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CHAPTER 2

Matrix Materials

1. INTRODUCTION

As presented in Chapter 1, composite materials consist of three main parts: fibers, matrix and interface between fibers and matrix. The functions and importance of the matrix were described in Chapter 1. The principles involving the matrix in the manufacturing of composites are covered in this chapter.

It is not the intention of this book to cover all matrices that are available for the manufacturing of composites. There are many excellent books that cover the topics and these should be consulted for the properties of these matrix materials. One example is the *Handbook of Composites* by Lubin [1].

The emphasis of this book is on the principles that govern the behavior of the matrix material during the manufacturing of composites. This involves an understanding of the basic chemical structure of the material, how this structure evolves during the manufacturing process, and how this evolution will influence the quality of the resulting composite structures. Both main categories of polymer matrix materials will be discussed: thermoset matrix composites and thermoplastic matrix composites.

2. DIFFERENT TYPES OF MATRIX MATERIALS AND THEIR PROMINENCE

Matrix materials are generally polymers, metals, or ceramics. In a way this sentence says that any material can serve as a matrix material. In reality, however, the majority of composites that exist on the market are made of polymer matrix composites. Among these, thermoset matrix composites are more predominant than thermoplastic composites.

The reason why there are more polymer matrix composites than metal matrix composites and ceramic matrix composites is due to the second requirement in the interface discussion in Section 3.3 of Chapter 1: Compatibility between the matrix and the fibers. It was shown in Chapter 1 that the surface energy of metals is on the order of 400–2000 dyne/cm while the surface energy of polymers is on the order of 30–45 dyne/cm. The surface energy of glass fibers is about 500 dyne/cm, that of graphite is about 50 dyne/cm and about 44 dyne/cm for Kevlar fibers. Thermodynamic requirements call for the surface tension of the matrix (in liquid form) to be less than that of the fibers to ensure bonding. Since the surface energy of liquid metals is much larger than that of the solid fibers, it is very difficult for liquid metals to bond onto the surface of solid fibers. As such, it is difficult to make metal matrix composites, in spite of the fact that metal matrix composites can offer desirable properties such as high temperature resistance. The same explanation can be used for ceramic matrix composites. This does not mean that metal matrix and ceramic matrix composites do not exist. They do, but only in rare cases of high temperature applications.

Among the polymer matrix composites, there are thermoset matrix composites and thermoplastic matrix composites. The differences between thermoset and thermoplastic resins are explained below.

2.1 Thermoset and Thermoplastic Matrix Materials

The similarities and differences between thermoset and thermoplastic composites can be understood if one compares the processes by which these two types of materials are made.

First consider a typical thermoset polymer such as epoxy. To make this material, one first starts with the epoxy molecules. The epoxy molecules are relatively small [on the order of about 20–30 carbon-carbon (C–C) links]. This is relatively short as compared to the order of a few hundreds or thousands of C–C links for thermoplastic molecules. Since the length of the thermoset molecules is short, the material consisting of them usually has low viscosity and appears in the form of liquid at room temperature or moderately high temperature (about 100°C). Figure 2.1(a) shows a schematic of the molecules in a thermoset resin. Since the material appears in liquid form, in order to make a solid out of it, the molecules must be tied together with molecules of some other type. The tying molecules are called the *linkers* or *curing agents*. Figure 2.1(b) shows a schematic of the linker molecules.

In some cases (such as polyester) the linker molecules may not react easily with the resin molecules when they come into contact. For these cases, the linker molecules can be mixed together with the resin molecule in a container for shipping purposes [Figure 2.1(c)]. When the linking is desired, one needs to add into the mixture an initiator (an unstable type of molecule) which will start the reaction.

In other cases (such as epoxies) the linker molecules may react easily with the resin molecules. For these cases, the linker molecules can not be mixed together with the resin molecules until the time the manufacturer is ready to incorporate the resin systems together with the fibers.

When the proper conditions for linking occur (discussed later in this chapter), the tying molecules will link the resin molecules together as shown in Figure 2.1(d). This 3-D linking network is a solid and it represents the solid thermoset resin. Since the ties (links) are made by chemi-

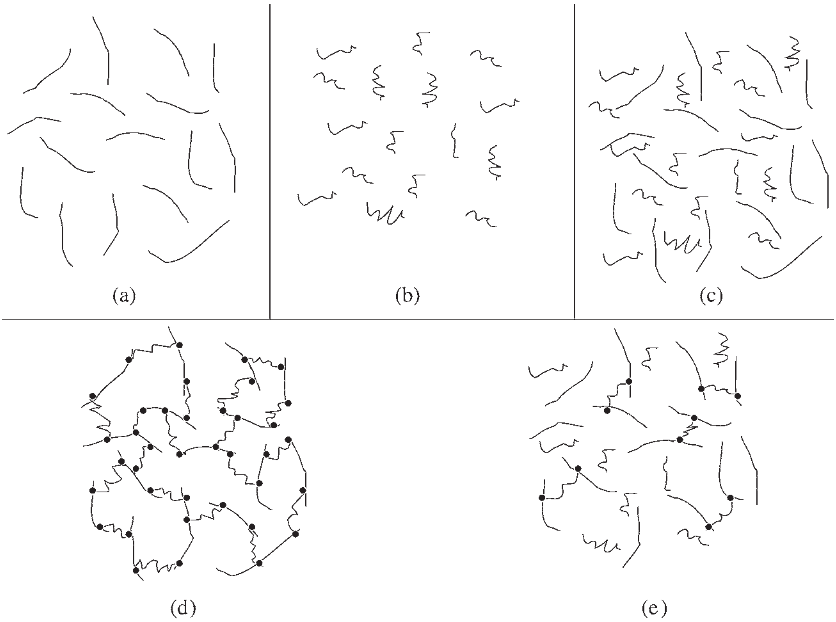


FIGURE 2.1 Schematic of (a) the molecules in a thermoset resin, (b) the linking molecules, (c) the resin molecules and the linking molecules in a container before linking reactions, (d) the thermoset resin network after linking reactions, and (e) a partially linked network.

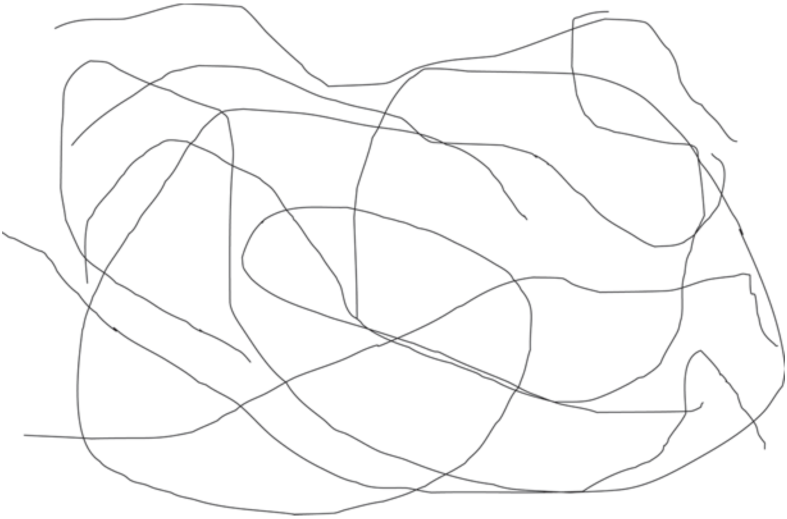


FIGURE 2.2 Schematic of the molecules in a thermoplastic resin.

cal bonding, once set, the shape of a component made of thermoset resin cannot be changed by heating.

The linking between the linker molecules and the resin molecules takes place whenever an active end of the resin molecule is in the vicinity of an active region of the linker molecule. All links (millions and millions of them) need to be complete in order to create a solid 3D network. This process takes time (several hours, sometimes several days). One can intervene in the process by allowing only a portion of the links to be formed and retarding the remaining reactions. This can be done either by lowering the temperature or adding in retarding molecules (called inhibitors) somewhere during the process. The result of this is a partially linked network [Figure 2.1(e)] which exhibits itself as a viscous liquid (or flexible solid) which can be handled like a liquid but remains tacky for bonding purposes. This is the process for making preimpregnated layers (prepregs).

Next consider a typical thermoplastic resin for composite applications such as polyetheretherketone (PEEK). Thermoplastic molecules can be very long. Each molecule may contain up to several hundreds or thousands of C–C links. Figure 2.2 shows a schematic of these very large molecules. Due to high molecular length, it is difficult for these molecules to move around at room or moderate temperature. In order for these molecules to be able to move relative to each other, high temperature needs to be applied. The viscosity of these resins is large even at high

TABLE 2.1 Viscosity (in centipoise) of a Few Thermoset and Thermoplastic Materials (1 Pa-sec = 10 Poise = 1000 centipoise).

Material	20°C	25°C	T°C
Air	0.0187		
Water	1		
Polyester	100–300		
Vinyl ester	100–300		
#10 Motor oil	500		
Golden syrup	2,500		
Epoxy (Shell Epon 828-14 phrMPDA, 15 phr BGE)	600		
Epoxy (Shell 826 16 phr MPDA, 10phr BGE)	750		
Epoxy (Dow 332-16 phr MPDA, 10 phr BGE)	500		
Molasses		10^5	
Epoxy 5208			100 @ 177°C
BMI			1000 @ 150°C
Ryton (thermoplastic)			10^7 @ 313°C
PEEK (thermoplastic)			10^6 @ 400°C
Utem (thermoplastic)			10^8 @ 305°C
Torlon (thermoplastic)			10^9 @ 350°C

temperature (Table 2.1). However when the material is cooled down, it becomes solid fairly quickly. The processing time therefore can be much shorter (on the order of minutes) as compared to thermoset resins (on the order of several hours or days) where time needs to be allowed for all the linking reactions to complete.

There are more thermoset matrix composites than thermoplastic composites. The explanation can be referred to the first condition discussed in the interface section (3.3) in Chapter 1, i.e., availability of the resin at the surface of the fibers. In order for the matrix to bond to the surface of the fibers, the resin has to be available at the surface of the fibers. This seems to be an obvious requirement but it has strong implications. For the resin to be available at the surface of the fibers, the manufacturer has to put it there. In the case of prepregs, the resin is already placed on the surface of the fibers and so this does not seem to be critical during the fabrication of the part (it is critical to assure the availability of resin at the surface of the fiber during the fabrication of the prepregs). For a process such as resin transfer molding, however, resin needs to be pumped so that it can flow to the surface of the fibers. The flow of resin depends on the permeability of the fiber networks, and also on the viscosity of the resin. At reasonably low temperatures (less than 100°C), the viscosity of thermoset matrix is much lower than that of thermoplastic matrix. Table 2.1 shows the viscosity of a few thermoset and thermoplastic matrix materials. Due to their low viscosity, thermoset matrix materials can flow to the surface of fibers more easily as compared to thermoplastic matrix. The difference in viscosity between thermoset matrix and thermoplastic matrix is the main reason for the predominance of thermoset matrix composites as compared to thermoplastic matrix composites.

3. THERMOSET MATRIX MATERIALS

The presentation on thermoset matrix materials will concentrate on two materials: polyester and epoxy, with some brief presentation on other types of materials. This is because the mechanism of operation of these two materials is representative for other materials.

3.1. Polyester Resins

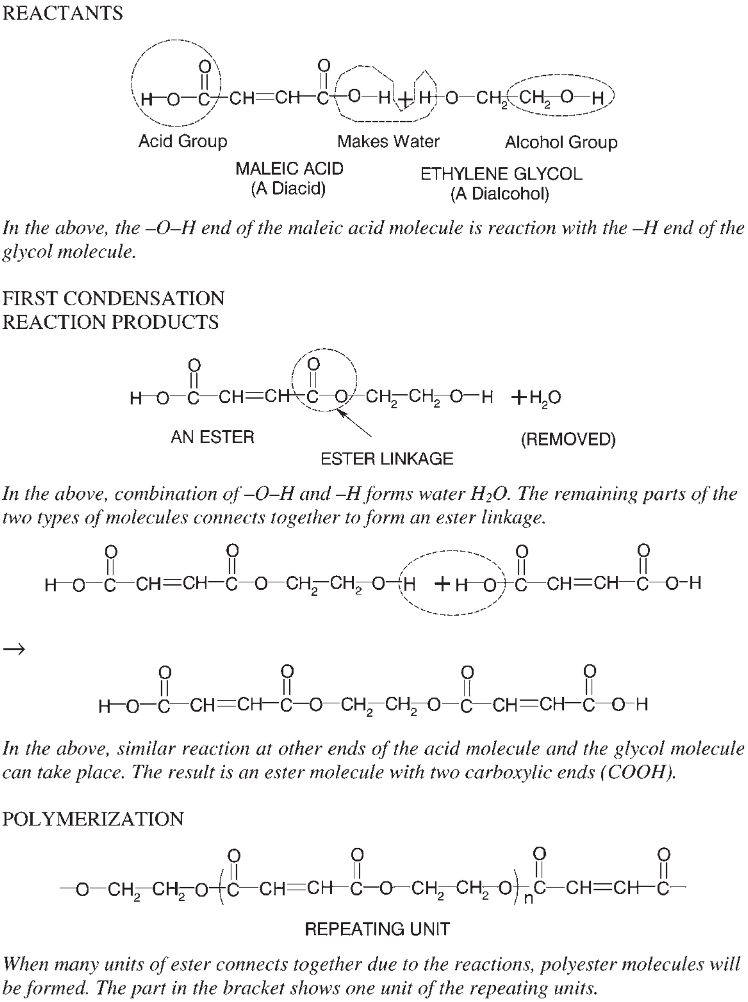
3.1.1. General

Compared with epoxy resins, polyester resins are lower in cost but limited in use due to less adaptable properties. Polyesters have been used mainly with glass fibers (normally E glass) to make many commercial products such as pipes, boats, corrosion resistant equipment, automotive components, and fiber reinforced rods for concrete reinforcement.

