28

THERMOSETTING POLYMERS

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28.1 INTRODUCTION

Thermosetting polymers (also called *thermosets*) are a family of plastics characterized by the fact that they are formed starting from a liquid solution that irreversibly leads to a solid material during a heating step. In this sense, they exhibit an opposite behavior than the one of thermoplastic polymers that, with some exceptions, show a reversible solid-to-liquid transition when heated to a convenient temperature. Although the irreversible liquid-to-solid transition can be also produced by other means such as UV or electron beam irradiation, the resulting products are also called *thermosetting polymers*. The process by which the initial liquid solution is transformed into a solid is usually known as the *cure of the material*.

The initial liquid solution is usually composed of several ingredients, the most important ones being a mixture of comonomers that can react among themselves by an external action such as heating, UV-irradiation, etc. The self-reaction of a single monomer can be also employed. The rest of the ingredients can be initiators, catalysts, rubbers, fillers, fibers, pigments, etc. The necessary condition to generate a thermosetting polymer is that the single monomer or one or more of the comonomers has three or more reactive groups per molecule. This produces a tridimensional crosslinked structure that occupies all the reaction volume. The chemical reaction is, in most cases, irreversible so that turning the resulting material into a liquid state would require the breaking of the generated covalent chemical bonds, a process that leads to degradation of the material instead of the recuperation of the initial comonomers. This imposes a severe restriction on the process leading to a thermosetting polymer. Once the chemical reaction has been completed, it is not possible to reshape the final material.

The only possible action is to mill the solid material and use it as a filler. Knowledge of the chemical reactions taking place and the reaction heat is essential to design a cure process. Thermoplastic polymers are easier to process in the sense that their transformation from a solid to a liquid (heating) and back to a solid (cooling) is reversible. If there is a mistake, the final material (e.g., without the required thickness, size, or shape) can be recycled to the process.

A large variety of families of thermosetting polymers is used in industry. Phenolics were the first synthetic plastic produced in an industrial scale since the beginning of the twentieth century. They are thermosetting polymers formed by the reaction of phenol (a monomer with three reactive sites located in o, o', and p positions) with formaldehyde (a comonomer with two reactive sites), and eventually another multifunctional comonomer, such as hexamethylenetetramine, added in a second step (for two-step processes). Of interest is the fact that they were produced by industry almost 15 years before the macromolecular structure of a polymer was formulated by Herman Staudinger, proving that on many occasions industrial innovations precede the formulation of the scientific background on which they are based. A second fact of interest is that phenolics still keep a niche in the market due to their outstanding dimensional stability, electrical properties, and resistance to creep at elevated temperatures. For example, formulations based on phenolics are used as the dielectric insulator in connectors for the space shuttle.

Many other families of thermosetting polymers have also found their niches in the global market. Some common examples are urea–formaldehyde and melamine–formaldehyde polymers, epoxies, unsaturated polyesters (UPs), and polyurethanes (PUs). Some typical

applications of these polymers are in wood agglomerates for furnishing (urea–formaldehyde polymers), laminates (melamine–formaldehyde polymers), coatings, adhesives, composite materials, electronic applications (epoxies), glass-fiber-reinforced plastics (UP), and insulating foams (PU). Formulations based on these polymers with a set of improved properties are continuously being developed by introducing new modifiers such as carbon nanotubes (CNTs), clays, or polyhedral oligomeric silsesquioxanes (POSS), or producing nanostructures using block copolymers (BCPs) or amphiphilic monomers [1]. These formulations are focused on high tech applications (optoelectronics and multimedia, telecommunications, energy storage and production, medical applications, etc.). New processing techniques with their corresponding equipment are continuously offered by several companies, proving the dynamic character of this field.

Although epoxies are mainly classified as thermosets, it is also possible to produce linear epoxy polymers using comonomers with two reactive sites per molecule. These linear polymers behave as thermoplastics and can be amorphous or semicrystalline. They exhibit some outstanding optical and barrier properties. Similarly, PUs can be either thermoplastics or thermosets depending on the number of reactive sites per molecule of monomers and comonomers.

Other thermosetting polymers are cyanate esters (CEs), benzoxazines, PU acrylates, bismaleimides (BMIs), dicyclopentadienes (DCPDs), diallyl phthalates (DAPs), etc. Formulations based on these polymers are used for specific applications where their particular properties are required. For example, DAP has long been the material of choice for electrical components where long-term reliability is required.

28.2 CHEMISTRIES OF NETWORK FORMATION

The description of the variety of chemistries that are used to produce thermosetting polymers can be the subject of a whole book and is beyond the scope of this chapter. A description of chemistries involved in the synthesis of several families of thermosets can be found elsewhere [2]. In this section, we focus on some aspects of the chemistry of epoxy polymers because it provides examples of both step-growth and chain-growth polymerizations employed in the synthesis of polymer networks.
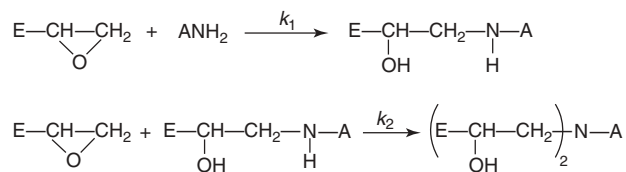
Scheme 28.1 Reaction of epoxy groups with amines.

