

4

Chemistry of polymer processing

4.1 Introduction

As indicated in Chapter 1, polymeric materials can be divided into two classes: *thermoplastics* which can be reshaped by heating and *thermosets* which cannot. Thermoplastics are formed from linear polymers and the monomers have a functionality of two, whereas thermosets are created from monomers with a higher functionality and each monomer becomes attached to a number of other molecules to form a three-dimensional structure. The challenges in processing these materials are very different and create very different physical characteristics in the final polymer.

4.2 Processing thermoplastic materials

Heating a thermoplastic will lead to the formation of a free-flowing liquid. The extent to which a polymer requires to be heated will depend on the molar mass of the polymer and the viscosity associated with the process. The processes usually used are:

- rotational moulding
- injection moulding
- compression moulding
- solution/melt casting
- plastisol moulding

The technology of each of the above processes is discussed in more detail in Chapter 5.

4.3 Thermosets: elastomers

A thermoset structure can be formed in a variety of different ways. Thermoset materials are created by cross-linking pseudothermoplastic materials. For instance, a thermoset can be created by the vulcanisation of rubber.

4.3.1 Rubbers and vulcanisation

Rubbers (elastomers) are used in applications where the ability to both stretch and carry a load is important. Traditionally, processed natural rubber has been the material of choice, but more recently materials such as the polyurethanes have been used. Natural rubber and gutta percha are artificial polyisoprene (see Figure 4.1).

Replacement of the methyl group by chlorine gives polychloroprene which has characteristics that are similar to those of natural rubber but are superior in some respects. A related material is chlorinated rubber that is produced by treating rubber with chlorine gas in hot carbon tetrachloride. The reaction produces free radical species which cause substantial substitution of hydrogen by chlorine to give a mixed chlorinated product which has properties which retain a rubber-like characteristic but also resemble polyvinylchloride.

In the early 1820s Mackintosh discovered how to vulcanise natural rubber using sulfur to produce a material with high durability. Goodyear refined this vulcanisation process in 1836

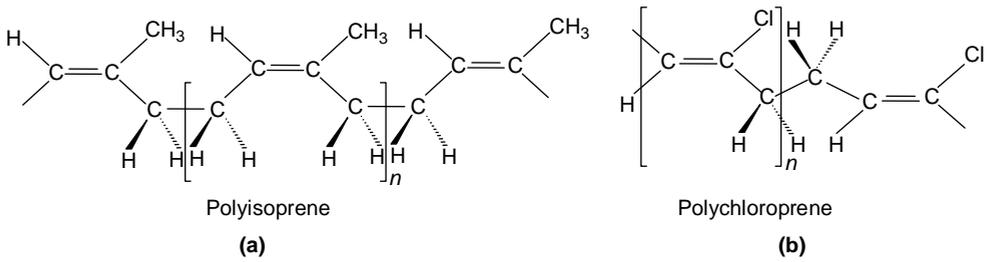


Figure 4.1 Structure of elastomers: (a) polyisoprene; (b) polychloroprene.

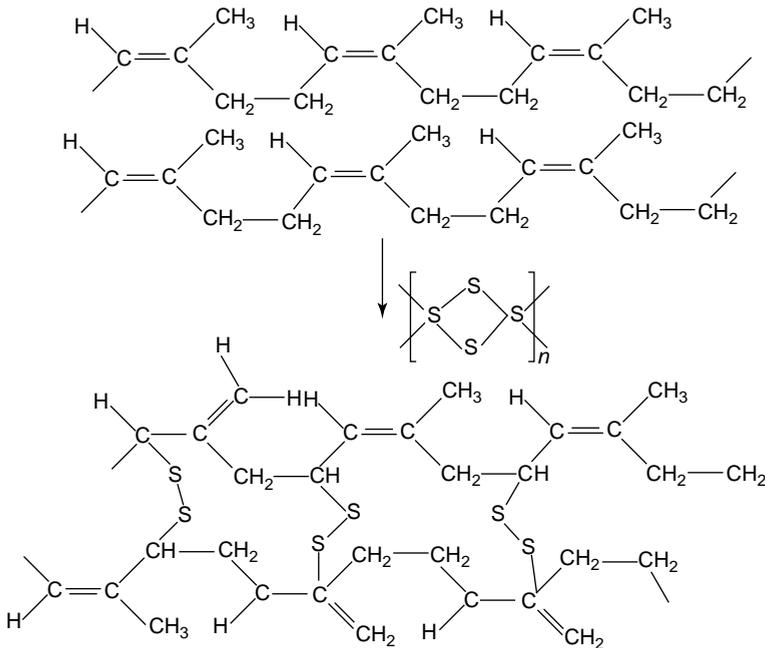


Figure 4.2 Schematic of cross-linking–vulcanisation process for polyisoprene.

to create flexible products that eventually evolved into the products used in the modern tyre industry. The chemistry is complex but can be represented by the diagram shown in Figure 4.2.

The vulcanisation process is complex and can be accelerated by the use of various sulfur containing compounds such as mercaptobenzothiazole (MBT) or diphenylguanidine (DPG) (see Figure 4.3), together with zinc oxide and surfactants for compatibility. In most applications,

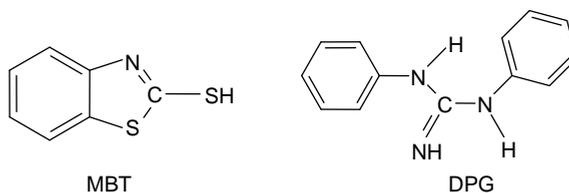


Figure 4.3 Schematic of accelerators used for vulcanisation of rubbers.

carbon black is added to rubber to act as a filler. If the density of the cross-linkages is very high then a very tough material, known as ebonite, is created.