3.1.2. Polyester Chemical Structure and Polymer Formation

Polyesters are formed by the condensation polymerization of a diacid and a dialcohol (a diacid means two organic acid groups are present in a molecule, and a dialcohol, sometimes called a diol, has two alcohol groups in the molecule). A typical reaction is shown in Figure 2.3, in which maleic acid is made to react with ethylene glycol to form polyester. In this reaction, the acid group (O=C–OH) on one end of the diacid reacts with the alcohol group (CH_2OH) on one end of the diol to form a bond linking the two molecules and to give out water as a byproduct. The linking group which is formed is called an *ester* (C–O–C=O). This step is called a condensation reaction.

The resulting product still has another acid group on one end and another alcohol group on the other. Both of these ends are still capable of undergoing further condensation reactions and then to repeat again and again. Therefore, with sufficient reactant materials, chains of alternating acid and alcohol groups will form and will have regularly repeated units as shown in the polymerization step of Figure 2.3. One unit of the repeating units is shown within the bracket at the bottom of the figure. Subscript *n* represents the number of repeated units. A large *n* value indicates a longer (or larger) molecule. Many polymers would have an *n* of several hundred, although some polymers exist with *n* of less than 20.



In the above, the –O–H end of the maleic acid molecule is reaction with the –H end of the glycol molecule.

In the above, combination of –O–H and –H forms water H_2O. The remaining parts of the two types of molecules connects together to form an ester linkage.

In the above, similar reaction at other ends of the acid molecule and the glycol molecule can take place. The result is an ester molecule with two carboxylic ends (COOH).

When many units of ester connects together due to the reactions, polyester molecules will be formed. The part in the bracket shows one unit of the repeating units.

FIGURE 2.3 Condensation polymerization of a polyester.

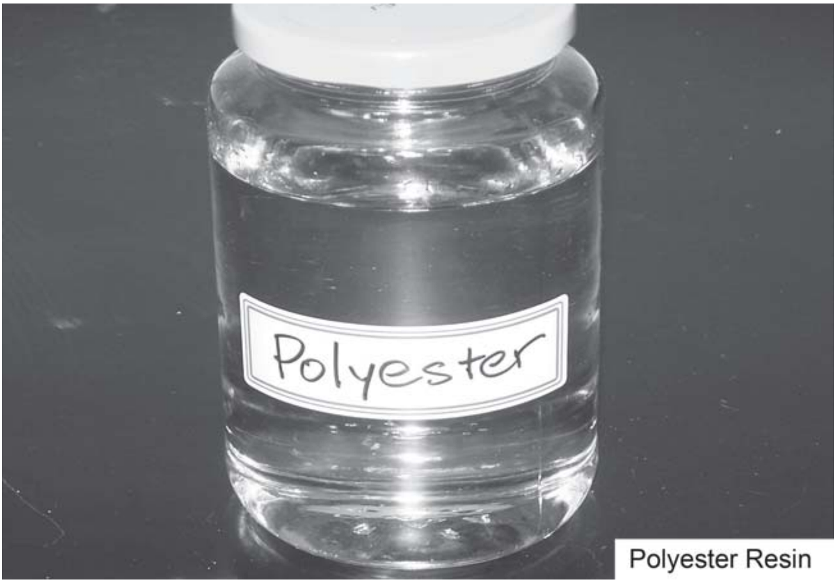


FIGURE 2.4 Glass container with liquid polyester.

These chains are called *polymers* (from the word for many parts). Because the linking group formed by acids and alcohols are esters, the term given to this type of resulting polymer is *polyester.* A quantity of these polyester polymer chains is collectively called *polyester resin*. (Polymers, in general, in the uncured state, are called *resins*.) For a certain amount of resin, there is a distribution of sizes of molecules, i.e. the resin is an ensemble of molecules of different lengths. This is because the formation of the molecules is due to the availability of the reactants. The molecular weight of the material is the average value of all molecules in the material. At room temperature, polyester appears as a liquid. Figure 2.4 shows a sample of polymer in a glass container.

Example 2.1

It is desired to make a polyester resin using 100 g of maleic acid and a corresponding amount of ethylene glycol. A stoichiometric amount of ethylene glycol is used. After the condensate is removed, how many grams of polyester are obtained?

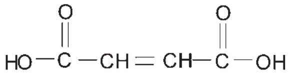
Mass of different atoms:

C = 12 g/mol, H = 1 g/mol, O = 16 g/mol, N = 14g/mol

Solution

The molecular structures of maleic acid and of ethylene glycol are shown below. From this, the molecular mass of each material is calculated as:

Maleic acid



$$HO-\overset{\overset{O}{\|}}{C}-CH=CH-\overset{\overset{O}{\|}}{C}-OH$$

Ethylene glycol

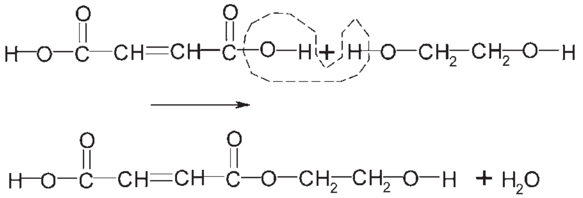
$$HO-CH_2-CH_2-OH$$

Maleic acid: 4C + 4H + 4O = 4 (12 + 1 + 16) =116 g/mole

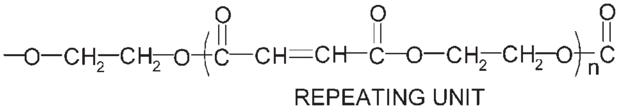
Ethylene glycol: 2C + 6H + 2O = 24 + 6 + 32 = 62 g/mole

The reaction takes place as shown in the following:

It can be seen that one molecule of maleic acid reacts with one molecule of ethylene glycol to make a unit of ester and two water molecules.



and



Mass of the water molecule: 2H + O = 18 g/mole.

Let M_p be the mass of the polyester made using 100 g of maleic acid, we have:

$(M_p/100) = (116 + 62 - 36)/116 = 1.224$

$M_p = 122.4$ g

3.1.3. Polyester Crosslinking

The polymers formed in the reaction illustrated in Figure 2.3 are not crosslinked since no chemical bond has been formed between the various chains. (The chains are often mechanically intertwined, but that is not crosslinking.) However, the diacid chosen in this case (maleic acid) con-

TABLE 2.2 Structures of Commercial Organic Peroxides [2].

Name of Peroxide	Chemical Structure
Hydrogen peroxide	H–OO–H
Hydroperoxides	R–OO–H
Dialkyl peroxides	R–OO–R
Diacyl peroxides	R–C(O)–OO–C(O)–R
Peroxyesters	R–C(O)–OO–R
Peroxy acids	R–C(O)–OO–H
Peroxy ketals	R_2–C–OO–R_2
Peroxy dicarbonates	R–OC(O)–OO–C(O)O–R

tained a carbon-carbon double bond which survived the polymerization reaction and is contained in every repeating unit of the polymer. (When a reactant or polymer contains a carbon-carbon double bond, the term unsaturated is often applied to it. Therefore maleic acid is an unsaturated diacid and the resulting polymer is an unsaturated polyester.) This unsaturation is critical since the carbon-carbon double bond is the location where crosslinking occurs.

The crosslinking occurs by the addition polymerization reaction as shown in Figure 2.5. In this figure, the RO– tends to react with another active site from another molecule [a dash (–) on the right hand side of the oxygen atom O indicates that it is reactive]. This reaction utilizes a crosslinking agent (styrene, in the example) that reacts with the polyester polymer chains to provide the crosslinks. (The styrene also lowers the initial viscosity to improve processing.)

Normally the styrene molecules are mixed together with the polyester molecules and shipped in a container. Under normal conditions [room temperature for a limited time (months)], the styrene molecules do not react with the polyester molecules. Initiators are usually required to start the reaction. The reaction steps shown in Figure 2.5 are explained below.

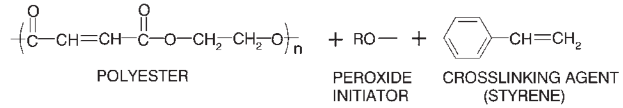
3.1.3.1. Initiation Step

The crosslinking reaction is initiated by a molecule that readily produces free radicals (a chemical species with unpaired electrons). The most common group of such molecules is the organic peroxides (for example, methyl ethyl ketone peroxide—MEKP).

Organic peroxides are useful as initiators or crosslinking agents because of the thermally unstable O–O bond which decomposes to form free radicals. Organic peroxides may be viewed as derivatives of hydrogen peroxides in which one or both hydrogens are replaced by organic radicals. Table 2.2 lists the structures of several commercially available organic peroxides.

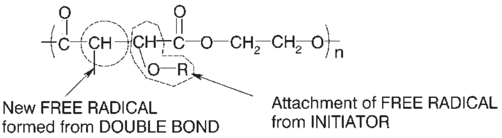
The rate of free radical production is highly temperature dependent, therefore, the reaction to produce free radicals, which in turn initiates the crosslinking reaction, can be accelerated by increasing the temperature.

REACTANTS



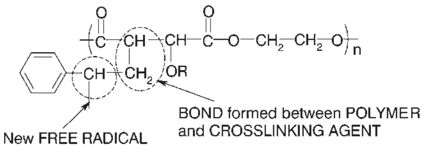
In the above reaction, a polyester material system consists of the polyester molecules, the peroxide initiator molecules (such as MEKP) and the curing (or cross linking) agents are mixed together inside a pot.

INITIATION STEP



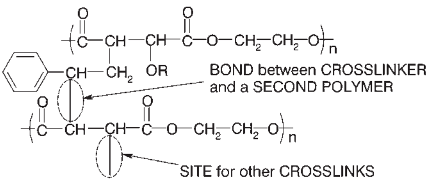
In the above, the initiator (–O–R) is making a reaction with one of the carbon atoms that had a double bond (=). After the reaction, the double bond in this carbon atom (and its partner carbon atom) is broken and it is replaced by a single bond (–). The partner carbon atom also has an active arm which is ready to make reaction with another adjacent molecule).

BRIDGING STEP



In the above, the active arm of the partner carbon atom makes a link with an adjacent styrene monomer. Due to this reaction, the double bond between the two carbon atoms in the styrene monomer is broken and is replaced by a single bond between the two carbon atoms. The carbon atom in the styrene monomer that is not connected to the ester molecule now has an active arm that is ready to react with another adjacent molecule.

CROSSLINKED POLYMERS



In the above, repeats of the reaction between the polyester molecules and styrene molecules gives rise to a crosslinking network between polyester molecule and styrene molecule. This is the polyester resin system.

FIGURE 2.5 Addition (or free-radical) cross-linking of polyester [3].

FIGURE 2.6 Small container of MEKP.

Since polymerization reactions take place at various temperatures, organic peroxides have been developed with different decomposition rates and these can be conveniently expressed by half-lives (the time required to decompose 50% of the peroxide in a diluent solution at a given temperature). The half-lives of most peroxides at about 100°C vary from 0.5 hours to 50 hours [2]. Initiator compounds are sometimes called *catalysts*. Figure 2.6 shows a small container of MEKP. These free radicals attack the carbon-carbon double bonds and bond to one of the double-bond carbons, reducing the double bond to a single bond and producing a new free radical on the other formerly double-bonded carbon. This new free radical is then free to react with any other carbon-carbon double bond. Since the styrene is more mobile than the polyester molecules, the most likely new double bond to react with would be in the styrene. Usually only a small amount of initiators (about 1%) is added to the polyester/styrene system to start the reaction. Adding large amounts of initiators is dangerous due to the simultaneous reactions of many links and this can cause a large amount of heat generated over a short duration of time.

3.1.3.2. Bridging Step

At the end of the initiation step, many radicals (the free bonds from the carbon atom C–) are produced. The radicals are produced from the breaking of the double C=C bonds in either the styrene molecules or in the polyester molecules. When these free radicals are in the vicinity of each other, they connect. The results are the single C–C bonds between the radicals. This forms the link between the styrene molecules and the polyester molecules. The formation of the single C–C bonds in turn creates new free radicals. These free radicals are again available for reaction with other carbon-carbon double bonds, and reactions with other polyester molecules would create further crosslinks. The reaction continues to propagate the crosslinks.

3.1.3.3. Crosslinking Step

The net result is a large network of interconnected polymers in which styrene serves as the crosslink (bridge) between the polymers. Since the peroxide is generally present in small quantities (typically 1%) the final structure does not show the peroxide attached to the polystyrene molecule as this would generally not be present except on the endmost crosslink. This crosslinking mechanism is called addition or free-radical crosslinking. This entire crosslinking reaction process is called *curing*.

Styrene is not the only crosslinker (sometimes crosslinkers are called *curing systems*) for polyester systems, although it is the most widely used. Other chemicals in use include vinyl toluene, chlorostyrene, methyl methacrylate, and diallyl phthalate. The physical and chemical properties of the crosslinked polymer are affected by the curing system. For instance, the use of chlorostyrene imparts flame resistance to the polymer.

