shrinkage, which helps give high bond strengths and adhesion to fibers, as well as good chemical resistance and good dimensional and thermal stability.

The main disadvantages are 1) relatively high cost compared with polyesters (especially the advanced aerospace epoxies); 2) moisture sensitivity; 3) less convenience than polyesters due to relatively slow cure and high viscosity; 4) limited resistance to some organic materials (particularly organic acids and phenols); and (5) a limited high-temperature performance even with the most advanced epoxy formulations.

4.3.2 Polyester Resins

The thermoset unsaturated polyester resins used in composite matrix resins are very different in character from the polyesters used in paints (alkyds) and thermoplastics (polyethylene-terepthalate), although they contain many of the same functional groups.

The polyesters used as matrices in composites are produced by first forming a low molecular weight (poly-) unsaturated polyester intermediate from a mixture of dibasic acids (including an unsaturated acid or anhydride such as maleic anhydride) and dihydric alcohols (glycols) or dihydric phenols as in Figure 4.10. These materials are usually viscous oils of molecular weight of 2000–4000 and are diluted with a reactive solvent such as styrene (35%) to improve flow properties and reactivity. When a source of free radicals is added (the initiator), and often a catalyst (the accelerator) as well, the styrene starts to polymerize. The polymerizing styrene radicals react with the unsaturated polyester sites to form a three-dimensional cross-linked network as shown in Figure 4.11. Higher

Maleic anhydride   glycol   Unsaturated polyester
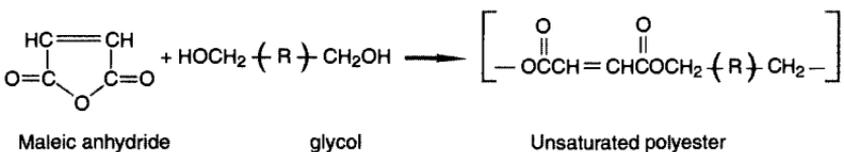
Fig. 4.10   Formation of unsaturated polyester resin.
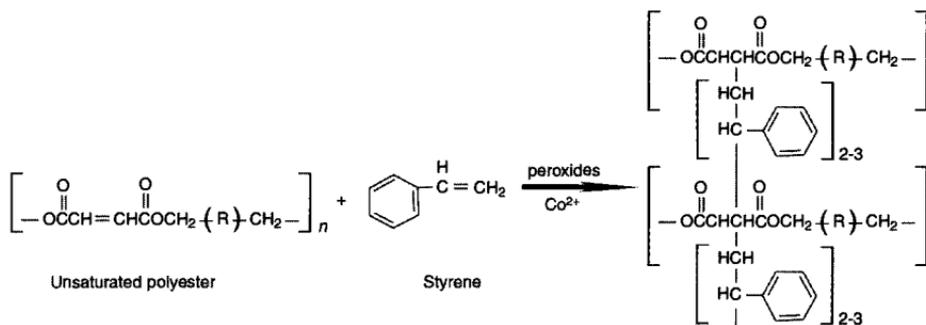
Fig. 4.11 Cure of polyester resin.

percentages of styrene lower the initial resin viscosity and increase reactivity but also increase the volatiles and the resin shrinkage.

4.3.2.1 Types of Polyester. The major commercial variations of polyester are based on modifications of the polyester component by partial replacement of the standard saturated phthalic acid or the glycol by alternative materials. For example, resins of improved strength and durability are obtained by replacing the normal (and lower cost) orthophthalic acid by isophthalic acid (isophthalic polyesters) or by the use of diphenylol propane in place of some of the glycol monomers (DPP resins). Another common variation is the use of adipic acid, which improves flexibility and increases the failure strain in the cured matrix. Halogenated anhydrides, such as tetrachlorophthalic anhydride, can be used in fire retardant formulations.

4.3.2.2 Curing of Polyesters. In contrast to the step growth cure of epoxy resins, polyester resins are cured by a free radical polymerization of unsaturated groups in a chain growth mechanism of polymer formation. This means that quite small quantities (0.5–3% of the resin) of an active initiator are used to start the reaction of a long "chain" of monomer double bonds. The speed of the polyester polymerization may be controlled over a wide range by adjustment of the quantities of this initiator and any accelerators that need to be added. However, the polymerization is strongly exothermic, and the use of high levels of initiator and accelerator will cause severe thermal damage in thick sections. The use of massive molds and the incorporation of fillers will reduce the exotherm by increasing the system thermal mass.