The epoxy group (oxirane ring) can react with both nucleophilic and electrophilic reagents. The most typical example of a step-growth polymerization of epoxy monomers is the reaction with amines, which are the most commonly curing agents/hardeners used to build up epoxy networks. The reactions shown in Scheme 28.1 take place in this case.

The multifunctional monomer with more than two reactive sites per molecule may be either the epoxy monomer or the amine comonomer. Diglycidylether of bisphenol A (DGEBA), with two epoxy groups per molecule, is a typical epoxy monomer (Scheme 28.2).

The step-growth polymerization between the 2-functional DGEBA and a 4-functional diamine (containing four active amine hydrogens in the structure) leads to a polymer network. The reactivity of the amine increases with its nucleophilic character: aliphatic > cycloaliphatic > aromatic. While for aliphatic and cycloaliphatic amines, primary and secondary amine hydrogens exhibit similar reactivities, for aromatic amines the reactivity of the secondary amine is 2–5 times less than the reactivity of the primary amine hydrogen. This means that once the primary amine reacts, the generated secondary amine exhibits a lower reactivity, a fact that is called a *substitution effect*. Aliphatic amines are used in low temperature curing formulations such as adhesives and coatings, while aromatic amines are used for high temperature cure cycles as those used for the manufacture of composite materials.

Hydroxyl groups catalyze the reaction through the formation of a trimolecular complex that favors the nucleophilic attack of the amino group, as shown in Scheme 28.3.

Apart from species containing OH groups that may be added as catalysts, the epoxy–amine reaction generates OH groups. Therefore, the reaction is self-catalyzed by reaction products, a fact that leads to sigmoidal conversion versus time curves when the polymerization is performed at a constant temperature.
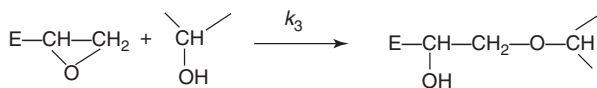
In most cases, when stoichiometric amounts of epoxy and amine comonomers are used, no side reaction takes
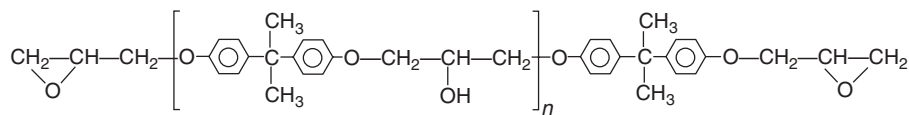
Scheme 28.2 Structure of diglycidyl ether of bisphenol A (DGEBA).
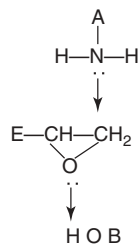
Scheme 28.3 Trimolecular complex that catalyzes the epoxy-amine reaction.


Scheme 28.4 Reaction of epoxy groups with secondary alcohols.

place. When there is an excess of epoxy groups, the reaction shown in Scheme 28.4 can take place after most of the amine hydrogens have reacted.

Epoxy monomers undergo a chain homopolymerization in the presence of both the Lewis acids as boron trifluoride complexes (cationic homopolymerization) or bases such as tertiary amines, imidazoles, and ammonium salts (anionic homopolymerization). These acids and bases are called *initiators* of the chain polymerization. In this reaction, each epoxy group acts as a bifunctional reagent in the propagation step, and therefore, a diepoxy monomer such as DGEBA becomes a 4-functional monomer leading to a polymer network. Figure 28.1 shows initiation and propagation steps of the anionic homopolymerization of epoxy groups. The scheme is completed by transfer reactions involving the transfer of an H from an OH group to the propagating chain, and complex termination reactions that depend on the particular formulation.

Initiation and propagation steps taking place in the cationic polymerization of epoxy monomers initiated by BF_3 complexes are shown in Figure 28.2.
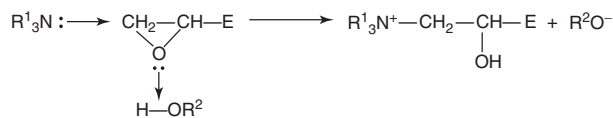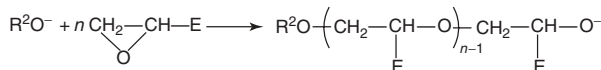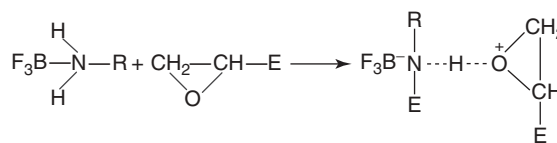

Figure 28.1 Initiation and propagation steps of the anionic homopolymerization of epoxy groups.

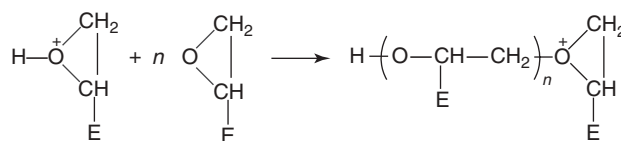• Initiation with BF_3 complexes

• Propagation

Figure 28.2 Initiation and propagation steps taking place in the cationic polymerization of epoxy monomers initiated by BF_3 complexes.

An usual way to generate a strong acid as an initiator of cationic polymerizations is by the UV decomposition of a complex aromatic salt of a Lewis acid. Cycloaliphatic epoxy monomers are used in this reaction because they exhibit higher reactivities than those of glycidylether epoxies such as DGEBA. These formulations are used in photopolymerization processes whose main advantage apart from the fast reaction rate is the insensitivity to oxygen (contrary to free-radical polymerizations).