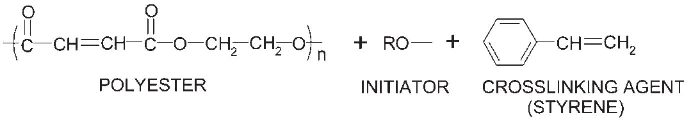
Example 2.2: Crosslinking of Polyester

It is desired to make a polyester using 100 g of maleic acid and ethylene glycol. A stoichiometric amount of ethylene glycol is used. Cross linking is done using styrene. Assume that one styrene monomer corresponds to one oligoester (this assumption is to simplify the calculation to illustrate the principle; in reality the crosslink between oliester molecules can be in the range from 1 to 4 styren monomers). From the cross linking process, how many C=C bonds are broken, how many C–C bonds are formed?

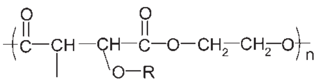
Solution

Continuing from the same problem in Example 2.1:

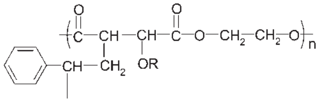
Number of bonds broken and formed



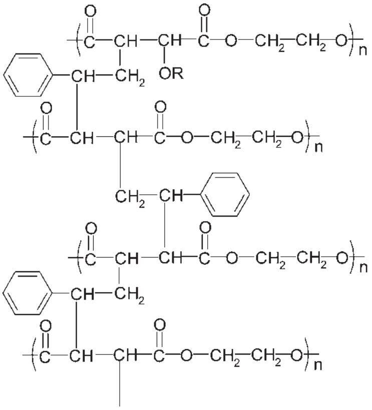
Initiating Step



Bridging Step



Crosslinking Step

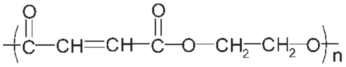


The crosslinking process is illustrated above.

For each pair of polyester units, it can be seen that four C=C bonds are broken and eight C–C bonds are formed. For the C=C bonds, two are from the two polyester units, and the other two are within the structure of the two styrene molecules. For the eight C–C bonds, two are replacing the two C=C bonds within the ester units, the other two are replacing the two C=C bonds within the two styrene molecules, the other four are connecting the two styrene molecules with the two ester units.

Therefore for each polyester unit, there are two C=C bonds broken and four C–C bonds formed.

The chemical formula for a polyester unit is:



$$\left(\overset{O}{\overset{\|}{C}}-CH=CH-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O\right)_n$$

The mass of a polyester unit is:

6C + 6H + 4O = 72 + 6 + 64 = 142 g/mole

Since there are 122.4 g of polyester made, the number of bonds involved is:

C=C bonds: (122.4/142) 2 = 1.724 mole or 1.038×10^{24} bonds. (Note that 1 mole = 0.602×10^{24}).

C–C bonds: 2 × 1.724 = 3.446 moles or 2.076×10^{24} bonds

3.1.4. Crosslinking (Curing) is an Exothermic Reaction (Heat is Generated)

The crosslinking of polymer from individual molecules into a polymer 3-D network is an exothermic reaction (i.e., heat is generated from the process). What this means is that the temperature of the material will increase as a result of curing. For the curing of thin laminates (about a few millimeters thick), this increase in temperature may not create a problem; but for the curing of thicker laminates the heat generated from inside the laminate may not be conducted away easily, due to the fact that polymers such as polyesters (or epoxies) do not conduct heat. Over a short period of time, the temperature increase at a given location can be quite large, resulting in the burning or degradation of the matrix material.

From the thermodynamic point of view, to break a bond, one needs to add energy into the system. For example, to break a piece of chalk with one's fingers, it has to be pulled apart or bent. Energy is added to the piece of chalk by the pulling or bending motion of the fingers. On the other hand, if the bonds between the broken pieces of chalk were to be bonded together again, energy would be generated from the bonds by the law of conservation of energy. This energy will increase the temperature of the chalk unless the heat is conducted away.

Example 2.3: Heat Generation and Temperature Increase

It is desired to make a polyester using 100 g of maleic acid and ethylene glycol. A stoichiometric amount of ethylene glycol is used. Crosslinking is done using styrene.

Continuing from the same problem in Examples 2.1 and 2.2:

a. The energy required to break a C=C bond is 680 kJ/mole and the energy created by forming a C–C bond is 370 kJ/mole. How much energy is generated during the polymerization process? 1 mole = 0.602×10^{24}
b. The heat capacity of polyester is 0.25 cal/g/°C. Assuming no heat loss, what is the increase in temperature of the polyester?

Mass of carbon C= 12 g/mole, H = 1 g/mole, O = 16 g/mole
1 calorie = 4.18 Joule

Solution

a. Energy generated:

Considering the energy in the bonds, one has:

Energy inputted into the system to break the double bonds:

(1.724 mole) (680 kJ/mole) = 1172.32 kJ

Energy generated from the system to form the single bonds:

(3.446 moles)(370 kJ/mole) = 1275.02 kJ

Net energy generated:

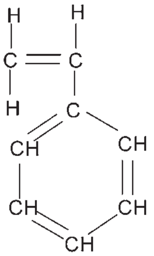
1275.2?1172.32 = 102.7 kJ

b. Temperature increase:

Heat stored in the material:

$Q = mc\Delta T$ or $\Delta T = Q/(mc)$

For the mass of the material, apart from the polyester, there is also the styrene. Each unit of the polyester corresponds to each unit of the styrene for complete crosslinking. The chemical formula for styrene is shown in the following:



The mass of a styrene molecule is therefore:

8C + 8H = 96 + 8 = 104 g/mole

Mass of styrene corresponding to 122.4 g of polyester is:

(122.4/142)104 = 89.65 g

Total mass of polyester and styrene:

122.4 + 89.65 = 212.05 g

The temperature increase can now be calculated using the above equation:

$$\Delta T = \frac{(102.7\ \text{kJ})(1\mathit{cal} / 4.18\ \text{J})}{(212.05\ \text{g})(0.25\text{cal} / \text{g}^\circ\text{C})} = 463^\circ\text{C}$$

Note that the temperature increase is very high. The reason for this is because of the assumption of no heat loss. In reality, there is heat loss to the surrounding environment. Also not all the heat is generated instantly. The process of bonding takes time. The curing process may take hours and even days, depending on the surrounding temperature. As such in real applications the temperature increase will be a lot less than the number above.

TABLE 2.3 Energy Associated with the Atomic Bonds.

Bond	Energy (kJ/mole)
C–C	370
C=C	680
C–H	435
O–H	500
N–H	430
C–O	360
C=O	535

On the atomic level, there is an amount of energy associated with the breaking or forming of each of the bonds. The energy associated with some of the bonds is shown in Table 2.3.

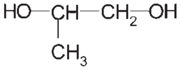
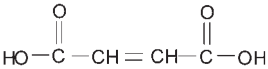
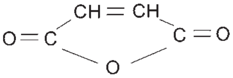
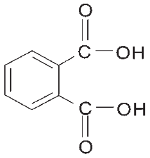
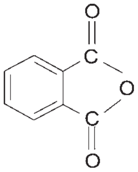
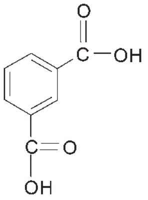
3.1.5. Photo-Activated Curing Systems

The initiators for curing described above (such as MEKP) are readily activated agents. They start acting as soon as they are mixed together with the resin systems. There are also initiators that are activated by ultraviolet rays. These photo-initiators can be mixed in the resin system but they are not activated until photon energy provided by ultraviolet light is introduced. Once activated they start reactions similar to the case of conventional initiators. The use of photoinitiators allows some control over the time for the reaction to start but requires that the resin be translucent enough for light to be transmitted.

3.1.6. Polyester Properties

One of the advantages of polyester resins is that the reactants, which are called monomers (Table 2.4), can be chosen from a wide assortment of diacids and diols to meet specific physical and chemical properties desired. Apart from maleic acids, one can also use maleic anhydrides, orthophthalic acids, isophthalic acids or orthophthalic anhydride. The difference between orthophthalic acids and isophthalic acids is that due to the location of the bonds on the benzene ring, the molecule of the isophthalic acids is straighter. Straighter molecules provide better packing of the material, and this in turn gives higher density, better strength, stiffness and environmental resistance. The anhydride on the other hand has a close ring which must be broken by the application of more energy (heat) before further reaction can occur. As a rule of thumb, when a molecule contains benzene rings rather than just straight C–C bonds it dis-

TABLE 2.4 Choices of Reactants for Polyester Resins [3].

Reactants	Chemical Structure	Advantages
Ethylene Glycol	$HO-CH_2-CH_2-OH$ *This molecule is aliphatic since it contains mainly linear chains.*	Basic reactant
Propylene Glycol	 $HO-\underset{\displaystyle CH_3}{\underset{\mid}{CH}}-CH_2-OH$ *This molecule is aliphatic and branched.*	More compatible with styrene than ethylene glycol
Maleic Acid (also Fumaric Acid)	 $HO-\overset{\displaystyle O}{\overset{\parallel}{C}}-CH=CH-\overset{\displaystyle O}{\overset{\parallel}{C}}-OH$ *This molecule is aliphatic.*	Flexible, Low cost
Maleic Anhydride	 *The anhydride has a ring which needs to be opened before reaction can occur.*	—
Orthophthalic Acid (Ortho)	 *This molecule is aromatic since it contains the benzene ring.*	Rigid Relatively low cost
Orthophthalic Anhydride	 *This aromatic molecule has the ring which needs to be opened before reaction can occur.*	Rigid
Isophthalic Acid (ISO)	 *The isophthalic molecule gets its name from the relative position of the connection between the COOH group with the benzene ring.*	Resilient (tough) Thermal stability

plays better mechanical properties and environmental resistance. Molecules that contain benzene rings are usually called aromatic while those that do not are called aliphatic.

Apart from the variation in the type of matrix material to make a composite, the manufacturer may use different types of resins at different locations in the structure for various reasons. For example, in the case of a fiberglass/polyester pipe used for transporting corrosive liquids, where the inside surface of the pipe is exposed to the corrosive environment, it is necessary to use a resin that is more corrosion resistant such as isophthalic resin (as compared to orthophthalic resin). However isophthalic resin is more expensive than orthophthalic resin. In order to save cost, the manufacturer may use a thin layer of isophthalic resin only on the inside of the pipe while the remaining part is constructed of orthophthalic resin. A layer of resin meeting particular requirements applied on the surface of a structure is usually called the *gel coat.*

There are disadvantages and advantages in using different types of resins at different locations within a structure. One disadvantage is that checking the quality of the product becomes difficult. Normally one can check the quality of the material by testing the surface for properties such as hardness or chemical resistance. But when the material at the surface is not the same as the material below, one cannot translate the finding at the surface to the material inside. One advantage is cost saving. Another possible advantage is that one can use resins with different thermal conductivities (such as the increase in thermal conductivity by adding carbon nanotubes) at different locations across the thickness of the structure to help dissipate the heat generated during the manufacturing of thick composite parts.

3.1.7. Polyester Use and Storage

Polyester resins are generally shipped and stored as a resin system (consisting of the polyester resin, curing agent, fillers and inhibitors) in a large container (drums), and the initiator in a separate container. Even though the polyester resin and the curing agent (such as styrene) are mixed in the same container, reaction does not take place if no activation occurs. Activation can occur in the form of addition of initiators, raising of temperature, or strong mixing activities. Figure 2.1(c) shows a schematic of the co-existence of the polyester molecule and curing agent molecule without reaction. The contents of the containers are mixed in appropriate proportions (usually about 40 phr of styrene and small amounts of inhibitors and fillers) depending on the applications. The styrene molecules not only serve as linking agents but they also reduce the viscosity of the polyester. For processes like liquid composite molding, low viscosity (less than 1000 cP) is required while for processes such as hand-lay-up for filament winding, higher viscosities may be required.

Occasionally the resin mixture will begin to crosslink spontaneously (without the addition of the initiator). This may happen when the temperature is raised or some violent sloshing occurs in the liquid resin. Since the crosslinking reaction is exothermic, once begun the reaction can proceed quite rapidly. To prevent this from occurring, molecules that absorb free radicals are added to the resin mixture. These molecules are called *inhibitors* and a typical example is hydroquinone. Even with inhibitors, however, after a sufficiently long time, the resins can crosslink, so the resin mixtures should be discarded after a specified length of time or at least tested to see if too much crosslinking has occurred. The length of time that they can be stored and still remain useful is called the *shelf life* or *storage life*. The test that is often performed to see if the resin is still acceptable for use is to check the viscosity. Viscosity of uncured polyester resin at room temperature is about 100–300 centipoise. If the viscosity is too high the resin mixture should be discarded.

Other chemicals that might be added to the container are *coupling agents*. These chemicals enhance the bond between the cured polymer resin and the fiberglass reinforcement. Typically these chemicals have one end that is a silane derivative and is, therefore, compatible with the fiberglass, and another end that is compatible with the resin. Hence, they act as bridges between matrix and reinforcement. Coupling agents will be discussed more in Chapter 3.