Although the free radical mechanism of cure means that the stoichiometric ratio of monomers is not important (so it is possible to obtain matrix materials with a wide range of properties), it is easy to kill the free radicals with impurities or oxygen. In fact, the resins are stabilized by quinone stabilizers that do just this and use up significant quantities of the initiators in the early stages of the cure. This means that unless precautions are taken, cure may be incomplete at

free surfaces. Also, almost all free radical initiators are very sensitive, unpredictable, and dangerous chemicals that have to be handled with care, especially in a concentrated form.

The most commonly used initiator for the ambient temperature cure of polyester resins is methylethyl ketone peroxide (MEKP), usually supplied as a solution in dimethylphthalate. Metal salts such as cobalt naphthenate, supplied as a solution in naphtha, are used as accelerators with MEKP. MEKP is an extremely hazardous material that can cause permanent eye damage, skin burns, etc. and can also lead to serious fires and explosions if used incorrectly. Of particular importance is the admixture of the initiator and accelerator, which will spontaneously inflame and may explode if not properly diluted by the bulk resin. This can occur if the two materials are accidentally added successively to the resin without intermediate stirring.

Another common initiator is benzoyl peroxide (BzP), which is sold as a paste in dimethylphthalate. The appropriate accelerator for BzP is a tertiary amine. It should be noted that the accelerators for MEKP and BzP are not interchangeable. Systems cured with BzP without an accelerator, or cured with one having a very low accelerator content, are stable at room temperature but can be cured at elevated temperatures. A range of free radical initiators similar to BzP is available that will allow resin cure at a particular limiting temperature; for example, BzP is stable to 70 °C, whereas t-butyl peroxide is stable to 140 °C. Heat-cured polyesters are generally used in matched die molding, where fast cycle times are required.

As with epoxy resin chemistry, the cure of polyesters progresses from the liquid resin through a soft rubbery gel state. Cross-linking proceeds rapidly and establishes the structure of the three-dimensional network in which polymers and monomers are immobile. However, in the intermediate gel state, there is a decrease in the termination rate constant, a net increase in free radical concentration, an exponential jump in copolymer growth, and an increase in heat generated before a rigid plastic forms. This gel effect in free radical polymerization is in contrast to the slow-down effect seen in epoxy polymerization.

4.3.2.3 Advantages and Disadvantages of Polyesters.

The major advantages of polyesters are 1) initial low viscosity that allows easy wet-out of the reinforcement; 2) low cost (all raw materials are readily available and relatively inexpensive with easy long-term storage of starting materials); 3) cure conditions that can be modified easily with little operator experience; 4) easy manufacture in a range of modifications for particular applications; and 5) excellent environmental durability.

The major disadvantages are 1) high exotherm and high shrinkage on cure (both factors lead to a poor fiber/matrix bond strength due to in-built stress and thus poorer mechanical properties than epoxy resins); 2) systems with adequate shear strength tend to be brittle, and toughening additives appear to be ineffective; and 3) poor chemical resistance to even very dilute alkali.

4.3.3 Vinyl-Ester Resins

In many ways, vinyl-ester resins are an intermediate class of materials between epoxy resins and polyesters. The major ester ingredient is the product of the reaction of a standard epoxy resin such as DGEBA and methacrylic acid to give active ester products with structures such as those shown in Figure 4.12.

The unsaturated end groups are very reactive with the styrene diluent but tend to form linear, saturated polymer chains with less cross-linking, so they are tougher and more chemically resistant than polyesters. The resins are cured by the same, low-cost type of free radical reaction process as the polyesters, with many of the same process characteristics. A wide variety of epoxy systems have been used as starting materials for vinyl esters, therefore there is a large commercial range of vinyl esters with different mechanical properties. Examples include resins made from phenolic epoxies for high heat distortion temperatures and rubber-toughened resins.

The major advantages of vinyl esters are 1) they can combine the chemical resistance of epoxies with the easy processing of polyesters; 2) reactive double bonds only on the end of the polymer chains and their high relative reactivities with styrene result in a lower cross-link density and better mechanical properties in the cured polymer; 3) improved bond strength between the fiber and matrix exists. The major disadvantages of vinyl esters include 1) their higher costs when compared to polyesters and 2) higher shrinkage levels than epoxy resins.