Another usual family of hardeners employed to cure epoxy monomers are cyclic anhydrides, with the reaction initiated by tertiary amines or ammonium salts. The reaction proceeds through an alternating chainwise copolymerization, as shown in Figure 28.3.

The reaction of an alkoxide group with a cyclic anhydride is much faster than the reaction of a carboxylate group with an epoxy ring.

Several epoxy formulations are cured by both step-growth and chain-growth polymerizations occurring sequentially or in parallel. For example, BF_3 complexes or tertiary amines may be added as catalysts of an amine–epoxy reaction, leading to different reaction mechanisms taking place whose relative significance depends on the cure temperature (or thermal cycle) and the initial stoichiometry. The structure and properties of the resulting polymer networks depend on the relative contribution of both mechanisms.

28.3 STRUCTURAL TRANSFORMATIONS DURING NETWORK FORMATION

28.3.1 Gelation

Gelation occurs at a conversion where percolation of a giant molecule takes place throughout the system. At this critical
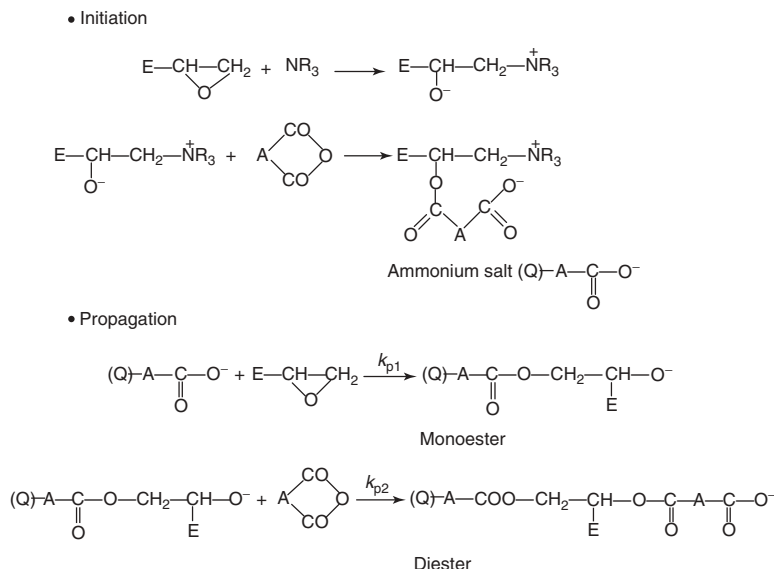
Figure 28.3 Chainwise copolymerization of epoxy monomers with cyclic anhydrides.

conversion, the system consists of a large number of finite molecules (the sol fraction) and one giant molecule (the gel fraction). From the macroscopic point of view, this implies the irreversible transition from a liquidlike to a solidlike behavior, which enables its characterization by monitoring the viscoelasticity of the sample during reaction. Gelation can be estimated as the time (conversion) where the elastic modulus becomes higher than the loss modulus. A more precise definition of gelation arises from the time (conversion) at which the ratio of both moduli (tan δ) becomes independent of the frequency of the experimental run [2]. The gel conversion depends on the functionality (number of reactive sites) of comonomers. The higher the functionality, the lower the gel conversion.

28.3.1.1 Stepwise Polymerizations

For stepwise polymerizations of stoichiometric formulations of comonomers with f and g active sites per molecule exhibiting an ideal behavior (equal reactivity of functional groups, absence of both substitution effects and intramolecular cycles), the gel conversion (x_{gel}) is given by:

$$x_{gel} = \frac{1}{\left[(f-1)(g-1)\right]^{1/2}} \qquad (28.1)$$

For the ideal step-growth polymerization of a diepoxy monomer such as DGEBA ($f = 2$) with a diamine ($g = 4$), the gel conversion is $x_{gel} = 0.577$. Experimental values close to 0.60 have been reported for many DGEBA–diamine formulations in close agreement with the theoretical prediction. The slight departure from the ideal value is often ascribed to the presence of substitution effects.

28.3.1.2 Chainwise Polymerizations

A typical example of a thermoset produced by a chainwise polymerization is the case of the cure of unsaturated polyesters with styrene by a free-radical mechanism. Styrene is a bifunctional monomer, A_2, characterized by the presence of one C=C group that is transformed into a –C–C– bond in the polymerization reaction. The unsaturated polyester is a multifunctional monomer, A_f, characterized by the presence of ($f/2$) C=C groups in its chemical structure. The molar fraction of C=C groups belonging to the multifunctional monomer is given by:

$$a_f = \frac{f A_f}{2 A_2 + f A_f} \qquad (28.2)$$

The gel conversion for the ideal chainwise polymerizations of an $A_2 + A_f$ system is given by the following equation [3]:

$$x_{gel} = \frac{2}{\left[a_f (f-2)(DP_w - 1)\right]} \qquad (28.3)$$

where DP_w is the mass-average degree of polymerization of primary chains produced by single activation and termination steps. Its value is given by:

$$DP_w = \frac{1 + q + \zeta}{1 - q} \qquad (28.4)$$

where

$$q = \frac{R_p}{R_p + R_t + R_d + R_c} \qquad (28.5)$$

$$\zeta = \frac{R_c}{R_t + R_d + R_c} \qquad (28.6)$$

Once initiated, a chain propagates at a rate R_p until termination takes place by one of the following events: chain transfer (rate R_t), chain disproportionation (rate R_d), or chain combination (rate R_c). For free-radical polymerizations, the probability of chain propagation is very much larger than the probability of termination by any one of the possible mechanisms. This means that $q \to 1$ and $x_{gel} \to 0$. In practice, the polymerization is far from being ideal. A large fraction of intramolecular cycles is produced leading to high crosslinked domains (microgels) embedded in a solution of unreacted monomers. Eventually, these microgels form an interconnected structure and macrogelation is produced, typically at conversions in the range of 5–15%.