In the case of polychloroprene, cross-linking is achieved by the addition of zinc and magnesium oxides without the use of sulfur. The chemistry is complex but rearrangements involve the removal of chlorine and the creation of ether linkages. This process is more acceptable in applications where the release of smelly thio compounds is deemed unacceptable.

4.3.2 Siloxanes

A very important class of elastomers is based on siloxanes. Polydimethylsiloxane (PDMS), is a very versatile polymer which is liquid at ambient temperatures and even the very high molar mass materials show viscoelastic rather than solid behaviour. The long Si–O bond and large distance between the methyl groups makes the backbone very flexible. The polydimethylsiloxane polymer is a thermoplastic, with a simple linear chain polymer with terminal OH groups at each end of the chain. The glass transition point (T_g) of the backbone is about -90°C ; however, the siloxane chains can form a crystalline phase at about -60°C , but still retain their rubbery characteristics down to the T_g . PDMS can be converted into a stable solid and is used as a sealant. The process of cross-linking the PDMS can be achieved by the addition of a hydrolysable tetrafunctional silane (see Figure 4.4). The hydrolysis process liberates silanol which rapidly condenses with the terminal hydroxyl group on the end of the PDMS to form a cross-linked structure. This process is known as *room temperature vulcanisation* (RTV) and is used to form the common sealants used for baths and showers and other applications where gaps are to be filled with a water impervious, flexible material.

The cross-linking process will liberate CH_3COOH (acetic acid, the chemical name for vinegar) and this can sometimes be detected as the RTV systems cure. An alternative cross-linking agent is based on tetraethoxysilane $(\text{C}_2\text{H}_5\text{O})_4\text{Si}$ and the generation of the silanol $[\text{Si}(\text{OH})_4]$ liberates $\text{C}_2\text{H}_5\text{OH}$ (ethanol). This latter cross-linking agent is preferred as the smell is more acceptable than that of acetic acid.

A more stable matrix can be created using a process known as *high-temperature vulcanisation* (HTV). The polymer used for this process contains a proportion of vinyl substituted silane units of the type shown in Figure 4.5. The number of vinyl groups in a polymer chain can be varied and this will influence the physical properties of the material being created. The larger the number of vinyl groups, the greater the extent to which a carbon-based cross-linked structure is created. Since the carbon-based chain is resistant to hydrolysis, the HTV materials have

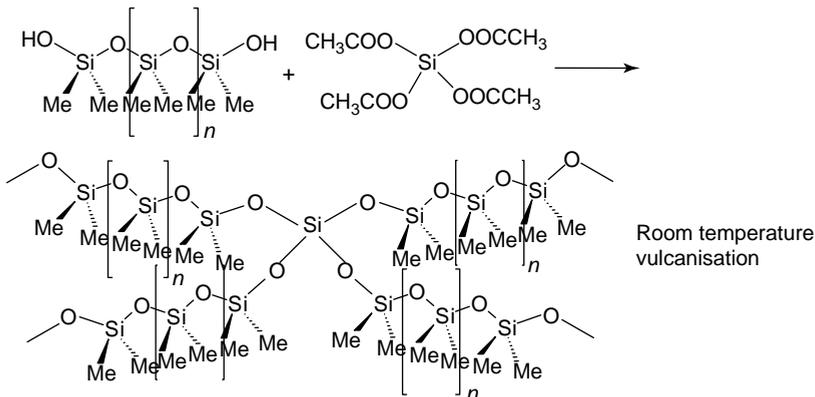


Figure 4.4 Schematic of cross-linking of PDMS to produce a siloxane rubber.

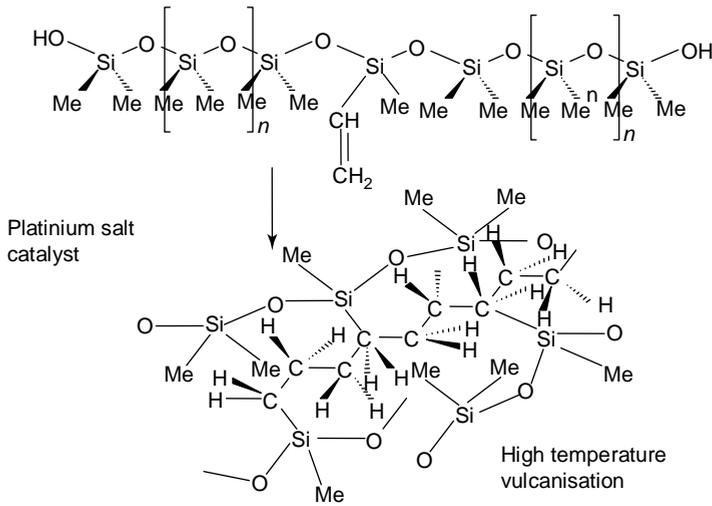


Figure 4.5 Schematic of high-temperature vulcanisation of vinyl substituted siloxanes.

superior resistance to alkaline attack compared with comparable RTV materials. The HTV is achieved by chain growth polymerisation initiated using a platinum salt that is heated to a temperature above 100°C. The resulting matrix has both Si–O and C–C chains and very good thermal and chemical stability. HTV siloxane polymers are used as a rubber coating for fuser rollers in photocopiers and other applications where operation to temperatures in excess of 150°C may be desirable.

Both RTV and HTV materials contain fumed silica as an active reinforcing agent. By adding 5–35% of fumed silica, it is possible to increase the hardness, modulus and tear strength of the material. An unfilled silicone rubber has very little tear strength and will readily snap if subjected to stress. However, the addition of fumed silica dramatically increases the tear strength and makes the material very useful as a sealant and filler. The surface of the fumed silica will contain SiOH groups which can undergo condensation reactions with silanol created by the hydrolysis process and incorporate the particles into the cross-linked matrix.