The incorporation of resins with fibers to make composites is done by either the wet process or dry process. Wet process means that liquid resin is introduced to the dry fibers at the time when the composite part is to be made. For the dry process the composite part is made in two stages. First, the liquid resin is introduced to the dry fibers and the resin is allowed to be partially cured. The result of the first stage is called *prepreg*. Prepregs are flexible sheets. When the manufacturer is ready to make the final composite parts, the prepregs are placed on the mold in different layers to build up thickness. The resin is then cured completely.

Even though there are recent efforts to make prepregs using polyester resin, most of the processes using polyester resins are wet. These include wet hand-lay-up, wet filament winding, and liquid composite molding. When the manufacturer is ready to make the part, a small amount of the resin system is transferred out of the large container and placed in a smaller container called a *pot*. A small amount of initiator (about 1%) is added and the crosslinking reaction then begins. The manufacturer needs to dispense all the resin in the pot before the viscosity becomes too high.

The duration that the resin stays in the pot without going bad is called the *pot life*. Different applications such as hand-lay-up, filament winding, pultrusion, or liquid composite molding may require different pot lives. The pot life can be modified by adjusting the amount of catalyst, inhibitor, or accelerator. Typical accelerators are cobalt naphthenate, diethyl aniline, and dimethyl aniline. They can be added by the resin system formulator or by the resin system user.

Curing agents such as styrene are unpleasant to the smell and are hazardous. There are government regulations that determine maximum amounts of styrene that may exist in the atmosphere of a working environment. Shops where styrene evaporation into the air exists should be well ventilated with high ceilings. Because of this problem, processes using polyester tend to go more toward the closed-mold approach (such as liquid composite molding) rather than the open-mold approach (such as hand-lay-up or filament winding).

3.2. Epoxy Resins

The most common matrix for advanced composites and for a variety of demanding applications is epoxy. Epoxies have been used extensively for these applications due to their excellent properties such as excellent adhesion, high strength, good corrosion resistance, low shrinkage (as compared to polyester resin), and processing versatility. In addition, the processing of epoxy resins does not involve toxic gases like styrene. Uncured epoxies emit some gas but these are not as unpleasant as styrene. The range of operating temperatures of epoxy resins can be up to 140°C. This is better than polyesters but lower than that of polyimides. On the other hand, epoxies are more expensive than polyesters and have higher viscosities than polyesters.

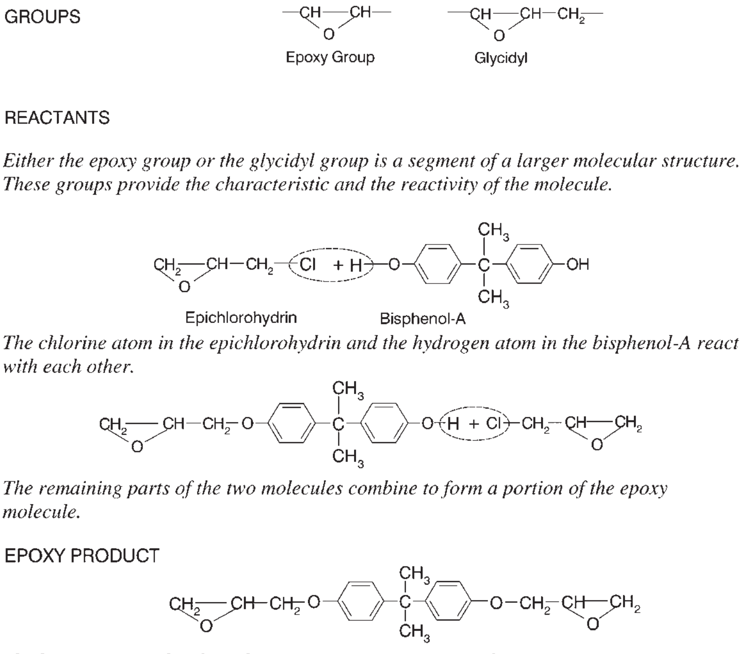
Figure 2.7 shows photographs of containers of Shell Epon 828 and

FIGURE 2.7 Photograph of a sample of Shell Epon 828 and TGDDM epoxy resin.

Vantico TGDDM epoxy resin. Shell Epon 828 is a low temperature cure resin (up to about 80°C). It has low viscosity at room temperature (about 600 cP) and appears in liquid form at room temperature. The viscosity of low temperature epoxy resins is about 500–2000 cP at room temperature. TGDDM is a high temperature cure resin (curing at 177°C). It is used as a base for many aircraft grade epoxy composites. It has high viscosity at room temperature and appears as a very viscous liquid. Its viscosity is about 20,000 centipoise at 50°C. Heat is usually required to reduce the viscosity of this resin in order to wet the fibers.

3.2.1. Epoxy Chemical Structure and Polymer Formation

Epoxies are characterized by the presence of an epoxy group—a three-membered ring with two carbons and an oxygen—as shown in Figure 2.8. The epoxy group usually occurs at the ends of the molecule. This epoxy group is the site of the crosslinking reaction in roughly the same way as the carbon-carbon double bond in polyesters, although the crosslinking reactions are quite different.



Either the epoxy group or the glycidyl group is a segment of a larger molecular structure. These groups provide the characteristic and the reactivity of the molecule.

The chlorine atom in the epichlorohydrin and the hydrogen atom in the bisphenol-A react with each other.

The remaining parts of the two molecules combine to form a portion of the epoxy molecule.

The basic epoxy molecule with two epoxy groups at two ends.

FIGURE 2.8 Epoxy groups and reaction to form epoxy [3].

The properties of the crosslinked polymer are more dependent upon the choice of curing systems in epoxies than in polyesters, so both the nature of the epoxy and of the curing system must be understood. Many epoxies use the slightly modified epoxy group with one additional carbon. This group is called the glycidyl group and is illustrated in Figure 2.8.

In addition to being the site that is used for crosslinking, the epoxy group is the reactive site and provides for good adhesion with the reinforcement or with the surface of another material.

3.2.1.1. Diglycidyl Ether of Bisphenol A (DGEBPA)

The most common of the epoxy resin systems is based upon the condensation polymer formed from epichlorohydrin and bisphenol A and is called *diglycidyl ether of bisphenol A* (DGEBPA) (see Figures 2.8 and 2.9). The reaction to form the resin from the reactants is shown in Figure 2.9. In this figure, the epichlorohydrin molecule is made to react with a bisphenol A molecule. Hydrogen will combine with chlorine to form hydrochloric acid. The epoxidyl group will connect with the bisphenol. Reacting with another epichlohydrin will form another molecule of hydrochloric acid and a basic segment of the epoxy is formed. This epoxy molecule has two epoxy ends. The reaction will continue to form epoxy molecules with longer length.

The number of repeat units in epoxy is generally small (less than 20) and the average molecular weight can therefore be fractional. For molecules of short chain lengths, the resin is a liquid. Generally, processing becomes difficult as the molecular length is increased although the physical and mechanical properties also increase. Therefore, a compromise must be made between processability and properties.

3.2.1.2. Specialty Epoxy Resins

Apart from the base resin DGEBPA, there are other epoxies that have been developed for specialty applications. A few of these are shown in Figure 2.10 along with their trade names. If one wants to have better mechanical strength, better chemical resistance and higher operating temperature, one can have more benzene rings in the molecule, as in the case of epoxidized phenolic novolacs (one trade name is DOW DEN 438), or tetraglycidylmethylene dianiline (THMDA) (trade name: CIBA MY-720). The presence of halogen atoms such as chlorine (Cl) or Bromine (Br) usually imparts flammability resistance. However these molecules emit toxic gases upon burning.

3.2.1.3. Diluents

In addition to the epoxy resins, sometimes diluents are also added. These serve to reduce the viscosity of the resin, to improve shelf or pot life, to lower the exotherm (exotherm is the peak heat release during the curing process; large exotherm can bring the peak temperature of the

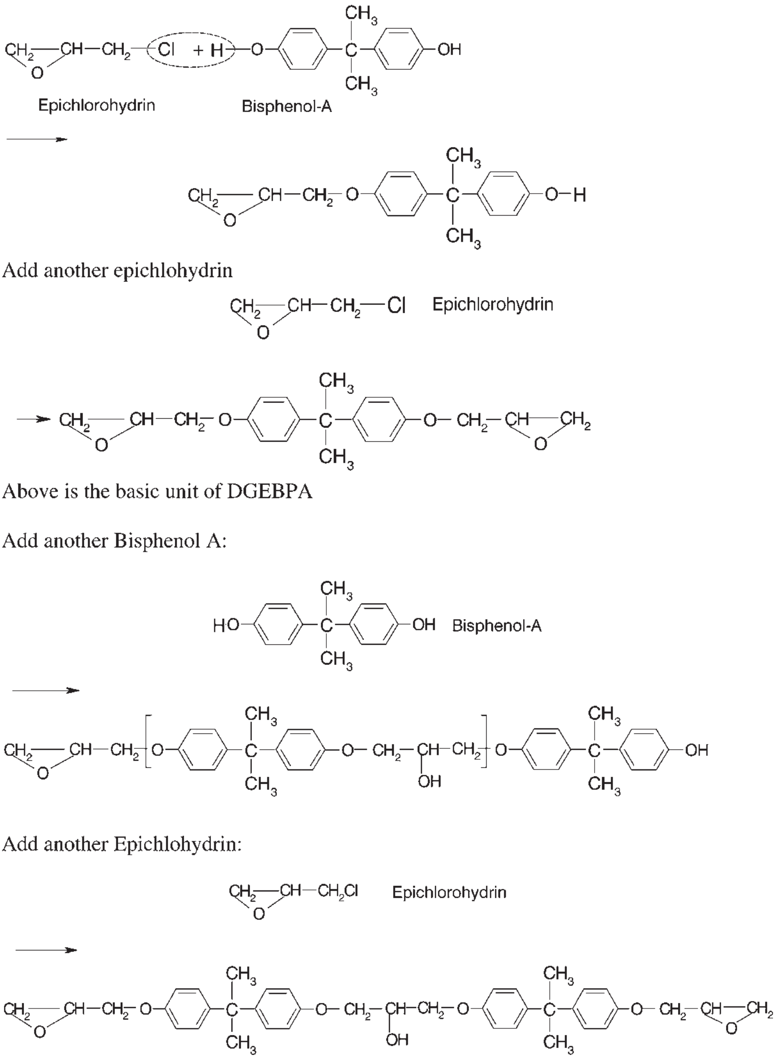
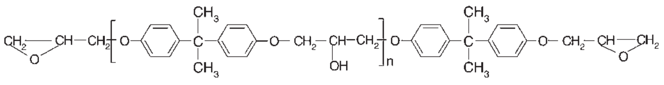
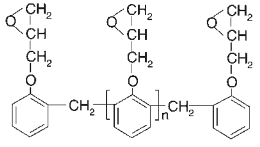


FIGURE 2.9 Epoxy groups and reactants for epoxy polymers.



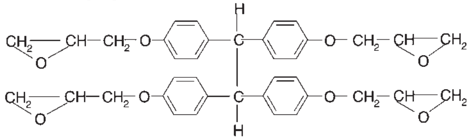
Diglycidyl Ether of Bisphenol A (DGEBPA)

DGEBPA is the basic epoxy resin that is used as the base for many commercial epoxy products.



Epoxy Novolac (Epoxidized Phenolic Resin)
Example: DOW DEN 438

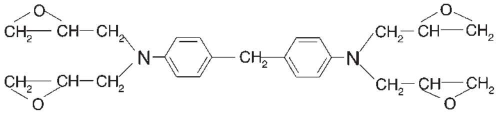
The epoxidized phenolic resin has many benzene rings which give rise to better mechanical and thermal properties.



Tetraglycidylether of Tetrakis (Hydroxyphenyl) Ether

Example: SHELL EPON 103

The tetraglycidylether of tetrakis ether has four epoxy groups and many benzene rings. This provides better mechanical and thermal properties.



Tetraglycidylmethylene Dianiline (TGMDA)

Example: CIBA MY-720

The tetraglycidylmethylene dianiline has four epoxy groups and many benzene rings. This gives better mechanical and thermal properties.

FIGURE 2.10 Major epoxy resin systems [3].

resin to dangerously high level such that damages due to burning can occur), and to reduce shrinkage.

For most applications, diluents that will react with the resin and become an integral part of the cured system are preferred. Such reactive diluents include butyl glycidyl ether, cresyl glycidyl ether, phenyl glycidyl ether, and aliphatic alcohol glycidyl ethers.

3.2.2. Curing Systems for Epoxies (Hardeners)

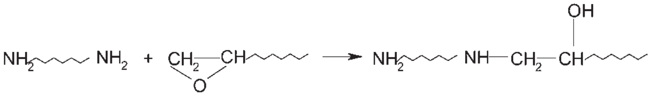
Three curing systems are of primary importance for epoxies: amines; anhydrides; and tertiary amines and accelerators.

3.2.2.1. Amines

The most common curing system is the amine, in which one of the amine hydrogens (an amine hydrogen is a hydrogen atom that is attached to a nitrogen atom) reacts with the epoxy ring to form a hydroxyl group which can then react with another group to crosslink the chains. These reactions are addition reactions, so no byproduct is formed as would be formed in a condensation reaction. Primary amines (RNH_2), which contain two active amine hydrogens, are therefore capable of reacting with two epoxy groups and achieving a greater crosslink density (number of crosslinks per polymer) than single functional hardeners. This greater crosslink density generally improves physical properties, although at the expense of flexibility. If the amine is aromatic, the overall stiffness, low shrinkage, and temperature capability is improved, although toughness is sacrificed. The chemical structures, and viscosities of the commonly used amine curing agents are shown in Table 2.5.