28.3.2 Vitrification

The other independent transformation that can take place during network formation is vitrification. This transition occurs at the particular conversion where the increasing glass-transition temperature (T_g) of the reacting system equals the instantaneous value of the cure temperature. At this time, the macroscopic behavior of the system changes from a liquid or rubber to a glass. This means an increase of several decades in the value of the storage modulus.

Several equations have been proposed to describe the increase of T_g with conversion (x). A particular expression that was used to fit experimental data of a large variety of thermosetting polymers is the following one [4]:

$$\frac{T_g - T_{g0}}{T_{g\infty} - T_{g0}} = \frac{\lambda x}{1 - (1 - \lambda)x} \qquad (28.7)$$

where T_g is the value of the glass-transition temperature at the particular conversion x, T_{g0} and $T_{g\infty}$ are, respectively, the initial ($x = 0$) and final ($x = 1$) values of the glass transition temperature, and $\lambda = \Delta C_{p\infty}/\Delta C_{p0}$ is the ratio of specific heats between liquid or rubber and glass, for the final material ($\Delta C_{p\infty}$) and the initial material (ΔC_{p0}). The evolution of T_g with conversion may be predicted by characterizing the initial and final materials using differential scanning calorimetry (DSC). For some polymer networks, full conversion cannot be attained due to limitations imposed by topology or by degradation when the temperature is increased to avoid vitrification. A specific system where full conversion cannot be attained is the reaction between epoxidized novolacs with aromatic diamines [5]. For these thermosetting polymers, Equation 28.7 can still be applied by replacing $T_{g\infty}$ by $T_{g\,max}$, x by x/x_{max}, and λ by $\lambda' = \Delta C_{p\,max}/\Delta C_{p0}$, where $T_{g\,max}$ and ΔC_{pmax} are the values obtained at the maximum attained conversion, x_{max} [5, 6].

28.3.3 Conversion-Temperature Transformation (CTT) Diagram

Gelation, vitrification, and degradation curves can be plotted in the conversion-temperature transformation (CTT) diagram shown in Figure 28.4 [2, 6, 7]. The degradation curve is the boundary of a high temperature region where chemical degradation of the polymer network takes place. It is assumed that the stability toward thermal degradation of the reacting polymer increases with conversion.

Below the degradation curve, the diagram shows four different regions separated by the gelation and vitrification curves. Below the vitrification curve, the partially reacted thermosetting polymer is in the glassy state, either as an ungelled or as a gelled glass. Above the vitrification curve, the reactive polymer is present as a liquid or as a rubber, depending on the location of its actual conversion with respect to the gel conversion.

How do gelation and vitrification affect the kinetics of network formation? Let us first consider gelation. This transition is related to the formation of a percolating structure in the reaction medium, a fact that does not alter the reaction probability of chemical groups (they do not sense the occurrence of percolation). This means that kinetic equations are not influenced by gelation. For stepwise polymerizations, reactions paths that describe the kinetics of network formation depend only on concentration of reactants and temperature. The same equations describe the kinetics before and after gelation. For chainwise polymerization, some of the elementary steps must be expressed as a continuous function of conversion (e.g., Ref. 8). An acceleration in the overall reaction rate is usually observed due to the decrease in the rate of termination steps requiring the mobility of long chains (the so-called Tromsdorff's effect). However, there is no special change in the kinetic
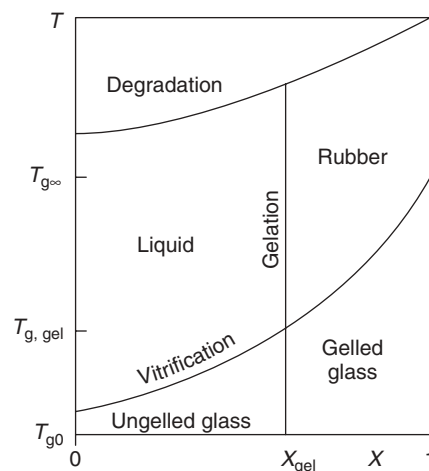

Figure 28.4 Conversion-temperature transformation (CTT) diagram.

equations due to gelation. On the other hand, vitrification produces a large decrease in the polymerization kinetics because it is directly related to the mobility of polymer segments. Kinetic equations must include a diffusional resistance that increases in importance as the system evolves beyond the vitrification curve. At some point, inside the glassy region chemical reactions become practically arrested and the polymer needs to be heated to the other side of the vitrification curve to continue the polymerization.

At room temperature, most thermosetting polymers are present as gelled glasses. Therefore, the most important properties of thermosetting polymers for practical purposes are those in the glassy state.