4.3.3 Rubber elasticity

We will discuss the theory of rubber elasticity in detail in Section 9.1. The siloxane, isoprene and butadiene materials exhibit behaviour which is close to that of a theoretically ideal rubber. If the chains between the cross-links are completely flexible then the effective modulus, E , of the material is directly related to the number of cross-links by the simple formula:

$$E = 3kTN_c \quad (4.1)$$

where N_c is the effective cross-link density of the material, k is the Boltzmann constant and T is the temperature. Cross-links are chemical and unlike the physical entanglements or hydrogen bonds found in thermoplastics cannot be broken. The net result is that the high temperature modulus does not show the expected drop above the values of T_g found with thermoplastics (see Figure 4.6). The high temperature drop in the modulus is associated with polymer chain degradation and results in the creation of monomer or small molecular species by chain scission. In certain systems, the degradation processes will lead to char formation and the modulus will increase as would occur if filler were incorporated into the rubber.

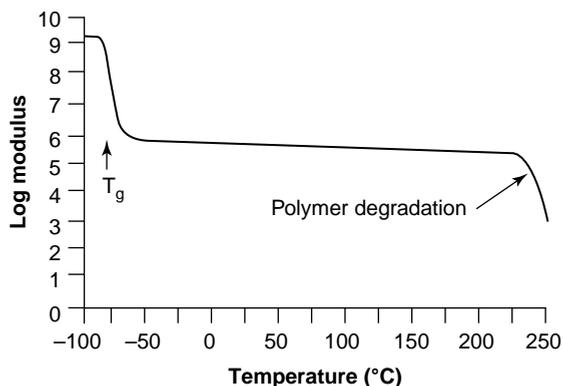


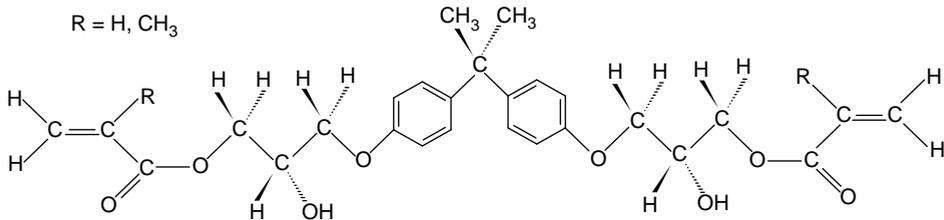
Figure 4.6 Schematic of DMTA trace for a cross-linked rubber.

4.4 Thermoset polymers: rigid materials

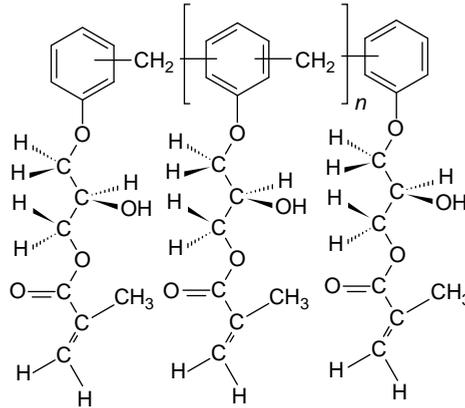
Rigid thermoplastic materials are produced predominantly from high molar mass linear polymers. In contrast, thermosets are formed from low molar mass starting materials and have to be created in the form of the final structure. The creation of a thermoset uses the same chemistry as the creation of thermoplastic material, the only difference being that one or more of the component monomers must have a functionality that is greater than two.

Thermoset materials are usually used where very good thermal stability is essential. If we are constructing an aircraft wing, we do not want it to change its shape when it is thermally cycled or after it has been exposed to a variety of climates. Typical materials used in thermoset chemistry include the following:

- *Epoxy resins*: These are the highest performance resins that are currently available. They will generally outperform most other resin types in terms of their mechanical properties and are resistant to environmental degradation. Epoxy resins are extensively used in aircraft fabrication. As a laminating resin, their increased adhesive properties and resistance to water degradation make these resins ideal for use in applications such as boat building. Epoxy resins may be cured with a difunctional amine which has *four* reactive hydrogen atoms and hence forms four bonds to epoxy groups (see Section 1.53), forming a cross-linked three-dimensional network. Epoxy resins are readily cured at any temperature in the range 5–150°C, depending on the choice of curing agent, and exhibit low shrinkage during cure, minimising fabric ‘print-through’ and internal stresses. High electrical insulation and good chemical resistance complement high adhesive strength and good mechanical properties to make these very useful resins.
- *Epoxy resins with anhydrides*: cationically initiated reactions and imadazole cured materials. The dominant reaction is the opening of the epoxy ring and a linear material bristling with epoxy groups is initially formed which is essentially a multifunctional macromonomer. Subsequent reaction of these pendant epoxy groups forms a very tight cross-linked resin and so they are excellent potting compounds for applications where high voltage electrical breakdown is a major concern.
- *Polyesters*: These are widely used and relatively cheap, but have only moderate mechanical properties. Their disadvantages include high styrene emissions in open moulds, and a large amount of shrinkage during cure. Polyester resins are widely used in the marine industry with a number of different acids, glycols and monomers being available. Two types of polyester resin are in use: orthophthalic polyester resin is the standard, cheapest resin, whereas isophthalic polyester resin is preferred when water resistance is desirable (see Figure 4.7).