4.3.4 Phenolic Resins

When phenol is condensed with formaldehyde under alkaline or strong acid conditions, polymerization occurs. If the system is carefully controlled, polymerization can be stopped while the polymer is still fusible and soluble. This prepolymer, when formed under basic conditions, is termed a *resol*. It will further polymerize under the influence of heat or of acidic or basic catalysts to

Fig. 4.12 Formation of vinyl ester resin.

give a densely cross-linked material of complex chemical structure (Fig. 4.13). Water and other volatile by-products are formed in this reaction, which requires that the polymerization be carried out under high pressure to avoid the formation of a friable foam. Cured resol-type phenolics usually have a high void content.

If the pre-polymerization is conducted under acidic conditions, a different polymerization path is followed, and a novolak resin is produced. This will not self-polymerize, but can be cross-linked under the influence of a complex amine, usually hexamethylene tetramine, to give structures such as those shown in Figure 4.14. Again, polymerization of the pre-polymer is carried out under pressure as volatile by-products are also formed in this reaction.

The phenolic pre-polymers for use in composites are solids and are usually supplied in solution. Due to the dilution effect, the solutions are stable at room temperature. Fibers, usually in the form of a cloth or mat, may be impregnated with the solution and the solvent evaporated to form a pre-preg. Alternatively, some acid-curing systems can be used in liquid molding processes (see Chapter 5) such as RTM and VARTM as the volatiles emitted during cure are controllable to the extent that excessive voiding (foaming) can be avoided.

4.3.4.1 Advantages and Disadvantages of Phenolic Resins. The princ-iple advantage of phenolic resins is their excellent resistance to high temperature, especially under oxidizing conditions. The fire-resistance of phenolics is related to their ablation properties, in other words, the speed at which they burn off when directly exposed to flame or other very high level heat fluxes. Under these conditions, phenolics char readily and thus give a high yield of a superficial layer of porous carbon. This protects the underlying composite, while the carbon slowly burns away. Most other resins usually provide a poor char yield and burn
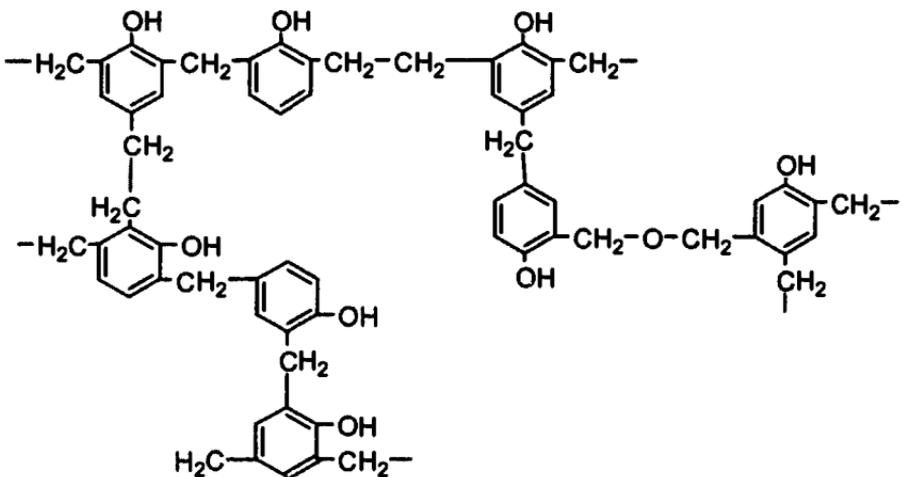
Fig. 4.13   Structure of a cross-linked phenolic resin (resol type).
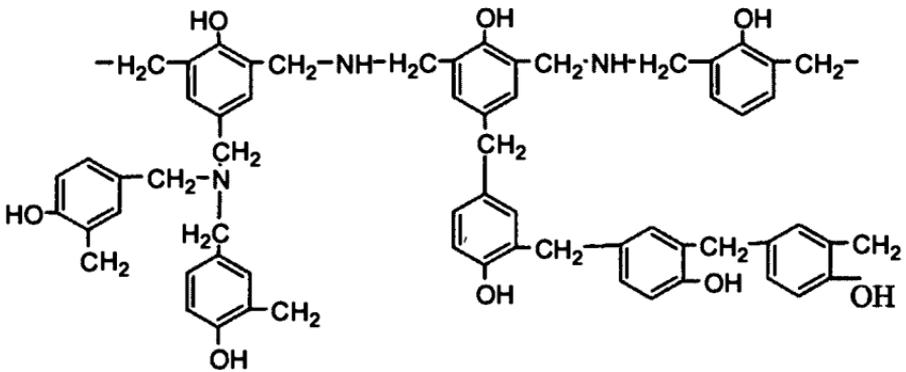
Fig. 4.14   Structure of a cross-linked phenolic resin (novolak type).