An amine is a substance that contains nitrogen, of which there are three types. A molecule containing a reactive group consisting of nitrogen that is attached to two hydrogens, is called a primary amine. When the reactive group consists of a nitrogen that is attached to one hydrogen, this is called a secondary amine. When there is no hydrogen attached to the nitrogen, this is called a tertiary amine.

It can be seen that many of the structures given in Figure 2.10 and Table 2.5 include reactive groups at each end. These permit the formation of crosslinks between epoxy molecules. For example, an amine end group with two hydrogens on the nitrogen (a primary amine) reacts with the epoxy molecule as follows:



When another amine hydrogen combines with a second epoxy molecule, a crosslink is formed. The curing agents in Table 2.5 that contain secondary amine end groups (one hydrogen on the nitrogen) react in much the same way.

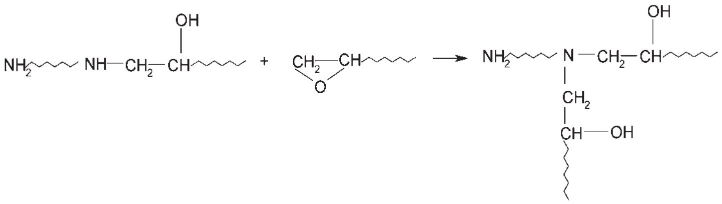
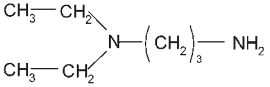


TABLE 2.5 Structures and Characteristics of Commonly Used Amine Curing Agents [1].

Amine Curing Agents	Amine Hydrogen Equivalent Weight (g/eq)	Viscosity @ 25°C (77°F), Pa.sec (cP)
Diethylenetriamine (DETA) $H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH_2$	20	0.0055–0.0085 (5.5–8.5)
Triethylenetetramine (TETA) $H_2N-((CH_2)_2-NH)_2-CH_2-CH_2-NH_2$	24	0.020–0.023 (20–23)
Diethylaminepropylamine (DEAPA) 	65	< 5.0

Amine Hydrogen Equivalent Weight (g/eq) and Epoxy Equivalent Weight

In Table 2.5, there is an expression of amine hydrogen equivalent weight (g/eq). What this means is the weight of the amine molecule over the number of hydrogen atoms that are attached to the nitrogen atoms. For example the DETA molecule has five hydrogen atoms that are attached to the nitrogen. These hydrogen atoms are called the amine hydrogens. The mass of the DETA molecule consists of 4C + 3N + 13H = 103 g/mol. Dividing this number by five gives the amine hydrogen equivalent weight of 20.6. The number reported in Table 2.5 is rounded off to 20.

The hydrogen equivalent weight is useful to determine the mass of amine required to react with a certain mass of epoxy for full reaction, as will be discussed later in Example 2.4.

A similar definition can be used for epoxy equivalent weight. This is obtained by dividing the molecular mass of the epoxy molecule by the number of epoxy groups in the molecule.

For thorough crosslinking, the hydrogens of the primary and secondary amines should be matched 1:1 with the epoxy groups. The amounts of curing agent and epoxy resin needed in order to obtain the 1:1 stoichiometric quantity are calculated as follows:

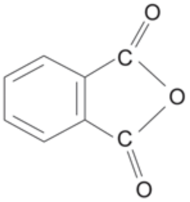
$$\text{Parts by weight of amine to be used with 100 parts by weight of epoxy resin (phr)} = \frac{\left(\dfrac{\text{Molecular weight of amine}}{\text{Number of available amine hydrogens per molecule}}\right)}{\text{Epoxy equivalent weight}} \times 100$$

FIGURE 2.11 Appearance of DDS amine curing agent.

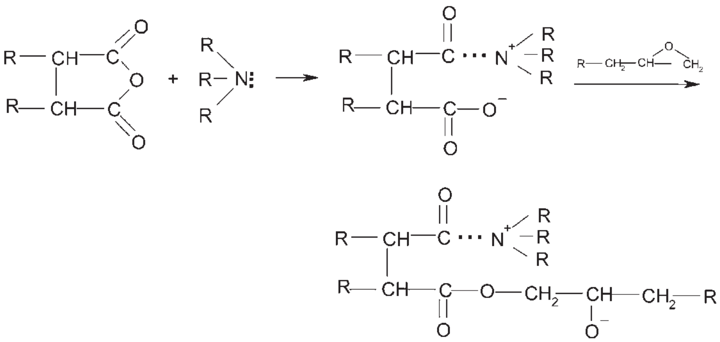
Figure 2.11 shows the appearance of the DDS (one type of amine) curing agent. It appears in powder form at room temperature.

3.2.2.2. Anhydride Curing Agents

The amine curing agents work well with epoxy resins. However, these amines may not be environmentally friendly. The alternative to amine curing agents is the anhydride curing agent, which has a closed ring. One example is phthalic anhydride (PA)with the chemical formula as shown below. The characteristic of the anhydride is the closed ring O=C–O–C=O. This ring needs to be opened (usually by catalysts) for the linking reaction to occur. Phthalic anhydride has an anhydride equivalent weight of 148 g/eq and a melting point of 130°C. The crosslinking reaction of anhydride with epoxy is shown schematically below.



phthalic anhydride (PA)



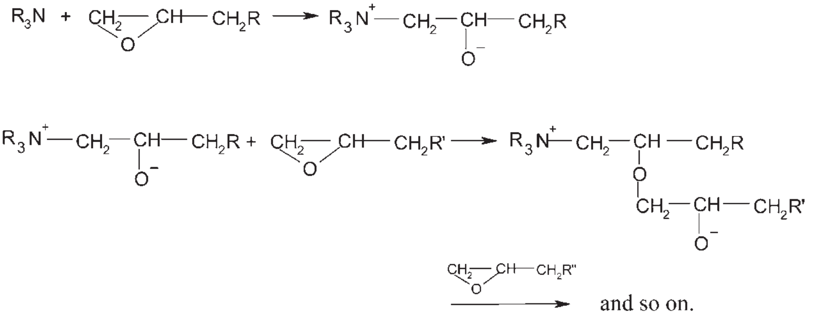
Theoretically, one anhydride group reacts with one epoxy group. The amounts of resin and curing agent that contain identical quantities of the two functional groups (i.e., 1:1 stoichiometrically) can be determined as follows:

$$\text{Parts by weight of anhydride to be used with 100 parts by weight of epoxy resin (phr)} = \frac{\left(\dfrac{\text{Molecular weight of anhydride}}{\text{Number of anhydride groups}}\right)}{\text{Epoxy equivalent weight}} \times 100$$

3.2.2.3. *Tertiary Amines and Accelerators*

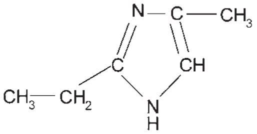
Tertiary amines (no hydrogen on the nitrogen) are Lewis bases that cure epoxy resins in an entirely different manner than the primary and the secondary amines. The curing agent operates as a true catalyst by initiating a self-perpetuating anionic polymerization. They are added to an epoxy resin in small non-stoichiometric amounts that have been empirically determined to give the best properties.

This type of reaction is also termed *homopolymerization* because the epoxy molecules react among themselves and there is no curing agent that forms part of the final structure.



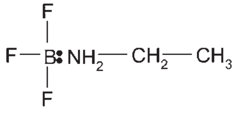
This homopolymerization of epoxy molecule to epoxy molecule results in a polyether. As such, this reaction is also called *etherification.* The ether linkages (C–O–C) are fairly stable against most acids (both organic and inorganic) and alkalis. Further, like ester linkages, they are more thermally stable than the carbon-nitrogen linkages formed by an amine cure.

One example of the accelerators is 2-ethyl-4-methyimidazole (EMI) with an amine hydrogen equivalent weight of 110 g/eq, a melting point of 25°C and a viscosity of 4000–8000 cP. EMI is a very efficient accelerator. It produces the highest degree of crosslinking and the highest heat distortion temperature.



EMI accelerator

Another example is boron trifuoride methyl amine (BF_3MEA) with an amine equivalent weight of 28 g/eq and a melting point of about 208°C. This Lewis acid has achieved great popularity as a curing agent for epoxy resins in composites. Added in small amounts to the epoxy resin alone, it functions as a catalyst by cationically homopolymerizing the epoxy molecules into a polyether. Boron trifluoride causes very rapid (occurring in minutes) and very exothermic polymerization of the epoxy resin, and blocking techniques to halt the room temperature reaction must be used when other than very small amounts of the resin are being used. When blocked with monoethylene amine to form the complex BF3MEA, boron trifluoride is a latent curing agent at room temperature, but becomes active above 90°C causing rapid cure of the epoxy resin with a controllable release of heat. For prepregs, which are often stored for weeks before fabrication into a component, the use of latent curing agent is an absolute necessity. Epoxy resin systems containing BF_3MEA are popular for use in potting, tooling, laminating, and filament winding. It has been found, however, that prepregs and cured systems containing BF_3MEA generally have poor resistance to humidity [3].



$F_3B\!:\!NH_2-CH_2-CH_3$

boron trifluoride-methyl amine

Normally the primary amine is preferred for the reaction over the secondary amine. However this also depends on the temperature. High temperature can activate the reaction with the secondary amines. Also the close proximity between the epoxy groups and the amines also has some influence. Usually at the beginning of the reaction the primary amines are involved. As the reaction proceeds, temperature is increased and the secondary amines may start to react.

3.2.3. Relative Concentrations [3]

The relative concentration of epoxy groups in the resin (active epoxy sites) and reactive sites on the hardener is very important in determining the physical and mechanical properties of the epoxy resin system. These effects can be summarized into four categories:

1. Large excess of epoxy. With a large excess of epoxy groups over reactive sites on the curing agent, a non-crosslinked epoxy-amine adduct is the predominant product. The physical properties of such a product are generally not as good as if it were highly crosslinked.
2. One reactive epoxy site for each reactive hardener site. At one epoxy group for each hardener reactive site, a crosslinked, thermoset polymer is obtained with most physical properties at a maximum. This gives a multidimensional crosslinked matrix because of the multiple crosslinking sites available.
3. One epoxy molecule for each hardener molecule. Because there are usually more reactive sites for each hardener molecule (typically four) than for each epoxy molecule (typically two), this case has slightly excessive hardener. When the concentration of curing agent reactive sites exceeds the number of epoxy groups, the material forms a thermoplastic resin and the physical properties again reduce and linear polymer results.
4. Large excess of hardener. The result is an amine epoxy adduct and the properties are those of thermoplastic polymer of low molecular weight. That is, poor physical properties compared to the other concentration options.

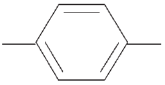
Example 2.4

Question

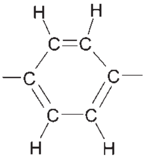
It is desired to cross link a DGEBPA epoxy resin using an amine curing agent called DETA. The formula for the two materials are as shown in Figure 2.8 and Table 2.5. How many grams of DETA should be used if 100g of the epoxy resin are used?

Solution

One repeat unit of the DGEBPA epoxy is shown at the bottom of Figure 2.8. Note that the symbol



means



Counting the number of atoms, each unit of DGEBPA has 21 carbon atoms, 24 hydrogen atoms, and 4 oxygen atoms. The mass of the epoxy unit is therefore:

$m_1 = 21(12) + 24(1) + 4(16) = 340$ g/mole

The DETA molecule (Table 2.5) has 4 carbon atoms, 3 nitrogen atoms and 13 hydrogen atoms. The mass of DETA is:

$m_2 = 4(12) + 3(14) + 13(1) = 103$ g/mole

In the epoxy molecule, there are two epoxy groups, the epoxy equivalent weight is therefore:

$m_3 = 340/2 = 170$ g/mole

There are 5 available hydrogens in the amine molecule. The value of molecular weight of amine over the number of available hydrogens per molecule is:

$m_4 = 103/5 = 20.6$ g/mole

Parts by weight of amine to be used with 100 parts by weight of epoxy resin are:

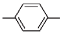
$\% = 20.6/170 \times 100 = 12.1\%$

For 100 g of epoxy, the amount of amine curing agent to be used is: 12.1 g.

3.2.3. Cured Epoxy Resin Systems

Some generalizations can be made concerning the relationship between the chemical structure and properties of a cured epoxy resin:

Aromatic Rings:

- The greater the amount of aromatic rings  a cured epoxy resin contains, the greater its thermal stability and chemical resistance.
- Epoxy resins cured with aromatic curing agents are likely to be more rigid and often make a stronger cured product than those cured with aliphatic curing agents. However, these epoxy resin systems require higher cure temperatures because their very

rigidity reduces the molecular mobility needed to properly position two reactive end groups for reaction.

Crosslink Density

Crosslink density is defined as the number of crosslinks per volume of the material. The crosslink density depends on the mass of the molecular segments between the cross links and on the ratio of mass of curing agent over that of the epoxy. It has the following effects on resin system properties:

- A lower crosslink density can improve toughness (if strength is not significantly lowered) by permitting greater elongation before breakage.
- A lower crosslink density can also result in reduced shrinkage during cure.
- A higher crosslink density yields an improved resistance to chemical attack.
- A higher crosslink density also leads to an increase in the heat distortion temperature (and glass transition temperature), but too high a crosslink density lowers the strain to failure (increased brittleness).