The CTT diagram may be employed to visualize the transformations occurring during specific thermal cycles selected for the polymerization. Isothermal trajectories at temperatures comprised between T_{g0} and $T_{g,gel}$ (temperature at which vitrification and gelation curves intersect) lead to a material that vitrifies before gelation. Vitrification is not a sharp transition, but it extends over a conversion range with its amplitude depending on the structure of the specific thermosetting polymer. For usual ways of defining the glass transition, the reacting polymer increases its conversion beyond the vitrification curve up to a point where the difference $(T_g - T)$ is in the order of 20–30 °C. If this point is located in the region of an ungelled glass, the partially reacted polymer may be reactivated and processed by heating to a temperature located in the liquid region of the CCT diagram.

A partially reacted thermosetting polymer located in the ungelled glass region is denominated (in some old literature) as the B-stage of the polymer. This simply means that the polymer can be reconverted to a liquid by heating and then processed with conventional techniques. However, keeping isothermal trajectories is not easy in industrial practice due to the high exothermic reaction heat of most thermosetting polymers. These thermal excursions can lead to degradation of the polymer, making it necessary to model the expected evolution of temperature profiles in the material through mass and energy balances [2]. These models enable to select cure cycles that conduct the reacting polymer through the liquid and rubbery regions, ending at a temperature higher than $T_{g\infty}$ at full conversion.

28.4   PROCESSING

28.4.1   Formulations

The monomers, comonomers (hardeners), catalysts, and initiators are the components of the formulation that define the thermosetting polymer. Depending on the desired properties of the final material, a variety of other components may be part of the initial formulation. Fillers

(e.g., calcium carbonate, sawdust, recycled powdered thermosets, etc.) are used to improve mechanical properties and/or to reduce costs. Short fibers (glass, carbon, cellulose, etc.) are used to improve mechanical properties. Continuous fibers (glass, carbon, aromatic amides, etc.) are used in the manufacture of composite materials where the thermosetting polymer acts as the matrix that fixes the structure made of continuous fibers. Main mechanical properties are determined by the structure of fibers. Other usual additives are pigments and processing aids (e.g., additives that facilitate demolding of a cured part).

The intrinsic brittleness of most thermosetting polymers is a problem for their use as adhesives and coatings. Toughening can be achieved by producing a dispersion of rubbery particles or thermoplastic polymers inside the thermosetting polymer [9]. Core-shell particles with a rubbery core and a thin shell compatible with the thermosetting polymer can be used for these purposes. These particles can be produced by a two-stage latex emulsion polymerization technique. The core is a graftable crosslinked elastomer ranging in size from about 30 nm to 2 μm. The shell is grafted to the core and its chemical composition is selected to be as compatible as possible with the thermosetting polymer. This enables to achieve the formation of stable dispersions that can eventually generate partial aggregates during the cure. Another way to produce a dispersion of rubbery or thermoplastic particles is to start with a solution of a rubber or a thermoplastic in the precursors of the thermosetting polymer. Solubility is achieved by using low molar masses and compatible chemical structures. During polymerization a reaction-induced phase separation (RIPS) takes place mainly due to the decrease of the entropic contribution to the free energy of mixing [10]. This produces a dispersion of particles of the linear polymer in the thermoset. In general, rubbers exhibit an expected better toughening behavior than thermoplastic particles but produce a decrease in the elastic modulus and the glass transition temperature. Some thermoplastics give a reasonable toughening without deleterious effects on thermal and mechanical properties.

28.4.2   Rules for Processing Thermosetting Polymers

The main characteristic of thermosetting polymers is that polymerization and final shaping are performed in the same process. For a clear understanding, the evolutions of viscosity and modulus during curing at constant temperature are schematically plotted as a function of reaction time as shown in Figure 28.5.

Before gelation the material is a liquid with a finite value of viscosity. As the reaction proceeds, the viscosity increases and it tends to infinite at the sol–gel critical transition when a giant macromolecule percolates through the sample. After gelation, the mass fraction of the insoluble
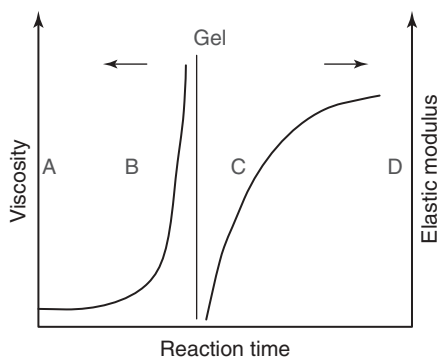
Figure 28.5 Evolution of viscosity and elastic modulus during the cure of a thermosetting polymer.

giant structure increases continuously and so does the elastic modulus of the sample. Shaping of the part has to be performed before the gel point where the material is still in the liquid state.

Most of the processing techniques have to take into account four different steps that depend on temperature, pressure, reaction rate, and the evolution of viscoelastic properties:

1. the pot life of the reactive system at the storage temperature (important before the beginning of the process);
2. flow inside the processing machine and into the mold (processing window);
3. reactions in the mold or on a substrate (for coatings and adhesives);
4. demolding and eventual postreaction.

The reactive system can be a one- or a two-pack system. Normally end users prefer a one-component system with a long pot life at room temperature and a high reactivity in the mold at a temperature as lower as possible. These two conditions are in contradiction with the Arrhenius law that can, however, be bypassed by the use of blocked reactants or by reactions activated by radiations.

The rheological evolution of the reactive system depends both on temperature and conversion. The chemoviscosity of thermosetting polymers is an important issue in relation to processing [11].