away to gaseous products relatively quickly. There are many applications of phenolic composite panels in non-structural internal panels where fire retardancy requirements, including smoke generation, are more critical than the mechanical strength properties. In recent times, some of these applications have been taken over by new thermoplastic matrix resin composites because their higher cost can be offset by their much better mechanical properties and their relative ease of processing by thermoforming.

The disadvantages of phenolics include 1) the difficulties in fabrication caused by the high pressures needed during polymerization; 2) their color (dark brown to black); and 3) the fact that the mechanical properties of derived composites are significantly lower than for those composites based on other resins due to the high content of the voids.

4.3.5   Bismaleimide Resins

Bismaleimide matrix resin formulations (BMIs) are highly cross-linked polymers produced by an addition-type polymerization of monomeric imide units synthesised from aromatic diamines and maleic anhydride. Varying the diamine precursor or the type of diamine mixtures used produces chemically different BMIs that in turn lead to unique matrix formulations. The most widely used building block is 4,4-bismaleimidodiphenylmethane (Fig. 4.15a) because the corresponding diamine precursor (Fig. 4.15b) is relatively available, is not costly, and the intermediate —CH$_2$— group provides some molecular flexibility in an otherwise very rigid molecule. In recent times there have been questions regarding the long-term health and safety aspects of this diamine and its products.

BMIs are thermoset resins, which are similar to epoxy matrix materials in their processability, although they can have better flow and wet-out properties. Typical glass transition temperatures range from 180–320°C, and the composites can operate in the range from 175–235 °C for short periods. However, long-term use at temperatures over 150°C, especially under hot/wet conditions, has been
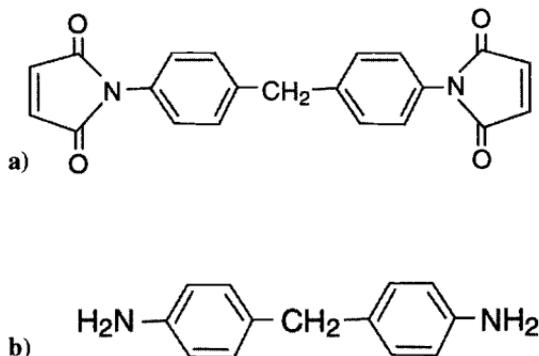
Fig. 4.15 *a*) **4,4-bismaleimidodiphenylmethane;** *b*) **diaminodiphenylmethane precursor.**

shown to not be advisable due to matrix embrittlement caused by continued cross-linking. The standard BMI generally provide a brittle end product, but the properties can be tailored by polymeric additives to give much higher fracture toughness. This is usually achieved at the expense of some of the high-temperature properties and at higher cost. BMI composites have been extensively used in high-speed military aircraft and other areas where thermal stability requirements exclude the use of epoxy resins. As military aircraft, in particular, have been flying at higher and higher speeds, the requirements for more thermally resistant (thermoset) composites for external structural applications have increased significantly in recent years. Although good aerospace epoxy resin-based composites have T_gs of up to 180°C, they are not suitable for continuous use much above 125°C, especially when combinations of heat and moisture are encountered. The next step up in thermal stability is usually taken by composites made with bismaleimide matrix resin materials and aircraft such as the F-22 contain high proportions of these composites.

In summary, there is a wide variety of BMI resins that can be used as composite matrix materials, but their use is generally restricted to situations in which their good mechanical properties at high temperatures outweigh their relatively high cost.