3.2.4. Pot Life and Prepregs

The pot life (working life) also must be long enough to allow fabrication of the desired component without the complications of rapidly advancing cure.

Aliphatic amine curing agents react faster with epoxy resins than do

In the manufacturing of composites, the resin usually is provided from the manufacturer in containers in the form of large drums. In the manufacturing process, it is necessary to transfer resin from the drum into smaller containers called pots. Curing agents are then added into the pot. While the resin system (resin and curing agent) is inside the pot, it should stay in liquid form for a certain amount of time. The manufacturing process should take place within this time. One should not wait too long so that the reaction has already taken place sufficiently and the viscosity becomes high. If the viscosity becomes high, the resin system is no longer of good usable liquidity. The time the resin stays in the pot and still retains its good liquidity is called pot life.

aromatic amines. The former have pot lives ranging from minutes to a few hours, whereas the latter have long pot livesoften 24 hours or more.

Anhydride curing agents can produce long pot lives (e.g., 2 months for NMA). However when an accelerator is used, the pot lives of the epoxy-anhydrated systems can be as short as a few hours, depending on the amount and type of accelerator used.

Prepregs are normally stored at low temperatures to inhibit further reaction of the partially cured (B staged) resin until desired.

The term prepreg stands for pre-impregnated. Prepregs are made by running fibers that are uniformly separated by tows into a resin bath for wetting. The wetted fibers are then conditioned so that a small portion of the bonds in the resin is formed. In this state, the resin is a viscous liquid. This makes the prepreg a flexible sheet of fibers and resin. The resin is neither liquid nor solid [schematically represented in Figure 2.1(e)]. This state allows the prepregs to be rigid enough to be handled and yet liquid enough so that they can be draped onto a complex shaped mold and be bondable. One analogy to the prepregs is wet wallpaper, except that prepregs are sticky on both sides. In order to provide handlability, usually a piece of non-stick paper is placed on one side of the prepregs to prevent them from sticking to each other. As such, prepregs can be provided in roll form. Usually prepregs are shipped in refrigerated bags to slow down the reaction. Under storage, the resin in the prepregs may continue to crosslink. As such prepregs should be stored at low temperature (about –3°C). If enough bonding has occurred in the resin in the prepreg, the prepreg becomes too stiff for forming, and also the tackiness (stickiness) of the prepreg is no longer sufficient for further processing. The time that the prepregs can stay in storage before becoming stiff or non-sticky is called the shelf life.

For the manufacturing of aircraft composites, prepregs are usually used. A controllable and reproducible cure advancement that allows both sufficient pot life as well as shaping and arrangement of the prepreg is critically important.

3.2.5. Quality Control

The quality control of the resin takes place at two stages: the liquid stage and the solid stage.

3.2.5.1. Quality Control at the Liquid Stage

Before the liquid resin is used for making composite components, its quality should be checked. This is because resins or fillers may be blended with resulting mixtures of different qualities. Also if there is a significant amount of cure already taking place in the resin, then the resin does not have sufficient liquidity to flow to wet the fibers. Normally chromatography is used and viscosity of the resin is measured to determine the molecular weight/molecular weight distribution of the molecules in the resin and the state of liquidity of the resin.

3.2.5.2. Degree of Cure of the Solid Resin

In the manufacturing of polymer composites, it is very important to ensure that the resin cures properly. Proper cure (almost 100% cure) will give the proper mechanical properties such as strength, stiffness and hardness. On the molecular level, curing means that crosslinking has taken place. Complete curing means that all the crosslinks within the microstructure of the resin have already taken place. It is difficult to achieve 100% cure inside the composite material but a degree of cure approaching this limit (in the order of 95% or more) is desirable. The reason why it is difficult or it takes a long time to attain 100% cure is due to lack of accessibility of the species required for curing. If one epoxy end is at one location in the container while the amine end is at a location far away, being separated by other cured material, it would be very difficult for that epoxy end and amine end to react.

There are many methods used to monitor the degree of cure. These can be classified into methods using chemical, thermal, electrical or mechanical principles:

a. Method using chemical principle
   - Wet chemical or physical analysis method (solvent swell) is often used to directly measure the chemical reaction during cure. The molecules of a solvent for an epoxy can diffuse into the space between the epoxy molecules when the epoxy is still not completely cured. By applying the solvent onto the surface of a piece of the solid epoxy, if some portion of that epoxy is not yet completely cured, the diffusing action will take place and this usually gives rise to discoloration or gumminess of the material.
   - Infrared spectroscopy has been used to determine the degree of cure. Figure 2.12 demonstrates the use of near-infrared

spectroscopy for monitoring the appearance or disappearance of the epoxy groups with time. The infrared microscopy measures the vibration resonance of a certain bond inside the material. If a bond exists, it will show more resonance. If a bond disappears over time, the resonance will diminish.

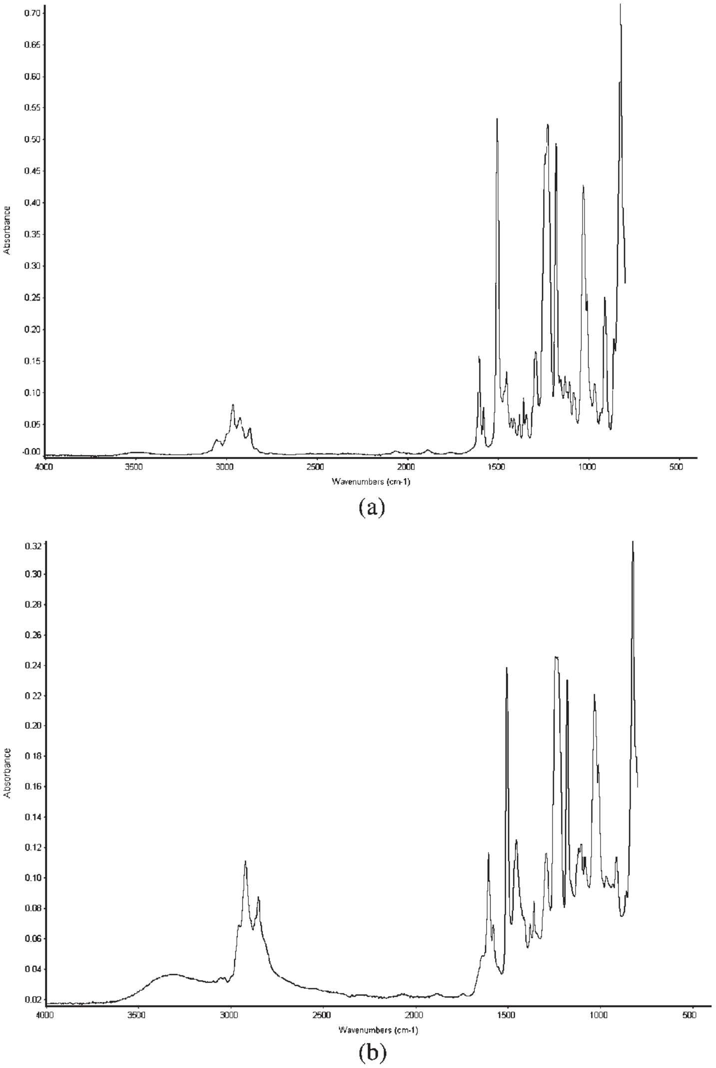


FIGURE 2.12 FTIR curve for Shell Epon 828. (a) Resin only, (b) Resin and curing agent 3046.

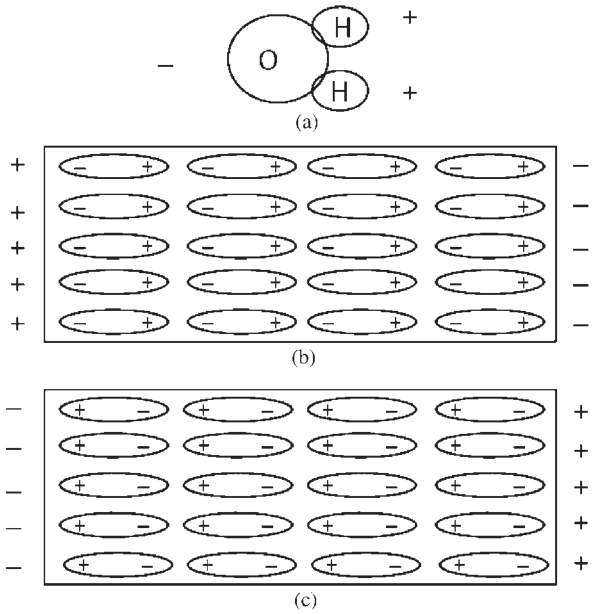


FIGURE 2.13 Switching of dipoles due to alternating electric field: (a) dipoles in water molecule, (b) two polar ends of the molecule in an electric field, and (c) switched dipoles due to switching of electric field.

b. Method using electrical principle

Dielectric measurement has become an increasingly popular cure monitoring technique. The mobility of the molecular segments and therefore the extent of cure is inferred by the response of molecular dipoles to an oscillating electric field. For polar molecules such as water, one end of the molecule has a positive charge and another end has a negative charge (Figure 2.13). If the molecules are subjected to an alternating electric field, the poles of the molecules will be switched back and forth. If the molecules are in the liquid state, it takes less energy to switch the dipoles. However, if the molecules are in a more solid state, it takes more energy for switching. By measuring the loss of energy due to the switching, one can infer the state of cure (or solidifying) of the molecules. Epoxy molecules also have positive locations (around the H atoms) and negative locations (around the oxygen atoms) and these dipoles are switched when the molecules are subjected to an alternating electric field. Figure 2.13 shows the switching of dipoles due to alternating electric field.

c. Method using mechanical principle

The degree of cure can be estimated from the mechanical properties of the resin. The available methods can be:

- Simple hardness test (Barcol Hardness test). In this technique, a simple hardness tester projects a sharp needle against the surface of the cured epoxy. If the epoxy is well cured, its surface is hard and the penetration of the needle is shallow. If the epoxy is not well cured, the penetration is deep. The machine gives the measure of the penetration. This method is good qualitatively and is useful for quick, quality control purposes.
- More complicated mechanical tests or sensitive dynamic mechanical tests such as the dynamic mechanical analyser (DMA). DMA is a machine that imposes mechanical and thermal loads onto the sample. The resistance of the sample against these loads provides the indication of stiffness which, in turn is a result of the degree of cure.
- Detection of the change of modulus of the material (E') or the damping capacity of the material (η) by the speed of propagation of the ultrasonic signals (ultrasonic cure monitoring). In this technique, ultrasonic signals are sent through the thickness of the sample. The time of flight of the signal through the sample is a function of its stiffness and its damping capacity. These in turn are indicators of the degree of cure of the sample.

d. Method using shrinkage measurement

As the resin cures, its volume decreases. There is a correlation between the degree of cure and the degree of shrinkage [4]. Monitoring shrinkage during cure can give an indication of the degree of cure.

e. Method using thermal principle

The thermal properties (such as thermal conductivity, specific heat, and heat content) of an epoxy resin depend on the extent of cure and can be used to assess cure advancement. Heat content measured by differential scanning calorimetry (DSC) has been used successfully to this end. The DSC machine enters a certain amount of heat into the sample and measures the net amount of heat coming out of the sample (heat out minus heat in). Figure 2.14 compares the DSC traces of a sample after being subjected to a few cycles of heating. The ordinate of the curve gives the net heat. Exotherm means net heat is coming out while endotherm means net heat is coming in. The area under the peak in the curve indicates the amount of heat. If there are uncured portions in the sample during the test, these portions will un-

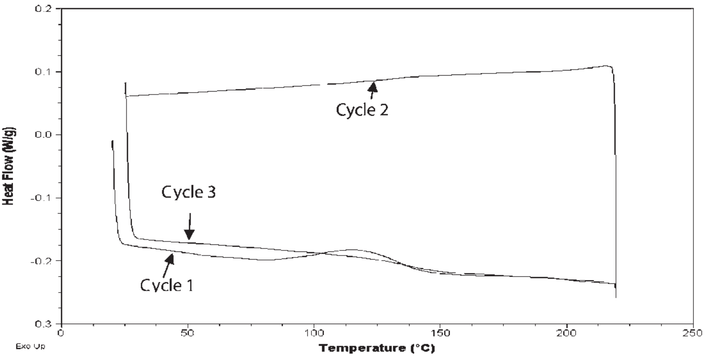


FIGURE 2.14 Comparison of DSC traces for two cycles of test on the same resin sample.

dergo curing during the test. The curing reaction will generate heat due to the formation of chemical bonds.

Figure 2.15 shows schematics of the heat flow curves obtained from two different types of DSC tests: the dynamic scanning test and the isothermal scanning test. In the dynamic DSC test, the temperature increases continuously from the start temperature up to the maximum temperature. The heat is measured as a function of time. In the isothermal DSC test, the temperature is quickly brought from the start temperature to the test temperature. The sample is then held at the test temperature for the duration of the test. Heat is measured as a function of time during the isothermal hold. Figure 2.16 shows the actual heat flow curve for an aircraft resin system.