Bisphenol-A epoxy-based (methyl) acrylate vinyl ester resin



Phenolic-novolac epoxy-based (methyl) acrylate vinyl ester

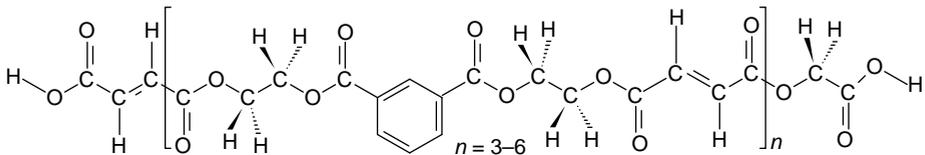
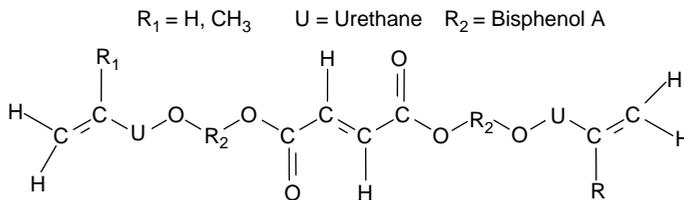


Figure 4.7 Idealised structure for a polyester resin.

The monomers are dissolved in styrene monomer and radically polymerised to produce a cross-linked structure in which polystyrene chains are bridged by the polyester groups which act as cross-links. The ester groups (CO–O–C) increase the reactivity of the vinyl –CH=CH– bonds. The most common resins are based on bisphenol A, fumaric acid or urethane groupings (see Figure 4.8). Polyester resins are viscous, pale coloured liquids which contain up to 50% styrene. These resins can be moulded without the use of pressure and are called ‘contact’ or ‘low pressure’ resins. Small quantities of inhibitor are usually added during resin



Urethane bisphenol-A fumaric acid-based polyester

Figure 4.8 Chemical structures of commonly used polyester resins.

manufacture to slow the gelling process. These resins are very important for engineering applications and form the basis of glass-reinforced plastic (GRP) composites.

- *Vinyl esters*: These resins are similar in their molecular structure to polyesters, but differ primarily in the location of their reactive sites, being positioned only at the ends of the chains (see Figure 4.8). The whole length of the chain is available to absorb shock, making vinyl ester resins tougher and more resilient than polyesters. The vinyl ester resin contains fewer ester groups that are susceptible to degradation by water and other chemicals. These resins are used for pipelines and chemical storage tanks and as a barrier or 'skin' coat for polyester laminates, such as boat hulls, which are immersed in water. Resins having isophthalate groups cure more slowly than resins without these functionalities.
- *Phenolics*: These are based on resole or novolac structures and are cured with a source of methylene radicals, usually hexamethylene tetramine. Phenolics are used where high fire-resistance is required. The condensation nature of their curing process tends to lead to inclusion of voids and surface defects unless pressure is used during moulding. The resins tend to be brittle.
- *Cyanate esters*: These are primarily used in the aerospace industry and have excellent dielectric properties that make them useful for the manufacture of radomes. These resins exhibit temperature stability up to 200°C.
- *Polyurethane*: This can be moulded to form a tough material, sometimes hybridised with other resins. Mixed PU/polyester materials are used for certain coating applications.
- *Bismaleimides*: These are used in aircraft composites where operation at higher temperatures (230°C wet/250°C dry) is required, e.g. engine inlets and flight surfaces of high-speed aircraft.
- *Polyimides*: These resins can operate at higher temperatures than bismaleimides and can stand up to 250°C wet/300°C dry. Typical applications include missile and aero-engine components. Polyimides tend to be difficult to process due to the condensation reaction emitting water during cure and are relatively brittle when cured.

4.5 Cure of thermoset resins and time-temperature transformation diagrams

The cure process in all these thermoset resins involves conversion of a low viscosity fluid into a hard solid (Pethrick, 2002). The cure process can involve either a step-wise addition or a chain reaction depending on the nature of the monomer. In the case of a monomer that involves a step-wise reaction, the viscosity of the resin stays very low for much of the curing process. It is only when cure has advanced well into the polymerisation reaction that the viscosity starts to increase and does so in an almost exponential manner. The viscosity-modulus plotted against time (see Figure 4.9), shows a break at the point at which *gelation* occurs. At *gelation* a three-dimensional

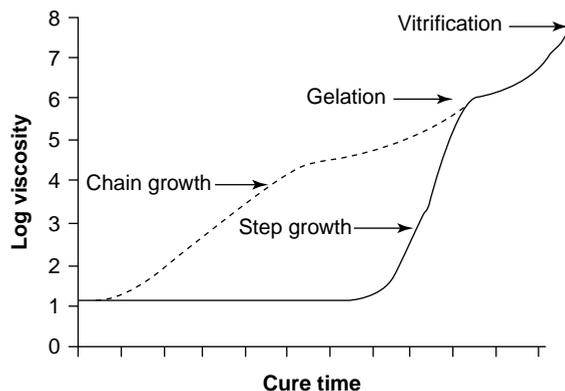


Figure 4.9 Typical viscosity against cure time plots for chain and step growth processes.

network is formed and the final shape of the article is fixed. Further reaction will convert the gel into a rigid solid (see Figure 4.9).