4.3.6 Polyimide Resins

Polyimide resin matrices are unique in that they exhibit extremely high temperature resistance compared with almost all other polymers. These aromatic/heterocyclic systems can have glass transition temperatures between 220–400°C. Extensive research has been carried out on polyimide matrix resins in composite products in recent years, and a large number of different types of materials have been produced. However, relatively few of these are commercially relevant.

There are two classes of polyimide matrices used in advanced composites: those produced by condensation reactions and those produced by addition reactions. Condensation polyimides are generally thermoplastic materials whereas the addition polyimides are considered to be thermoset resins. The former materials are usually produced by reacting aromatic diamines with aromatic dianhydrides, and large volumes of water are evolved. Condensation polyimides include materials such as DuPont's Avimid-N and Kapton, LARC-TPI from NASA, General Electric's Ultem, and Mitsui's Aurum. Apart from their use in thermoplastic composites, they have been applied as toughening additives in some high-temperature epoxy composite formulations.

Addition polyimides are produced by an addition reaction (no release of volatile chemicals) of unsaturated end groups on a previously formed imide-containing unit. BMIs are a subclass of this type but the polymerisable monomeric reactant (PMR) type, originally developed by NASA Lewis Research Center are the major commercially available matrix resin materials of this type. In this case, the reactive end groups are unsaturated cyclic units that are postulated to react by a complex series of addition reactions to give a highly cross-linked polyimide resin system when cured. In practice, the reaction does not proceed wholly as described, and large quantities of volatiles can be liberated unless the composites are fabricated under high pressures and temperatures in a very controlled fabrication program. However, high-quality composite parts can be produced under the correct conditions.

PMR-15 is the most common example of these addition resins types, and quite large structural composite parts have been produced in this material and used in advanced aircraft systems that are subject to high-temperature environments, in for example, engine components, such as casings or in the structure of high-speed military aircraft. Extensive engineering and material science studies have been carried out with both the neat resin and carbon fiber composite parts in an effort to qualify the product for service in extreme conditions including possible use in the new supersonic airliners. However, because PMR-15 composites lose their physical properties in long-term use above 170°C (due to microcracking and embrittlement), a family of new PMR-type resins has recently been developed from oligoimides with fluorinated groups in the molecule. This includes materials such as Avimid N (DuPont), PMR-II 50, AFR 700B, and others. All are very expensive, difficult to process, and do not have particularly good mechanical properties except at high temperatures, so their applications are very limited.

Composites based on PMR-15 matrices are generally manufactured by the pre-preg route, which involves hot-pressing layers of fibers pre-impregnated with the uncured polymer, as described in Chapter 5. However, this is a costly method of manufacture, especially with these polymers, because of the high temperature and pressure required to prevent voiding. Thus efforts are being made to develop the use of resin transfer molding (RTM), as described in Chapter 5. To achieve this, methods are being developed to reduce viscosity of PMR-15 type polymers to levels less than 1000 centipoise and to extend their working life to allow

sufficient time for impregnation. Most of the PMR-type resins have viscosities around 2×10^5 centipoise. A number of approaches are being attempted including 1) dissolving the resin in a solvent; 2) dissolving the resin in a low-viscosity reactive polymer which subsequently forms part of the cured matrix; and 3) introducing molecular twists into the backbone of the polymer. In the case of 1), the solvent is removed under vacuum before curing the resin; this process is called solvent-assisted RTM.

A final range of addition (thermoset) polyimide resins with very good high-temperature stability properties, as well as good mechanical properties, are the phenylethynyl terminated imide (PETI) materials developed by NASA. These were candidates for structural applications on the previously planned Boeing supersonic airliner. The complex aromatic structure of these materials, combined with their very high processing temperatures ($\sim$370 °C), make these materials extremely expensive, but their advantages include a high T_g ($>$270 °C), long-term thermo-oxidative stability, and excellent mechanical properties. These qualities mean that they have applications in unique situations.

4.3.6.1 Advantages and Disadvantages of Polyimide Resins. The major advantage of polyimide resins (thermosets) is their stability at high temperatures and resistance to most chemicals. They can be formulated to have very good mechanical properties at these temperatures unlike the much cheaper phenolic resins. The major disadvantages of polyimides are their high cost and the difficulty of processing.

4.3.7 Cyanate Resins

Cyanate resins, also known as cyanate esters, cyanic esters, or triazine resins, contain the polymerizable functional group —O—C≡N on an aromatic ring structure. The commercial dicyanate monomers used fit the model compound structure shown in Figure 4.16a and are derived from standard phenolic compounds.