The important information to obtain from curves such as those in Figure 2.15 is the equation modeling the rate of cure $d\alpha/dt$ where α is the degree of cure. This is essential for the heat transfer model for

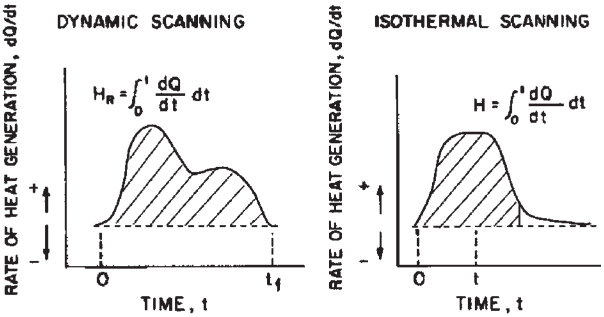


FIGURE 2.15 Schematic of heat flow curves for different types of DSC tests.

the processing of the composites as will be discussed in Chapter 4. The rate of cure is usually expressed as: $d\alpha/dt = H_R(dH/dt)$where H_R is the total amount of heat generated during the whole curing process (this is the area under the whole curve). It can be seen from Figure 2.15 that the rate of heat generation dH/dt is a function of time. This is because the degree of cure changes as time progresses. In addition the rate of heat generation is also a function of temperature. One can therefore write a general expression for the rate of cure as $d\alpha/dt = f(\alpha,T)$. By carrying out an isothermal DSC test, one can keep the temperature fixed, and the rate of cure will be only a function of the degree of cure. One can see from the isothermal curve in Figure 2.15 that the rate of heat generation (or rate of cure) is a function of time. The rate first increases with time up to a certain maximum and decreases. This shows that for low degree of cure, the rate of cure increases up to a certain value of the degree of cure. As the degree of cure gets larger, the rate of cure decreases. A significant amount of work has been done on the modeling of the kinetic behavior of the resin (equation for rate of cure as a function of the degree of cure and temperature. More details of this are presented in Chapter 4.

3.2.6. Use of Epoxies

One of the reasons for the widespread use of epoxy systems in advanced composites is its adaptability to manufacturing methods. The

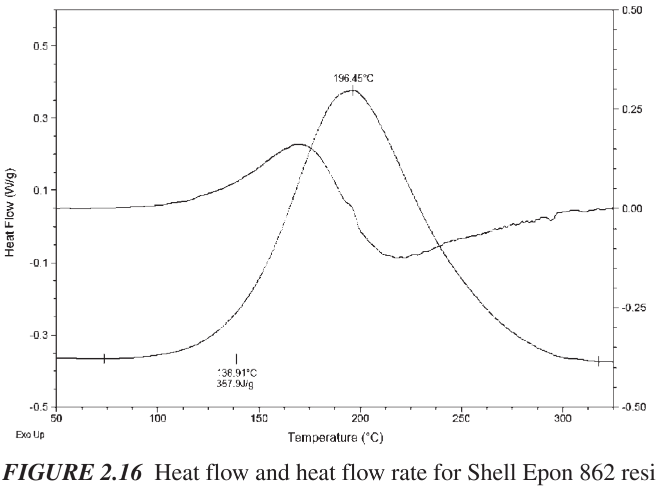


FIGURE 2.16 Heat flow and heat flow rate for Shell Epon 862 resin.

large variety of epoxy types and cure systems commercially available allow the cure rates and performance to be tailored.

High performance aircraft applications use a material form called a prepreg in which fibers are sold pre-impregnated with resin. The fibers can be unidirectional or woven. These prepregs can be made using epoxies and cure systems that are not reactive at freezer temperatures to provide long storage times for customers, yet can be cured quickly at high temperatures and provide service temperature capabilities of 121°C–177°C.

For prepregs, normally an autoclave needs to be used. Recently there is a push toward out-of-autoclave curing process in an effort to cut down the processing time. Liquid composite molding processes have been developed. For these processes, the resin needs to have low viscosity (less than 1000 cP). Special resin systems (such as RTM 6, CYCOM 890) have been developed for these applications.

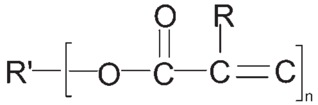
Epoxy systems have also been developed for rapid cure even under cold conditions (such as gluing reflectors to road surfaces). In general, the temperature capabilities of the cured resin will be similar to the cure temperature. Room temperature cured resins will soften somewhat at temperatures just above room temperature. High temperature capability requires high temperature cures.

In the part, the high degree of crosslinking needed to achieve temperature performance reduces the toughness of the epoxy resins. However, recent advances have boosted the level of toughness of composites based on epoxies to equal or surpass the toughness of other resin systems. Techniques to improve toughness of epoxies include the incorporation of rubber particles, thermoplastic particles or nanoclays. The addition of rubber improves the toughness significantly but with reduction in glass transition temperature. The introduction of thermoplastic or nanoclay particles can provide enhanced toughness without significant impact on operating temperature. In addition, these higher toughness systems can be processed like the earlier, brittle systems. In this way, high performance composites can be fabricated with existing facilities and equipment designed for thermoset chemistry without the modification needed to handle a different curing technology.

3.3. Vinyl Ester Resins

3.3.1. Chemical Definition

Vinyl ester resins are thermosetting resins that consist of a polymer backbone R′ with a reactive termination. The general formula for the vinyl ester resin is shown in Figure 2.17.



$$R'-\left[-O-\overset{\overset{O}{\|}}{C}-\overset{\overset{R}{|}}{C}=C\right]_n$$

FIGURE 2.17 General formula for vinyl ester resin.

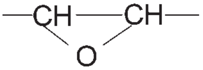
In Figure 2.17, R′ represents the rest of the molecule and R represents either the atom H (for acrylate vinyl ester) or CH_3 (for methacrylate vinyl ester). Vinyl ester resins have intermediate properties between polyester resins and epoxies. The cost of vinyl ester resins are also intermediate between the cost of polyesters and epoxies.

Figure 2.18 shows the chemical formula for a few commonly used vinyl ester resins. In this figure, the top molecule is bisphenol A epoxy based (methacrylate) vinyl ester resin. The phrase bisphenol A comes from the presence of two phenol A groups in the middle of the molecule. The word methacrylate comes from the existence of the CH_3 group at the end of the molecule. Note the star symbols (*) placed below the second carbon from the ends of the molecule. These symbols are used to denote that these are the reactive locations of the molecule. During the curing reaction (or crosslinking reaction), the double bond associated with these carbon atoms opens up and connects with the curing agent. Also in this molecule, the number *n* denotes the number of times the repeating unit will repeat itself. The range of $n = 0–3$ indicates the range of the size of the molecule. Other molecules in Figure 2.18 can be understood in a similar way.

Although vinyl ester resins have sometimes been classified as polyesters, they are typically diesters that (depending on the polymer backbone) contain recurring ether linkages. The backbone component of vinyl ester resins can be derived from an epoxide resin, polyester resin, and so on, but those based on epoxide resins are of particular commercial significance.

3.3.2. Vinyl Ester Resin Manufacture

Vinyl ester resins are produced by the addition of ethylenically unsaturated carboxylic acids (methacrylic or acrylic acid) (these molecules have the COOH termination) to an epoxide resin (usually of the bisphenol A-epichlorohydrin type). Molecules with the ring

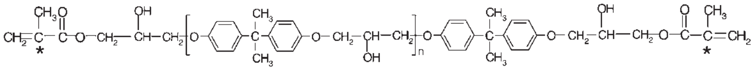


An illustration of the reaction between an epoxy resin and a carboxylic acid is shown in Figure 2.19. The reaction of acid addition to the epoxide ring (esterification) is exothermic and produces a hydroxyl group without the formation of byproducts (e.g., as in polyesterification, where water is produced.) As such the production of the vinyl ester resins is less messy than the production of polyester resins where condensation occurs. Appropriate diluents and polymerization inhibitors are added during or after esterification.

Epoxides that have been used to produce vinyl ester resins include the bisphenol A types (general purpose and heat resistance vinyl esters), and the tetrabromo bisphenol A types (fire retardant vinyl esters).

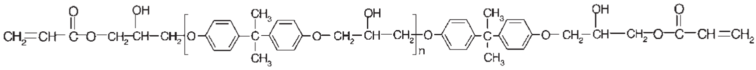
3.3.3. Curing Vinyl Ester Resins

Vinyl esters, like unsaturated polyesters, contain double bonds that react and crosslink in the presence of free radicals by chemical, thermal and radiation sources. Figure 2.20 illustrates the curing reaction. Initiators such as methyl ethyl ketone peroxide (MEKP) need to be introduced



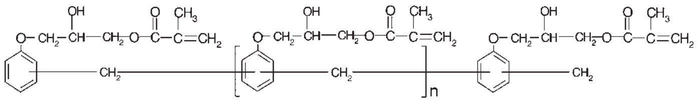
BISPHENOL A EPOXY BASED (METHACRYLATE) VINYL ESTER RESIN (*n* = 0-3)

This resin is called methacrylate due to the presence of the CH_3 group connecting to the C atom that has a radical (represented by the symbol (*) at the end of the molecule.



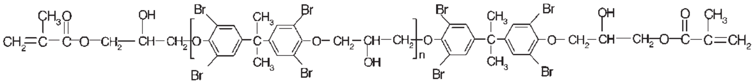
BISPHENOL A EPOXY BASED (ACRYLATE) VINYL ESTER RESIN (*n* = 0)

This resin is called acrylate due to the presence of the H atom that is connected to the C atom that has a radical (represented by the symbol (*) at the end of the molecule.



PHENOLIC-NOVOLAC EPOXY BASED VINYL ESTER RESIN (*n* = 0-1)

This resin has branches which give better mechanical and physical properties



TETRABROMO BISPHENOL A EPOXY BASED VINYL ESTER RESIN (*n* = 0-3)

This resin has bromine which gives its flammability resistance. However bromine is toxic and is banned fromr use in Europe.

FIGURE 2.18 Examples of commonly used vinyl ester resins [3].

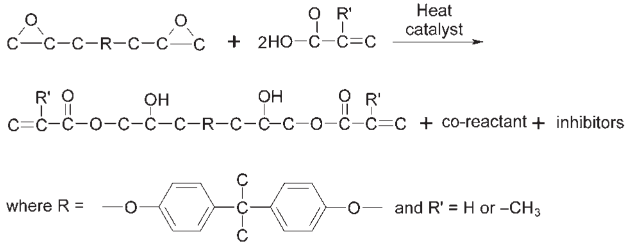


FIGURE 2.19 Reaction between an epoxy and a carboxylic acid to make vinyl ester [1].

to start the reaction. The curing proceeds by a free radical mechanism comprised of initiation (induction period), propagation, and termination. The rate-determining step is initiation, in which the catalyst swamps out the inhibitors, followed by reaction with the double bond of the vinyl esters and the curing agents (e.g., styrene).

3.4. Polyimide Resins

For applications requiring temperature stability up to 600°F (316°C), or even up to 700°F (371°C), the resin of choice is generally a polyimide rather than an epoxy, as epoxies have a normal upper use temperature of 350°F (177°C) to 400°F (204°C). Polyimides are higher in cost than the epoxies. They are often limited to aerospace applications where the higher performance can justify the increase in cost.

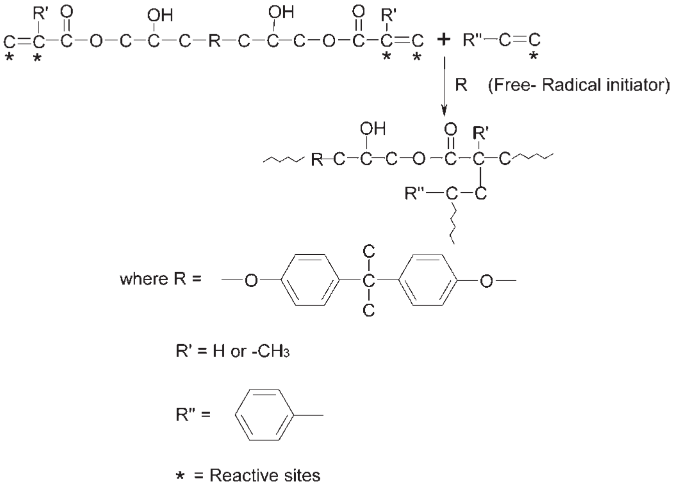


FIGURE 2.20 Curing reaction of vinyl ester resin [1].

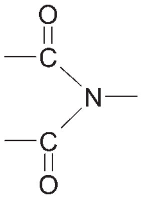


FIGURE 2.21 Chemical formula for the imide group.

Polyimides are characterized by the cyclic group containing a nitrogen and two carboxyl groups (carbons that are double-bonded to oxygens). The imide groups are structurally planar and are very rigid, which contribute to the high stiffness and stability of polymers containing these groups. Figure 2.21 shows the imide chemical group. Usually large aromatic groups are incorporated into the polymer to further enhance the temperature and stiffness properties.

3.4.1. Bismaleimide (BMI) Resins

Another type of addition polymerization is based on reactions involving bismaleimide (BMI) derivatives. The major advantage of BMI resins is that this resin can be cured at 350°F (177°C), which is the same range as is used for epoxies, therefore standard process equipment used for epoxies can be used. However, a postcure at 475°F (246°C) must be performed on the BMI resins to complete the polymerization and achieve properties that are significantly higher than epoxies. For postcure equipment, only an oven is required, without the need for vacuum and pressure as normally required for an autoclave. This is because the part already has taken shape after the preliminary curing.