Processing techniques for thermosetting polymers are described in what follows in relation to the most extended applications.

28.4.3 Thermosetting Polymers for Adhesives, Coatings, and Paintings

28.4.3.1 Chemistries
A large majority of adhesive and coating films in the end-use state exist in the form of a polymer network. Chemistries for adhesives and coatings are either classical step-growth (epoxy/amine, epoxy/acid, isocyanate reactions, phenolics, trans-reactions of melamine, etc.) or chain-growth polymerizations (radical polymerization of acrylic or unsaturated polyesters, cationic polymerization of epoxies, etc.). Network formation is a very important process in film formation and the structure of the thermosetting polymer determines the application properties of the film [12]. Formulations are rather complex and additional components such as solvents, pigments, fillers are usually introduced to control the final properties.

Because of their excellent photooxidative durability, acrylic monomers are most often used in coatings. Hardness and softness, refractive index, chemical and humidity resistance, degree of durability, and degree of crosslinking are easily designed with an acrylic copolymer. Inherently, however, acrylic copolymers are not very flexible. To solve this problem, low T_g oligomers with acrylic functional groups are introduced in the formulation.

Formulations containing aromatic molecules such as aromatic isocyanates or epoxies not only suffer from poorer durability than formulations based on aliphatic monomers but they yellow severely on exposure to sunlight.

28.4.3.2 Solvent-Borne Coatings
The majority of conventional coatings are solvent borne, traditionally containing about 25% solids. Organic solvents are added to coatings to disperse the different constituents of the formulation and to provide the low viscosity needed for conventional application methods (spray, roller coating, etc.). Once solvents are eliminated, the thermosetting polymer provides the physical properties of the coating.

Solvent-based coating films are formed by simultaneous crosslinking of polymer network precursors and solvent evaporation. This is a complex process in which the crosslinking rate and the development of the network depend on the content and nature of the solvent. Solvent evaporation depends not only on solvent volatility but also on the structure of the crosslinking system (thermodynamic interactions and chemical potential). The progress of chemical reaction and the rate of solvent evaporation determine the increase in T_g. When T_g approaches or exceeds the reaction temperature, the curing reaction becomes diffusion controlled and greatly retarded. The solvent evaporation slows down as well. The retention of residual solvent in the coating film even after long drying times (especially in the case of ambient temperature drying) is a very serious problem affecting the quality and durability of coating films [13].

As coating and paint producers as well as end users wish to reduce the volatile organic compound (VOC) emissions, progresses are made to increase the solids contents of solvent-based liquid coatings (high solid formulations). The challenges are finding more effective rheology-control agents, polymer architectures giving better control of the

placement of functional groups, and adequate catalysis to control the rate of curing.

28.4.3.3 Waterborne Coatings

Water-borne coatings are based on formulations in which water is the primary "solvent." Water-borne coatings constitute a strongly growing segment of the coatings' market. Not only do water-borne formulations result in lower odor, easier clean-up, and decreased fire hazards than their solvent-borne counterparts, but they are also one of the key choices for reducing VOC emissions.

The polymers used in waterborne coatings can be either soluble or dispersed in water (or a combination of water and a cosolvent). The problem of formulations containing soluble polymers is that the presence of polar/hydrophilic groups in the polymer makes the final films more sensitive to humidity. For this reason, a better solution is to formulate hydrophobic polymers that are stabilized in water by internal or external surfactants forming emulsions. Emulsified polymers have high molar masses but because they are dispersed in a particulate form, the viscosity of the media is not sensitive to their molar masses. Therefore, the physical properties are expected to be less dependent on the cure reactions.

An important class of waterborne coatings is the family of polyurethane dispersions (PUDs). Ionizable groups (usually carboxyl) incorporated to the PU backbone allow the polymer to be dispersed in water after neutralization with amines. The properties can be varied substantially depending on the structure of the polyol and diisocyanate used to prepare them. Aliphatic and cycloaliphatic isocyanates are preferred because of their low reactivity with water and

to prevent yellowing of the film. However, the key problem is to control the coalescence of the initially stabilized polymer particles. Coalescence of these particles is often incomplete in the final film and may take a long time to reach equilibrium. In some cases, the film is postcured by a polyisocyanate leading to isocyanurate (or uretdione) structures (Fig. 28.6), to increase its thermal stability. This is accomplished by the use of a two-component system.

28.4.3.4 Radiation-Cured Coatings

Radiation (ultraviolet light and electron beam) is a means of curing coatings that can be effectively used for heat-sensitive substrates because the curing can be carried out at ambient temperature. In addition, UV curing can bring many benefits to the coatings manufacturer in terms of increased productivity and lower labor costs as well as providing the possibility to reach the ever-increasing demands of legislation in terms of environmental compatibility. Within UV-cured coatings, the key and most critical part of the formulation is the photoinitiator. The two commonly used functional groups are (meth)acrylates (requiring free-radical initiators) and epoxies (that need cationic initiators). The other problem to solve is to find a compromise between the viscosity of the initial formulation, the final crosslink density, and the film hardness and toughness. This can be achieved by adjusting the ratio between different monomers and reactive oligomers of different molar masses [2]. However, as the morphology of photo-cured acrylate films is rather complex [14], properties of films such as elongation at break are limited compared to those of PU coatings.