Epoxy resins are very mobile initially but after a small degree of cure can be converted into a solid at room temperature. A mixture of an aromatic amine and an epoxy resin can form a solid phase at room temperature with a very low reactivity. On heating to a high temperature, the cure process (see Figure 4.9) will occur. This mixture of amine and epoxy is called a *one-part resin* and forms the basis of much of composite fabrication technology. The alternative is a two-part resin process, in which each of the reactants is mixed at the point at which the reaction is required. The *one-part resin* can be very stable when stored at low temperature and can have a useful life for several months and in certain conditions up to a year. On heating the resin mixture to temperatures of the order of 70–120°C, rapid reaction occurs and the liquid is transformed into the solid. The significant increase in viscosity occurs once the degree of reaction is of the order of 60–70%. A quick rule of thumb for the accelerating effect of heat on the rate of cure of a resin is that an increase of 10°C in temperature will roughly double the reaction rate. Therefore if a resin gels in a laminate in 25 min at 20°C it will gel in about 12 min at 30°C, provided that additional exothermal reactions do not occur. Curing at elevated temperatures is often required to ensure that the reaction is complete and many resin systems will not reach their ultimate mechanical properties unless the resin is ‘postcured’. The postcure involves increasing the reaction temperature after the initial cure has been completed. Postcuring increases the extent of reaction and increases the density of the cross-linkages in the material. Depending on the structure of the material, a three-dimensional gel phase will be formed and after further reaction a glass is created. Once the system has passed into the vitrified or glassy state, the reaction will cease. However, it is possible that groups will remain that are capable of further reaction. Increasing the temperature will transform a glassy solid into a rubbery phase, which will then undergo further reaction. These phase changes can be represented in a time–temperature transformation (TTT) diagram (see Figure 4.10). It is sometimes desirable to leave the matrix slightly undercured, residual

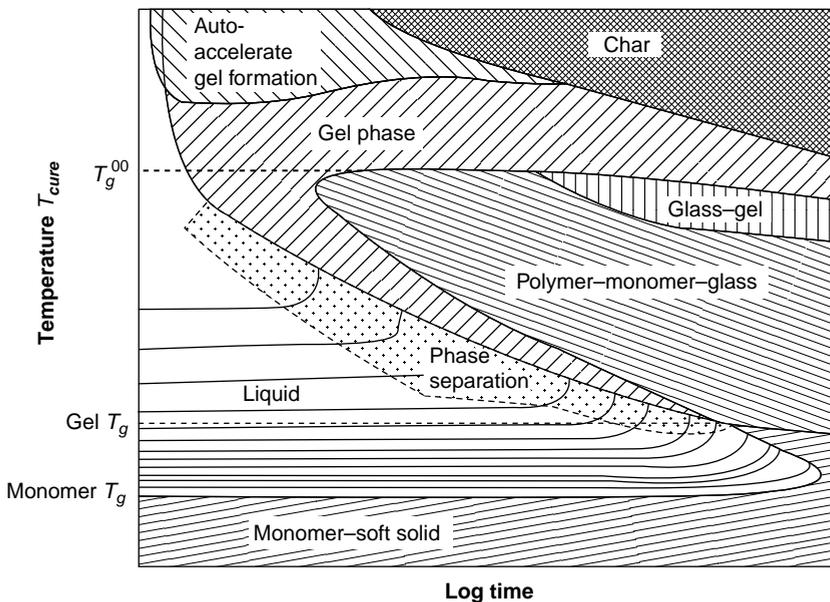


Figure 4.10 TTT diagram for a phase-separating epoxy resin system.

uncross-linked trails of chains effectively plasticising the matrix and improving the mechanical impact strength.

The TTT diagram describes the path by which the cure process proceeds at various temperatures and is typical of the behaviour of a one-pack epoxy resin system (see Figure 4.10). The characteristics features of the TTT diagram are as follows:

- At low temperatures, the *monomer* mixture forms a soft solid rather like butter. The monomer components will react only very slowly and it is possible to store this mixture for a long period of time without compromising its curing behaviour.
- If the *monomer* mixture is heated, it can be transformed to a liquid. The lines on the diagram represent the values of viscosity profiles during curing. For much of the period of the reaction, the viscosity is constant but rises dramatically as gelation is approached (see Figure 4.9). Increasing the temperature of the liquid will lower the viscosity, as reflected in the increased spacing between the lines. The rate of reaction will increase with the increase in temperature and this is indicated by the increase in viscosity decreasing in time with increasing temperature.
- In many systems, *phase separation* can occur. Because epoxy resins are intrinsically brittle it is common practice to toughen the material with either the addition of a rubbery phase or a thermoplastic. The point at which phase separation occurs depends on the solubility of the second phase in the epoxy mixture and the effect of the increasing molar mass on the solubility of the second phase in the matrix. In some systems, phase separation occurs at a relatively early stage in the cure, for other systems it is a processes that occurs just before gelation.
- As the polymerisation processes proceeds, a point is reached at which the network being formed effectively fills the whole reaction volume and this point is designated the *gelation* point. The gel will contain a significant amount of unreacted monomer and will have rubbery, elastomeric characteristics.
- Further reaction of the gel will lead to the unreacted monomer being incorporated into the matrix and the material is slowly converted into a glassy solid. The solid contains monomer yet has glassy characteristics and is designated a *polymer–monomer–glass* solid. The network will contain unreacted monomer and it will have a glass transition temperature (T_g) which is lower than that of the completely cured system, designated T_g^∞ .
- Heating the solid to the point at which it once more regains elastomeric characteristics produces a *glass gel*. The matrix will be fully formed but not all the groups may have been reacted into the matrix. This phase can also be produced as a consequence of chain degradation leading to the creation of short chains which will lower the T_g of the resin allowing the formation of a gel phase.
- At higher temperatures the fully formed resin network can be transformed into an elastomeric phase, known as the *gel phase* if the temperature is raised above the T_g of the fully cured system (T_g^∞). In principle, this is a stable elastomeric phase but it is clear from the phase diagram that if the material is held at these temperatures for a long period of time degradation can occur and a *char* will be formed.
- The *char* phase represents the creation of a degraded resin structure in which some elements of the structure will become very highly cross-linked and have very brittle characteristics whilst others may become very open and exhibit elastomeric or even liquid-type properties. A *char* is the same state which would be achieved if an object were burnt.
- If the curing temperature is raised to a very high value then it is possible for certain systems to exhibit *auto-accelerated* cure processes which are often accompanied by the premature formation of a gel network. High temperatures can be created if the heat generated during the cure process is not effectively dissipated. The heat created can lead to hot spots being generated which lead to volatilisation of the unreacted monomer and can produce an explosion! This type of problem

can be encountered in the cure of heavy composite structures and must be avoided at all costs. Very often the temperatures created will lead to the degradation of the resin and char formation.