3.5. Phenolic and Carbon Matrices

For high temperature applications, phenolic thermoset resins and carbon matrices can be used. Phenolic resins are manufactured by the reaction between phenol and formaldehyde. The resin is brittle and has high shrinkage. As for most applications, fillers need to be added. The vast majority of phenolic resin is filled with particular materials such as sawdust, nutshells, or carbon black. Phenolics have been used for many years as a general, unreinforced thermoset plastic in applications such as electrical switches, junction boxes, automotive molded parts, consumer appliance parts, handles, and even billiard balls. When subjected to high temperature, phenolic resins ablate (transform directly from solid to gas). The principal use for long fiber reinforced phenolic resins is for rocket nozzles, such as nose cones, where the ablative nature of the phenolic can be utilized.

Carbon matrix (carbon/carbon) composites have applications that are similar to phenolics and are used when phenolics may not provide the specific characteristics of very high temperature protection, or, occasionally, toughness that is needed. Applications of carbon matrix composites include rocket nozzles, tiles for space shuttle nose cones, aircraft, race car and truck brakes. Both the opposing parts are made of carbon matrix material reinforced with carbon fibers. This application takes advantage of the fact that carbon/carbon composites have the highest energy absorption (specific heat capacity) of any known materials.

Carbon/carbon composites are most often made from carbon fiber reinforced phenolics that may have been tailored slightly and then have been carefully charred. This process of charring is called pyrolysis. The charring process results in a porous structure because of the vaporization of certain parts of the phenolic polymer. The porous material is then reimpregnated with pitch, phenolics, or directly with carbon by vapor deposition. The resulting material is then carefully pyrolyzed again and the process is repeated as many times as necessary to fill the remaining void space with material. The entire process may take as long as six months because each charring step must be done slowly to avoid rapid vaporization and possible matrix damage.

4. THERMOPLASTIC MATRIX

As mentioned in Chapter 1, the composition of thermoplastic resins is different from that of thermoset resins. Whereas thermoset resins depend on the crosslinking of many small molecules to provide rigidity to the material, thermoplastic resins depend on the size (length) of the molecules (these molecules are non-reactive) to provide stiffness and strength for the material. Due to this inherent difference in microstructures, thermoplastic resins have advantages and disadvantages as compared to thermoset resins. The advantages of thermoplastic resins in thermoplastic composites are:

- There is no shelf life issue. The thermoplastic resin can be placed on the shelf infinitely without concern about the material becoming hard.
- The processing cycle can be short. Once the preforms have been arranged into a mold, the heating and cooling steps can be done on the order of minutes (rather than hours for thermosets).

- Thermoplastic composites have higher ductility and fracture toughness as compared to thermoset matrix composites.
- Thermoplastic resins can be melted and reused, making them recyclable.
- If there are defects in the thermoplastic composites, the material can be heated up to heal the damage.

The disadvantages of thermoplastic resin in thermoplastic composites are:

- The preform of thermoplastic composites (tapes made of thermoplastic resin and fibers) is fairly stiff and boardy. Placing sheets of these preforms requires efforts in alignment.
- The viscosity of thermoplastic resin is very high as compared to that of thermosets. This high viscosity requires high temperature and pressure for processing. It also creates the problem of occurrence of voids in the composite material.

The vast number of thermoplastic resins used in composite materials can be conveniently separated into two categories:

1. The traditional industrial thermoplastics that have been used with short fiber reinforcement for many years. Examples for these are polyethylene (PE), poly vinyl chloride (PVC), poly propylene (PP), polystyrene (PS), poly methyl methacrylate (PMMA), poly acrylonitrile butadiene styrene (ABS). The subject of traditional industrial thermoplastics has been covered extensively in the literature and it is not repeated here.
2. A new set of high performance thermoplastics that have been developed specifically for use in advanced applications. This is discussed in more detail below.

4.1. High Performance Thermoplastic Matrices

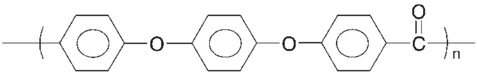
Several unique thermoplastic resin materials have been developed for use in composite materials. These resins generally have inherent thermal and mechanical capabilities beyond the conventional industrial thermoplastics. The high performance thermoplastics are usually more costly. The most important of these high performance thermoplastic matrices developed to date include the following:

- Polyetheretherketone (PEEK) and related molecules
- Thermoplastic polyimides

The current high performance resins are characterized by their high T_g's, which give good mechanical performance at temperatures much higher than the conventional thermoplastics, and in some cases, better than the polyester and epoxy thermosets.

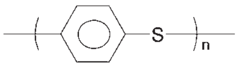
4.1.1. Chemical Structure

The chemical structure of the most common high performance thermoplastics is given in Figure 2.22. The names of some of the molecules, such as PEEK, are taken from the type of linkage between the benzene rings. Therefore, PEEK has an ether (C–O–C), then another ether linkage, then a ketone linkage (C–C=O) and is named polyetheretherketone.



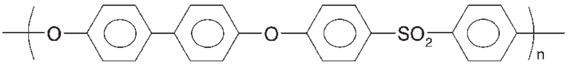
Polyetheretherketone (PEEK)

Note that the C–O–C bond is an ether bond andthe O–C=O is a ketone bond. There are 2 either bond and one ketone bond in PEEK.

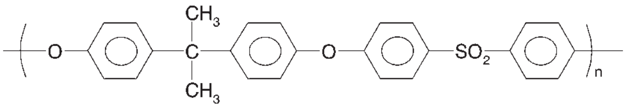


Polyphenylene sulfide

Note that C–S is a phenylene sulfide bond.

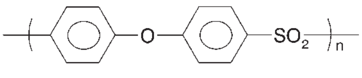


Polyaryl sulfone



Polysulfone

Note that C-SO_2 is a sulfone bond.



Polyethersulfone

The name of this molecule comes from the either bond C–O–C and sulfone bond C–SO_2

FIGURE 2.22 Chemical structure of a few high performance thermoplastics.

Other PEEK-related polymers are PEK with one ether linkage and PEKK with one ether linkage and two ketone linkages. Each of these polymers is characterized as highly aromatic, which increases the T_g and givse good thermal stability. The polymers generally have long repeating units that lead to a high degree of orientation in the liquid (melt) phase. Therefore, when these polymers solidify, they easily assume a crystal structure. This high crystallinity results in high modulus and low creep for thermoplastics because the tensile forces are immediately resisted by the rigid and strong crystal structure rather than by amorphous regions, as in many other thermoplastics. In addition, the crystal structure resists many solvents because the solvent molecules must also encounter these interatomic forces of the crystal structure to have any effect on the polymer. It must be remembered, however, that the polymers are not completely crystalline, so the effects of the amorphous regions can also be seen. Hence these thermoplastic polymers show much more elongation than thermosets (30%–100% versus 1%–10%) and this results in far greater toughness and impact resistance. This toughness is more pronounced at higher temperatures. In fact, at low temperatures, the thermoplastic becomes brittle.

The properties of a few commercial high performance thermoplastic resins are shown in Table 2.6. In this table, polyetherimide (PEI) has a high T_g with moderate processing temperature but low environmental resistance. Polyphenylene sulfide (PPS) has moderate processing temperature and good environmental resistance but low fracture toughness and low T_g. Polyetheretherketone has good fracture toughness, high T_g, good environmental resistance, and a large database but high processing temperature and high cost. A relatively new material, polyetherketoneketone (PEKK), has high T_g, moderate processing temperature, high toughness, and good environmental resistance, but a limited amount of information is available.

4.1.2. Fabrication of Composites

Because of the high melting point of these resins, they cannot be processed using typical plastics processing equipment unless this equipment has been upgraded to handle higher temperatures and pressures.

Many of the typical thermoset processes, such as filament winding and pultrusion, are also difficult to apply to high performance thermoplastics because of the high viscosity of their melts, 10^4–10^7 poise versus 1000 poise for noncured epoxy (molasses is about 10^5 poise).

The high viscosity in thermoplastics makes wet-out of the reinforcement very difficult. Increasing the temperature lowers the viscosity, but

TABLE 2.6 Properties of a Few Thermoplastic Resins (with permission from Cytec Engineered Materials Ltd.).

	PIE	PPS	PEEK	PEKK (DS)
Morphology	Amorphous	Semi-Crystalline	Semi-Crystalline	Semi-Crystalline
T_g (°C)	217	90	143	156
Typical Process Temperature (°C)	330	325	390	340
Comments	✓High T_g ✓Moderate Processing Temperature * *Environmental resistance*	✓Excellent environmental resistance ✓Moderate Processing Temperature * *Low* T_g * *Low Toughness* * *Poor Paint Adhesion*	✓Extensive database ✓Excellent environmental resistance ✓High toughness * *High process temperature* * *High polymer cost*	✓Excellent environmental resistance ✓High toughness ✓Lower process temperature than PEEK ✓Bonding and painting * *Limited database in composite form*

too high temperature can cause decomposition before sufficiently low viscosities are reached. High consolidation pressures are commonly employed to enhance flow of the resin.

4.1.3. Shear Thinning

One method to alleviate this wet-out problem is to take advantage of the shear sensitivity of some thermoplastics. These resins are non-Newtonian and undergo shear thinning. Therefore reinforcements can be impregnated by forcing the resin and fibers through a die at high temperature and under conditions that create high shear.

Strategies addressing the high viscosity issue for the manufacturing of thermoplastic composites will be discussed in Chapter 8.

5. FILLERS, COLORANTS AND OTHER RESIN MODIFIERS

Fillers, colorants and other resin modifiers are added into the resin for various purposes. These may produce side effects such as the reduction of mechanical properties or adhesive ability of the resin. As such they are only added into resins used for applications where load bearing is not critical. Normally these fillers are added into polyester or vinyl ester resins but not very often in epoxy resins used for aerospace applications.

5.1. Reasons for Use of Fillers

5.1.1. Cost Reduction

The most common purpose for adding fillers to resin is to lower the cost since the fillers are generally much less costly than the resin or reinforcements. Common fillers used for this purpose are powdered inorganic materials such as calcium carbonate, talc, clay in aggregate form, alumina trihydrate and glass microspheres.

5.1.2. Shrinkage Reduction

Many of the fillers also help prevent problems such as shrinkage when curing the resins. In this application, the fillers are called *low profile additives* (LPA) and are most important in polyester formulation. LPA are normally particles of thermoplastic resins.

5.1.3. Improvement of Flame Resistance

Fillers may also impart flame resistance, especially if the fillers contain chlorine, bromine, iodine, or water molecules (hydrated). Nanoclay particles can also provide resistance against flammability.

5.1.4. Alter Mechanical Properties

Fillers can also influence stiffness, electrical properties, expansion coefficients, and uncured resin viscosity. Addition of carbon nanotubes can increase the electrical conductivity and thermal conductivity of the resin. Thixotropic fillers are added to increase the viscosity of the uncured resins.

5.2. Colorants, Dyes, and Pigments

Colorants, dyes, and pigments can be readily added to most resin systems. Addition of dyes or pigments affects the cure rate. Some dye systems are also affected by the temperature changes that occur during curing.

Some pigments affect the weather resistance of the composites. Carbon black and titanium dioxide, for example, will absorb or modify ultraviolet light and prevent or diminish ultraviolet degradation of the resin.

6. CERAMIC MATRICES

Ceramic materials are attractive due to their strong resistance against high temperature and corrosion. A high degree of chemical and thermal stability is characteristic of the oxides, carbides, nitrides, and borides that form the basis for ceramic materials. However, as mentioned in Chapter 1, due to their high surface energy, it is difficult for ceramic in liquid form to adhere to fibers. As such the number of available systems is limited. One example is carbon/carbon composites where the carbon matrix is deposited on a bed of carbon fibers by chemical vapor deposition. Other forms are short fibers incorporated into a bulk ceramic for fracture toughness improvement.

7. METAL MATRIX [3]

Due to their high surface energy, it is difficult for liquid metal to bond with fibers. However a few systems of metal matrix composites have been developed. High pressure and introduction of roughness on the surface of the fibers is usually used to compensate for the lack of wetting. Metal matrix composites (MMC) have the advantage of high temperature resistance. They can be classified into two forms: short fiber metal matrix composites and long fiber metal matrix composites.

Short fiber MMC consist of high performance reinforcements (such as SiC) in a metallic matrix (aluminum, titanium, magnesium, copper). The reinforcements can be in the form of particles, whiskers, or fibers. MMCs have been used (or investigated for use) as piston ring inserts, pistons, connecting rods, impellers, brake calipers, sway bars, critical suspension components, and tennis racquets. The incorporation of a second phase (the reinforcement) into a metal significantly affects the propagation of pressure waves through the material by acting as sites for scattering and attenuation. This provides good dynamic damping capacity. The high thermal conductivity of the metal matrix, combined with the low thermal expansion coefficient of the composite, allow the design of high performance heat sinks for electronic applications. Carbon reinforced copper is of particular interest for this application.

To manufacture long fiber reinforced MMCs, continuous fibers are aligned to form a bed of fibers. Metal matrix is introduced by casting, hot molding, or plasma spraying around the fibers. Individual layers can be formed and then stacked in any ply orientation to give the desired mechanical properties.

8. REFERENCES

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9. HOMEWORK

1. Show the chemical reaction that forms a polyester made of maleic acid and propylene glycol. Also show the chemical reaction for crosslinking using styrene.

2. It is desired to make a polyester using 100 g of maleic acid and propylene glycol. A stoichiometric amount of propylene glycol is used. Crosslinking is done using styrene.
    a. After the condensate is removed, how many grams of polyester are obtained?
    b. How much heat is generated?