28.4.3.5 Powder Coatings

Powder coatings are produced by an extrusion process. The two-component powder
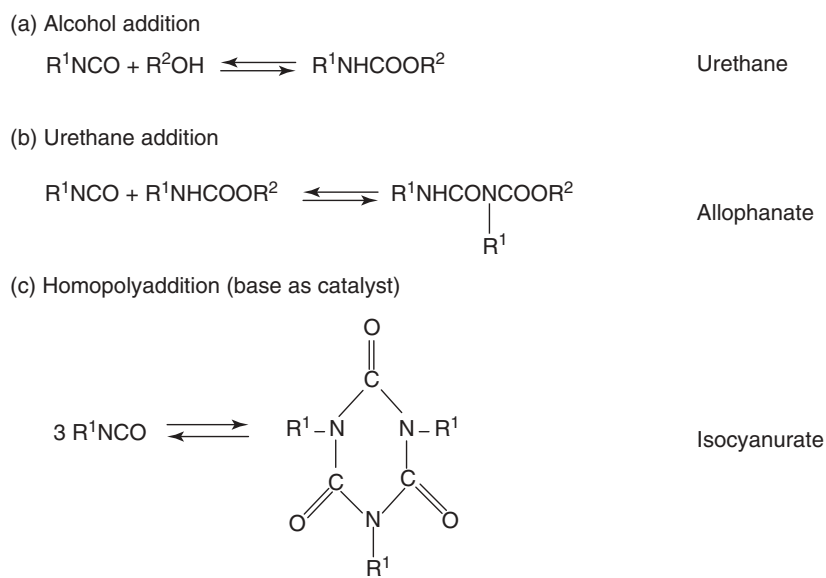

Figure 28.6 Different reactions of isocyanate groups.

(plus additives) is applied onto the substrate by electro-spray; then, the substrate is heated above T_g (or the melting temperature, T_m) to produce film flow and crosslinking. The requirements for a powder coating formulation are as follows:

1. T_g (or T_m) must be at least $20–30\,°C$ above ambient conditions to store and handle powders.
2. Low molar mass to allow enough flow above T_g (or T_m), to obtain smooth films before the beginning of cure (processing window).
3. The cure temperature must be placed at $40–50\,°C$ above T_g (or T_m) to achieve a convenient flow leading to film homogeneity. If the flow is controlled by T_m instead of T_g, the situation is slightly eased because the melting point is a much sharper transition than the glass transition.

Various systems are available depending on the end use. Typical systems are based on saturated polyesters, α,ω-acid-terminated cured with an epoxy (triglycidyl isocyanurate TGIC), or α,ω-OH-terminated cured with an isocyanate (or a blocked isocyanate). Recently, bio-based formulations with aliphatic nonyellowing monomers have been proposed [15].

The generation of a convenient processing window is difficult for most known crosslinking chemistries. This has limited the use of powder coatings at temperatures lower than about $130\,°C$, a fact that precludes their use on many plastic substrates. Efforts to develop radiation-curable powder coatings are ongoing.

28.4.4 Reaction Injection Molding

Reaction injection molding (RIM) is similar to thermoplastic injection molding except that thermosetting polymers are used, making it necessary a curing reaction to occur within the mold. The process involves the high speed mixing of two or more reactive chemicals, just as they are injected into the mold. The low viscous mixture fills the mold at relatively low temperatures and pressures. The reactions must be synchronized with the process so that gelation does not occur during the filling time [16].

The high pressure metering unit is one key element of the process. It must deliver the highly reactive starting ingredients to the mixhead with precise synchronization of two liquid streams, and within a few seconds inject them into the mold under high pressure using an impinging mixer. The other key element is the mixhead, which must deliver each stream at high velocity into the mixing chamber, accomplish this under precisely synchronized conditions, develop turbulence in the mix chamber so that the two streams are fully and rapidly mixed, and clean the chamber so that there is no build-up. The mixture is allowed to stay in the mold up to the time necessary to advance the cure to the point where mechanical properties of the part allow demolding. For some formulations, reaction is accompanied by foaming. Heat generated by the chemical reaction helps to cure the material, but the mold must be heated so that the edges do not cool more rapidly than the core. The entire process, from mixing to demolding, typically takes less than 1 min.

From the perspective of a life cycle analysis (LCA), the RIM process presents two winning cards with respect to thermoplastic injection molding: the use of liquids instead of thermoplastic granules and the necessity to use much less clamping force during the molding process.

Because isocyanate/alcohol and isocyanate/amine reactions are very fast, give no by-products, and attain high degree of conversion, they are well suited for RIM. For PU-RIM, part A in Figure 28.4 is filled with the diols plus a catalyst and usual additives such as antioxidants, pigments, etc., and part B with the isocyanate. Several nonisocyanate chemical systems such as the metathesis polymerization of a diolefin monomer, DCPD, epoxy, and free-radical chemistries have also been developed for RIM. The required temperatures to generate convenient processing windows vary for each of these systems. For a DCPD-RIM formulation, part A contains DCPD monomer, initiator, activator, and other additives; part B also contains DCPD monomer, the coinitiator, and additives. Ring opening polymerization of caprolactam adapted to RIM leads to a linear polymer, polyamide 6.

Common items made via RIM include rigid structural foams (for business equipment, housings, furniture, and building materials), low modulus elastomers (for automobile fascias, bumper, air spoilers, and fenders), high modulus elastomers (for large industrial and consumer parts requiring toughness and rigidity), and also some specialties such as ophthalmic lenses [17].