4.3.7.1 Curing Chemistry. It is postulated that the cyanate functionality undergoes cyclotrimerization to form symmetrically substituted triazine structures of the type shown in Figure 4.17. Cure catalysts are normally required to achieve high conversions under practical fabrication conditions (170–250 °C), and generally the process is carried out via partially reacted prepolymers, where the degree of trimerization is between 25–40%. The materials are then tacky semi-solids that have a molecular weight range between 1000–2000 or hard resins, about 4000. Cure advantages of these materials can include fast cure cycles and very low shrinkage problems compared with most thermoset materials. They are very susceptible to moisture at the partially cured stages.

4.3.7.2 Properties of Cyanate Resins. The major advantages of cyanate ester resins are their low dielectric loss and low moisture-absorption properties.

Fig. 4.16 Idealized structure of the PMR-15 polymer.

They have good high temperature strength and toughness values and can be coreacted with epoxy resins or alloyed with a number of engineering thermoplastics for advanced composite applications. They have found extensive use in areas such as printed circuit boards and satellite dishes. While short-term thermal stability is often superior to matrix resins such as bismaleimides, there have been problems with long-term stability in moist conditions, which has troubled the aerospace industry. The problems of composite blistering in these cases may be due to moisture reaction with incompletely reacted monomer groups in the resins.

Fig. 4.17 Formation of cyanate ester monomer and its reaction to form cross-linked cyanate ester.

4.4   Thermoplastic Systems

Thermoplastic polymers can be very broadly classified as amorphous or crystalline. Most thermoplastics suitable for use as matrices for high-performance composites exhibit some degree of crystallinity—because this type of structure has better resistance to chemical attack by fuels, hydraulic oil, and paint stripper.

Thermoplastics, compared with thermosetting polymers, absorb much less moisture with less consequential reduction in elevated temperature mechanical properties. Thermoplastics are much tougher than thermosets, therefore they have much better interlaminar strength and resistance to impact. Because no chemical reaction is required, they have very short processing times, although the temperatures and pressures are much greater than those required for thermosetting systems, with a concomitant increase in costs. Another major advantage is that matrix flaws can be healed (at least in principle) and components welded. Table 4.3 provides details on some of the important thermoplastic systems for aerospace composites.[4,11]

4.4.1   Amorphous Thermoplastic

Polymer chains in an amorphous thermoplastic are in a random coil status without any high degree of local order. Because amorphous thermoplastics are often dissolvable in common industrial solvents, the reinforcement can be impregnated with low-viscosity solution, thus avoiding the problem of high-melt viscosity, but, as may be expected, the resultant composite is not solvent-resistant. Because these composites are of particular interest to the aerospace industry, where hydraulic fluid, aviation fuels, and the use of paint stripper are widely encountered, soluble thermoplastics are placed at a severe disadvantage. Amorphous polymers also tend to be more subject to creep deformation and fatigue damage than semi-crystalline polymers. The lack of solvent resistance relegated some of the amorphous materials to non-structural applications, where their good fire, smoke, and toxicity characteristics and toughness could still be exploited. Nevertheless, amorphous thermoplastic composites are being used in various areas in the aerospace industry, especially where high-temperature performance is required, and some solvent susceptibility can be accommodated.

4.4.2   Semi-Crystalline Thermoplastic

In several thermoplastics, polymer chains may, under certain conditions, align themselves into a regular, preferred, low-energy configuration—crystal formation. In reality, it is not possible to achieve complete crystallinity, due to the interference of long molecular chains. Polymers possessing the ability to crystallize are referred to as semi-crystalline. In the solid phase, these locally ordered regions, or crystallites, act as physical cross-links, giving the polymer a

good solvent resistance and preventing the dissolution of the entire molecular structure. The crystallinity also improves high-temperature mechanical properties, including creep resistance. The level of crystallinity can be varied by differences in processing history. In addition, rapid cooling from the melt causes low crystallinity, where as very slow cooling, or annealing near the crystalline point may lead to excessive crystallinity. Semi-crystalline polymers shrink more than amorphous polymers upon solidification. The main difficulty in using semi-crystalline polymers is in finding methods for coating the fibers. Because solvents normally cannot be used to dissolve such polymers, coating the fibers with molten thermoplastic is often the only option.