- The glass transition point, T_g , of the mixture designated *monomer* T_g will be the temperature at which there is sufficient fluidity in the mixture for curing to effectively start to occur. The *gel* T_g corresponds to the lowest temperature at which a three-dimensional matrix has been formed. At this point there will be large quantities of monomer present which will plasticise the resin and the value will be relatively low. The T_g achieved at a particular cure temperature T_{cure} will usually be slightly higher than the cure temperature used and reflects the influence of the unreacted monomer on the resin.

4.5.1 How do we effectively cure resins?

The objective of the cure process is to achieve a material in which almost if not all of the monomer has been converted into polymer. The most obvious approach would be to raise the reaction mixture to a value close to the ultimate T_g^∞ value. This could have several effects. First, it is possible that a phase-separated structure might not be created and this could have consequences for the impact properties. Secondly, the material would gel very quickly making the processing very difficult. Thirdly, in the case of the resin being the matrix for composite manufacture, the viscosity may have been so decreased that it flows away from the fibres, forming a resin-rich region and leaving fibres that are no longer surrounded by resin. Fourthly, the thermodynamic state of the gel structure created will correspond to the temperature at which the cure process is carried out. As we have seen before, the chemical structure will adopt conformations that reflect the temperature the material is at. In the case of the cure process, the gel network structure will retain a memory of the temperature at which it is formed. When cure is completed, the object is cooled and the conformations trapped at the stage of gel formation may not be able to adopt the appropriate lower thermodynamic state corresponding to the lower temperature. This frozen-in thermodynamic strain can be very large and may be sufficient to lead to chain scission. On an object that has thick sections, it has often been observed that the use of a high temperature for the cure can lead to major cracks being formed when the object is cooled. Thus, it is normal to start the cure process at a relatively low temperature where the reaction is sufficiently slow for the resin to be easily handled and the gel is formed with a structure which leaves the object with minimal strain when cooled to room temperature. However, the T_g of the object will be rather low and it is normal to *postcure* the object. *Postcuring* may be part of the overall cure cycle and is achieved by slowly heating the article once gel has been formed to a value that approaches T_g^∞ . An alternative approach is to hold the article at some elevated temperature that is below the value of T_g^∞ , for a longer period. Which approach is used depends on the circumstances under which the article is fabricated.

4.5.2 Thermoset cure resins

Polyesters, vinyl esters and epoxy resins account for ~90% of all structural composites. Any resin system for use in a composite material will require the following properties:

- good mechanical properties
- good adhesive properties
- good toughness properties
- good resistance to environmental degradation

4.5.3 Mechanical properties of the cured resin system

The stress–strain curve for an ‘ideal’ resin system (see Figure 4.11) indicates that the material has a high ultimate strength, stiffness and strain to failure. Changes in resin type will be reflected in the tensile strength and stiffness. Figure 4.12 compares the values for typical polyester, vinyl ester and epoxy resin systems cured at 20°C and 80°C. After a curing period of seven days at room

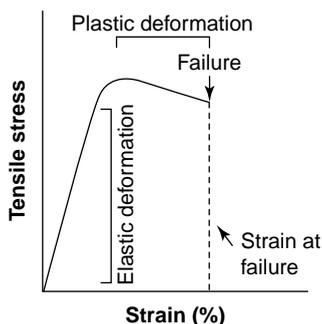


Figure 4.11 Stress–strain plot for an ideal resin.

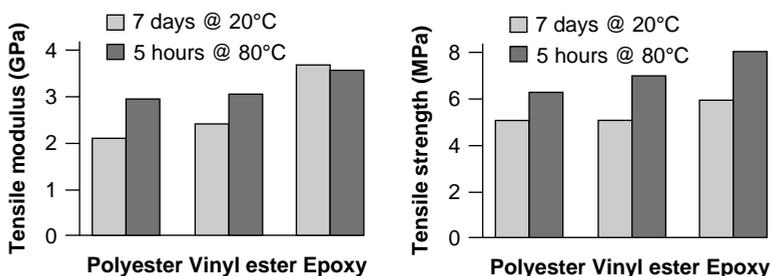


Figure 4.12 Typical mechanical properties for polyester, vinyl ester and epoxy resins obtained using different times and temperatures of cure.

temperature, a typical epoxy will have higher mechanical properties than a typical polyester and vinyl ester for both strength and stiffness. Postcuring at 80°C leads to significant enhancement of the mechanical properties.

4.6 Commercial thermoplastic polymers

The composition of a commercial polymer will depend on its intended application. Most systems will contain: polymer 40–100%, fillers 0–40%, plasticisers 0–60%, antioxidants 1–6% and processing agents 0–5%. All the above may influence the physical properties of the material. Fillers may be especially beneficial and can increase the modulus of a plastic but can also lead to a reduction in some physical properties.

4.6.1 Antioxidants

These are organic molecules which are added to the mixture to stop the depolymerisation reaction and inhibit the reduction in molar mass which occurs when the polymer approaches its ceiling temperature. At the ceiling temperature a polymer will spontaneously decompose to produce radicals. Many antioxidants are hindered amines which are able to scavenge the free radicals and suppress the degradation processes.