4.4.3   Polyketones

The group of thermoplastic resins known as polyketones are crystalline polymers with exceptionally high temperature resistance. There are numerous aromatic polyketones, such as polyetherketone (PEK), polyetherketoneketone (PEKK), etc., the most common is polyetheretherketone (PEEK); Figure 4.18 depicts the molecular structures. PEEK possesses high mechanical properties, high temperature tolerance, and good solvent resistance. The level of crystallinity achieved in PEEK polymer depends on the processing history. Very rapid cooling can produce an amorphous polymer. This can subsequently be annealed to achieve any desired level of crystallinity. The optimum level of crystallinity for PEEK resin is 25–40%.[3] With respect to resistance to hostile environments, PEEK is generally considered to be outstanding in the field of polymeric resins. PEEK is resistant to non-oxidizing acids (such as hydrochloric acid, alkalies, salts, and solvents). The only common material that will dissolve PEEK is concentrated sulphuric acid.[4] The cost of PEEK is high, but can be justified in composites for high-performance applications in the aerospace and defense industries. Besides continuous fiber reinforced products, PEEK is also available in fiber and film forms.

4.4.4   Polyphenylene Sulfide

Polyphenylene Sulfide (PPS) is a highly crystalline polymer recognized for its unique combination of properties, including thermal stability, chemical

PEEK
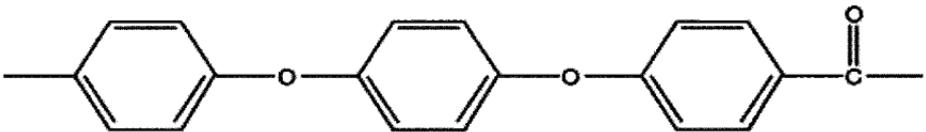
Fig. 4.18   Molecular structure of polyetheretherketone (PEEK).

resistance, and fire resistance. PPS polymer crystallizes very rapidly at temperatures above its T_g and usually has a crystallinity content in the range of 50–60%.[5] PPS exhibits intermediate mechanical properties and temperature tolerance. Its excellent corrosion resistance is attributed to its inertness to organic solvents, inorganic salts, and bases. PPS composites are not affected by aircraft fluids. PPS is soluble in aromatic hydrocarbons and chlorinated aromatic compounds.[6] PPS is inherently flame-resistant, and its composites pass The Ohio State University fire safety test required by the U.S. Federal Aviation Administration (FAA) for materials for use in aircraft interiors. Property retention at elevated temperatures shows that PPS composites exhibit classical deterioration above their T_gs. However, due to crystallinity effects, the loss in strength is gradual; even at temperatures of 200°C, considerable integrity is retained.
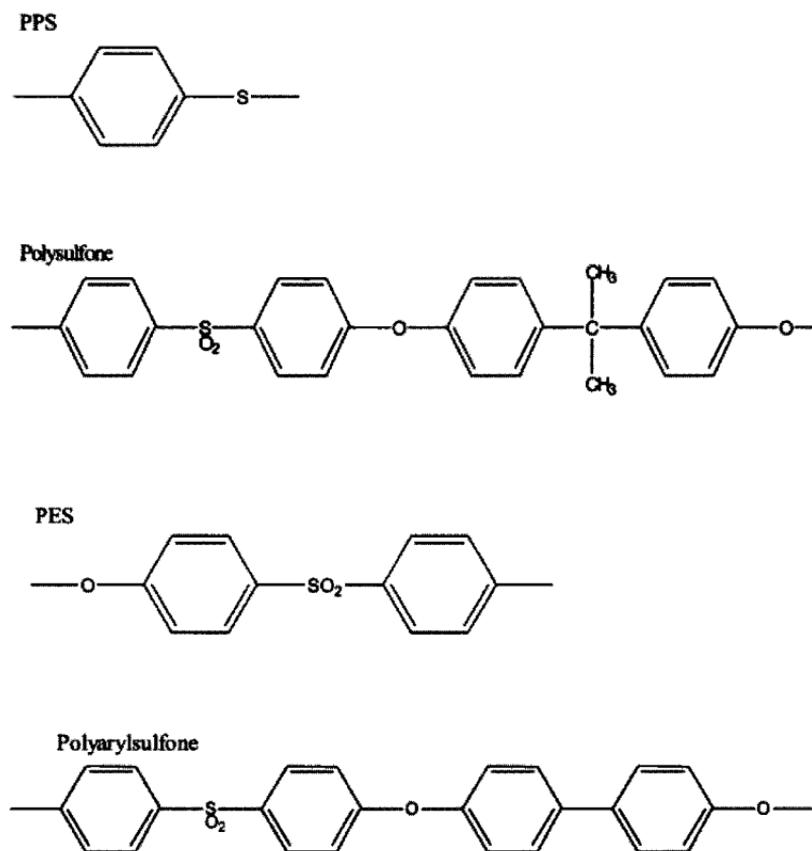
Fig. 4.19   Molecular structure of sulphur-containing thermoplastics.