4.7 Fillers

A variety of fillers are used with polymers. They can be divided into two types: reinforcing and nonreinforcing fillers. They differ in their interaction with the polymer. Hence, it is possible for a material to be a reinforcing filler in one situation and a nonreinforcing filler in another. Typical fillers are: quartz, fused silica, sand, talc, calcium carbonate, carbon black, carbon fibres, glass fibres, kevlar (polyimide), polyethylene fibres, wood fibres and sawdust.

4.7.1 Carbon black

Carbon black is commonly used to produce black plastic products. It is produced by the partial combustion of various organic media, usually high molar mass hydrocarbon materials. The process generates graphitic materials that have dimensions of typically 1–20 μm. A close examination of the particles indicates that they are porous and are created by the fusion of smaller particles. Using similar techniques, it is possible to create Buckminster fullerene (C₆₀), or nanotubes that are the cylindrical equivalent of the spherical C₆₀ structure. The typical carbon black is a less perfect fusion of graphite platelets and structures which resemble the more exotic spherical and tubular forms of carbon (see Figure 4.13).

There are a variety of different types of carbon black, their properties depending on the conditions used in their formation. Conducting blacks will contain larger graphitic structures and may have additional functional groups that reflect the nature of the gas stream used in their formation. Acid blacks are usually postoxidised using nitric acid, nitrogen oxides (N₂O₄, N₂O₅, NO) or ozone. The types of surface chemistry found on carbon blacks are illustrated in Figure 4.13.

The main physical differences between various carbon blacks are their surface area and porosity. Surface areas can typically range from ~100 m² g⁻¹ to over 600 m² g⁻¹. The pore size will influence whether or not polymer molecules can enter the internal structure of the carbon black and hence its ability to reinforce the matrix. Some carbon blacks will *not* reinforce the matrix whereas others can. However, it is possible that a nonreinforcing carbon black is capable of reinforcing a thermoset, where penetration of the monomer is possible.

There are at least seven different ways of producing carbon black:

- *Lamp-black process*: Produces carbon black from burning rubber or paint. The particle size can vary in the range 50–120 μm. The carbon black is produced by depositing the product of combustion in a flue.
- *Thermal process*: The process uses two furnaces that run alternately for about five minutes; one is heated with a mixture of natural gas and air and the other has a stream of 100% natural gas. A coke oven produces thermal decomposition and the carbon black particles have sizes in the range 120–500 μm.
- *Channel process*: This process burns natural gas through a large number of small luminous flames impinging on slowly moving cooled iron channels, forming fine particle blacks of ~5–30 μm.

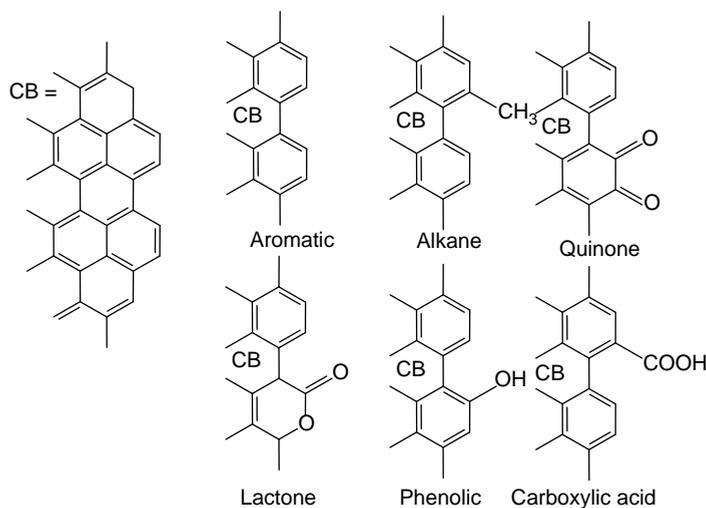


Figure 4.13 Types of chemical structure found on the surface of carbon black (=CB).

The product is removed mechanically from the channels and collected on a conveyor. The yield is only 3–6% of the theoretical maximum and channel blacks are expensive.

- *CK black process*: This is similar to the channel black process except that oil is used instead of gas. The average size of the particles is 10–30 μm and they are used as pigments.
- *Electric arc process*: The process is used to produce acetylene by hydrocarbon decomposition and yields large quantities of carbon black. The particle size is 35 μm, however, the particles are laminar or flaky, not spherical. This process also yields nanotubes and nanocarbon blacks.
- *Furnace process*: This differs from the channel process in that combustion of oil raw materials is carried out with a single large flame in a refractory lined furnace. The particle sizes are in the range 10–80 μm.
- *Acetylene black process*: The process is operated at 800°C and acetylene is decomposed into carbon and hydrogen in a self-sustaining exothermic process and the carbon is separated from the hydrogen gas stream. The particle size is typically 10–30 μm and contains nanomaterials.

Each carbon black has a different application depending on the media in which it is used and the extent to which conductivity is to be imparted to the object.

4.7.2 Quartz, silica and clay fillers

Silica in the form of sand, fumed silica and exfoliated clay is used to reinforce plastics. Many of the materials will have been derived from a geological source and are not perfectly defined from either the point of view of their chemistry or their physical properties. Two of the most abundant elements are silicon and aluminium and these combine to give a wide range of materials. Clays have been traditionally used as fillers for various plastics, and if treated with organic modifiers can be dispersed (exfoliated) to the level of the primary platelets and substantially enhance their physical properties. Clays can be classified according to their chemical composition, shape and size.

4.7.3 What is the structure of a clay?

The primary building block for a clay structure is a *tetrahedral sheet* composed of individual tetrahedrons based on silicon or aluminium which share three out of four oxygens. The primary units are arranged in a hexagonal pattern with the basal oxygens linked and the apical oxygens pointing up/down. The resultant sheet composition is T_2O_5 , where T is the common tetrahedral cation of Si, Al and sometimes Fe^{3+} and B. In many clays there are *octahedral sheets* in which individual octahedrons share edges composed of oxygen and hydroxyl anion groups with Al, Mg, Fe^{3+} and Fe^{2+} typically serving as the coordinating cation. The octahedral structures can be subdivided into dioctahedral (gibbsite) $Al_2(OH)_6$ and trioctahedral (brucite) $Mg_3(OH)_6$. If cation substitution occurs in the sheet structure, charge imbalances result and cations add into the layers to satisfy the charge imbalance or exchangeable cations (K, Ca, Mg, Na and many others). Variants on the structure of the layers arise from substitution of Al^{3+} and Fe^{3+} for Si^{4+} in the tetrahedral layer. In octahedral layered structures, the cations are usually Al^{3+} , Mg^{2+} , or Fe^{2+} , but such structures may also contain Fe^{3+} , Ti, Ni, Zn, Cr and Mn. In the octahedral layers, the anions are oxygen and a hydroxyl and some of the hydroxyls may be replaced by F or Cl ions.

Clays with an octahedral and a tetrahedral layer, e.g. kaolinite, which has a platelet dimension of 7 Å, are designated 1:1 clays. Clays which have an octahedral layer plus an interlayer are known as 2:1 clays, e.g. chlorite, which is trioctahedral and has a 14 Å basal spacing. The various clays are characterised by various charges. The neutral lattice structures are: talc (2:1), pyrophyllite (2:1), kaolinite (1:1), chlorite (2:1+1), all of which have a net charge of zero and their sheets are bound by van der Waals-type bonds. The high-charge 2:1 structures have charges in the range 0.9–1.0 created by ionic substitution, which is compensated for by an interlayer cation (K held firmly, dioctahedral). Low charge 2:1 structures have a 0.2–0.9 charge compensated for by loosely held ions which can easily be exchanged and have a tendency to swell. Dioctahedral clays (1:1 clays) include kaolinite $Al_2Si_2O_5(OH)_4$, dickite and halloysite $Al_2Si_2O_5(OH)_4$. The 2:1 clays include micas,

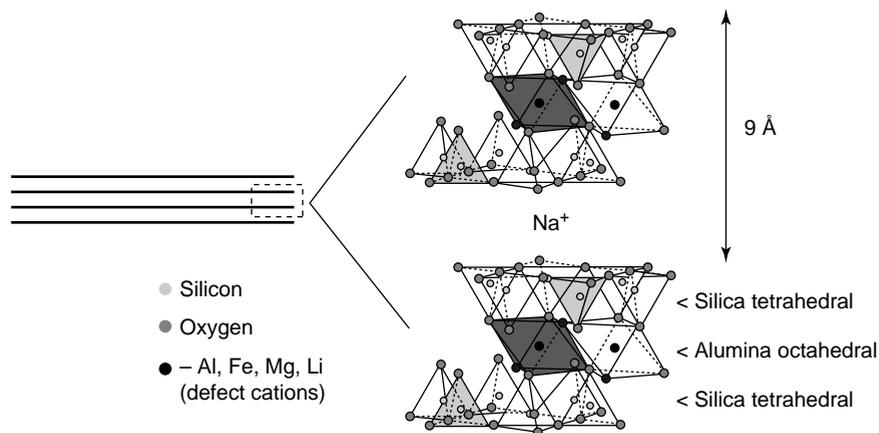


Figure 4.14 Schematic of platelet structure of montmorillonite.

pyrophyllite $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ and muscovite $\text{KAl}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$. Smectites include beidellite $\text{X}^+_{0.33}\text{Al}_2(\text{Si}_{3.67}\text{Al}_{0.33})\text{O}_{10}(\text{OH})_2$ and montmorillonite $\text{X}^+_{0.33}(\text{Al}_{1.67}\text{Mg}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2$. Vermiculites include altered smectite and illite $\text{K}_{0.8}\text{Al}_2(\text{Si}_{3.2}\text{Al}_{0.8})\text{O}_{10}(\text{OH})_2$. A typical layered structure is that of montmorillonite (see Figure 4.14). The silica and alumina elements fit together to produce a layered structure which is about 1 nm thick and will extend as sheets for distances of the order of one or more micrometres. In nature, the charge imbalances are matched by sodium hydrated ions which hold the platelets together. The exfoliation process is the dispersion of these platelets as individual sheets. To aid this exfoliation process organic cationic surfactant molecules are added to replace the sodium, increase the platelet separation and ease the exfoliation process.

These platelets have a large surface area and can reinforce the plastic raising the glass transition temperature by 10–20°C for the addition of 2–3% of exfoliated clay. The large sheets can overlap and are able to introduce barrier properties by increasing the percolation path for a gas moving through the material. Other clays have a ribbon structure and are useful as thixotropic index modifiers.

4.8 Plasticisers

These are usually low molecular weight polymers or small molecules. The necessary criteria are that they should be soluble in the polymer and this usually requires that they are chemically very similar to the polymer in which they are dispersed. Plasticisation has been discussed more fully in Section 2.5.3.

Brief summary of chapter

- Polymers can be broadly divided into two classes: thermoplastics and thermosets.
- The production of articles from these materials involves very different approaches to be adopted for the creation of useful structures.
- This chapter has summarised the chemical–physical issues associated with polymer fabrication.

Additional reading

Pethrick R.A. Cure monitoring. In: Kulshreshta A.K. and Vasile C. (Eds.) *Handbook of Polymer Blends and Composites, Vol. 1*, RAPRA, Shrawbury, UK, 2002, Chapter 10.

Pinnavaia T.J. and Beall G.W. *Polymer–Clay Nanocomposites*, Wiley, Chichester, UK, 2000.