4.4.5 Polysulfone

Polysulfone (PSU), polyether sulfone (PES), and polyaryl sulfone (PAS) are members of a family of thermoplastics based on sulphone derivatives.[7] They are high-performance amorphous polymers with good tolerance to high temperatures and fire. They are characterized by their high heat-deflection temperature, combined with excellent hydrolytic stability and an ability to retain mechanical properties in hot/wet conditions. They are self-extinguishing and, when they do burn, produce little smoke. Because polysulfones are amorphous, they are not resistant to all solvents, although their resistance to many chemicals is nevertheless very good. Figure 4.19 depicts the molecular structure of some of the relevant sulphur-containing thermoplastics.
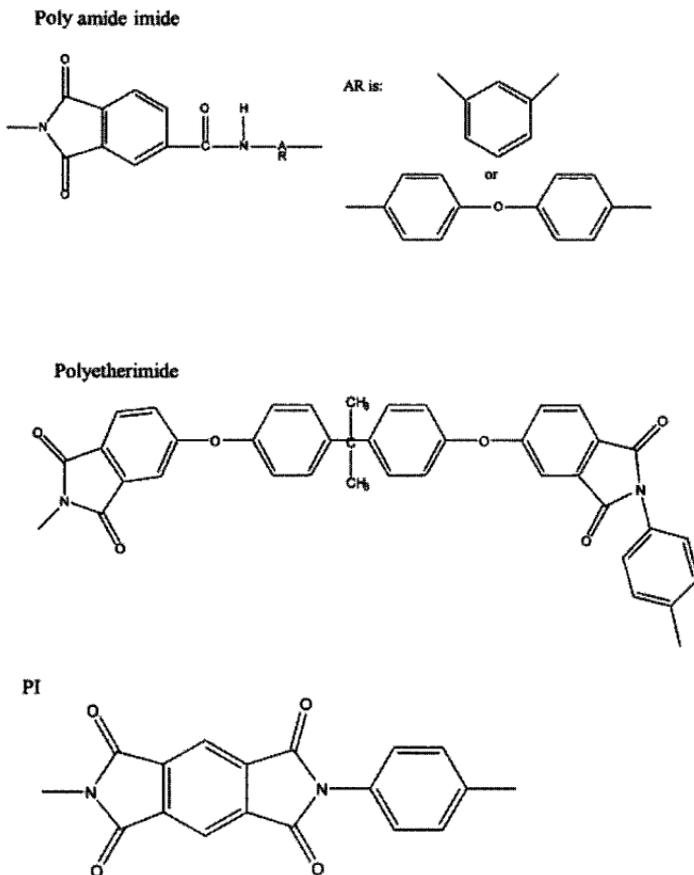
Fig. 4.20   Molecular structure of polyimide thermoplastics.

4.4.6   Polyetherimide

Polyetherimide (PEI) is an amorphous, high-performance thermoplastic. The amorphous structure of PEI contributes to its dimensional stability, low shrinkage, and highly isotropic mechanical properties compared with most crystalline polymers. The high T_g allows PEI to be used intermittently at 200 °C. Un-reinforced PEI is one of the strongest engineering amorphous thermoplastics and offers very good mechanical properties but has the forming disadvantage of very high viscosity in the molten state. Despite being amorphous, PEI is very tolerant to solvents and environmental exposure and resists a broad range of chemicals, including most hydrocarbons, non-aromatic alcohols, and fully halogenated solvents. The molecular structure of some of the polyimide resins is depicted in Figure 4.20.

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