When reinforcing agents such as short glass fibers are added to the mixture, the process is known as *reinforced reaction injection molding* (*RRIM*). This process is used to produce rigid foam automotive panels. A subset of RRIM is structural reaction injection molding (SRIM), which uses fiber meshes previously placed in the mold as reinforcing agent.

Another similar process is in mold coating (IMC). The IMC is similar to the RIM process: a thermosetting formulation is first introduced into a closed mold and then cured by the high temperature of an injected thermoplastic [18]. This produces a coating (surface finish) of the thermoplastic part reducing time, space, material, and machinery requirements compared to a conventional two-step process. The process allows painted parts to be produced in similar cycle times as those used to produce the uncoated parts.

28.4.5 Thermosetting Polymers for Composite Materials

28.4.5.1 Introduction   Composites are materials consisting of a combination at a macroscopic scale of high strength stiff fibers embedded in a matrix. In this section, the discussion is restricted to composites where the matrix is a thermosetting polymer. The matrix holds the reinforcement in the desired shape while the reinforcement improves the overall mechanical properties of the matrix. When designed properly, the new combined material exhibits better strength than the one of each individual material. This is the basic difference between reinforced and filled systems in which fillers are used to reduce cost but often degrade the mechanical properties.

Fiber-reinforced composite materials can be divided into two main categories normally referred to as *short fiber-reinforced materials* (*L/D* < 100) and *continuous fiber-reinforced materials* (*L/D* > 100). They can be also categorized by their fiber characteristics such as (i) type (glass, carbon, aramide, etc.), properties (strength, stiffness, tensile elongation), and content; (ii) form (discontinuous or continuous); (iii) fiber alignment (random or unidirectional); and (iv) composite's layout (e.g., laminar with a given stacking sequence of plies). All these parameters affect the strength and stiffness of the final material. With these data, the material can be classified as high fiber volume or high performance composite. As an example, materials made by a build-up of plies in which the continuous fibers are oriented unidirectionally are often referred to as *advanced* or *high performance composites*.

The matrix allows the necessary positioning of the fibers, transfers the load to the fibers and distributes the stress among them, and is also responsible for protecting the reinforcement from the environment. However, the matrix is often the weakest component of a composite. One important parameter for the material properties is the fiber–matrix interface (or interphase), which guarantees the stress transfer from fiber to fiber via the matrix. The interface/interphase is a finite thin layer with its own (very often unknown) physical and chemical properties that depend on the fiber–matrix combination. Because of the low viscosity of the thermoset precursors, they wet the reinforcement better than a thermoplastic polymer.

The matrix is the weakest component of the composite determining the allowed maximum stress and the maximum service temperature. Great efforts have been undertaken to develop thermosetting polymers with increased temperature resistance. Cyanate-esters (CEs), BMI, and polyimides are the actual thermosetting matrices with higher thermal resistance.

Unique to the composites industry is the ability to create a product using many different manufacturing processes. The matrix and reinforcement (short or long fibers) can be combined in different ways to produce a wide variety of preforms and prefabricates, including granules, pellets, prepregs, and textile fabrics. Their form and appearance determine the processing alternatives for converting them to structural parts. The thermoset precursors can be put in contact with the fibers before or after placing the reinforcement material into the mold cavity or onto the mold surface. Once they are combined, they are compacted and cured.

Manufacturing processes can be split into two categories depending on the use of an open or a closed mold. A universal disadvantage of open-mold processes is that the material is only in contact with one side of the mold. Processes included in the open-mold category are wet lay-up techniques and bag molding. Processes pertaining to the closed-mold category are transfer molding, compression molding, and injection molding.

The physical changes that take place during composite manufacture include heating and cooling, pressure changes, fluid flow, and solidification (Fig. 28.5). Many interrelated issues are common to all composite processing techniques based on thermosetting polymers: (i) kinetic, statistical, and rheological aspects of network formation (viscosity vs extent of reaction, gelation time); (ii) matrix–fiber interfacial interactions; (iii) macroscopic and microscopic flow of the reacting thermosetting polymer in a confined geometry, preform deformation; (iv) heat transfer and heat production by chemical reaction; (v) temperature and conversion profiles; and (vi) dimensional stability (control of the shrinkage due to reaction and temperature variation).

Each one of the previous issues can influence the performance of the processing technique and the resulting composite in a variety of ways. Insufficient cure may result in a low T_g and a consequent creep under stress. Inadequate flow may result in high levels of porosity or large voids. Online sensor systems permit process control [19] and are a useful tool toward improved quality in composites manufacture. Dielectric techniques have achieved the greatest success as commercial *in-process* monitoring systems. Optical-fiber methods show promise for further development, most notably where distinct features in chemical spectra can be obtained.

For the choice of a process, an important factor is the amount of material to be produced. Large quantities can be used to justify high capital expenditures for rapid and automated manufacturing technology. Small production quantities are accommodated with lower capital expenditures but higher work and tooling costs at a correspondingly slower rate.

The finishing of the composite parts is also critical in the final design. Many of these finishes will include exterior erosion coatings, which can be deposited *in situ* (IMC) or during a separate operation.

28.4.5.2   Processes for Small Series

Wet Lay-Up Process.   Formulations are impregnated by hand or sprayed into fibers that are in the form of woven, knitted, stitched, or bonded fabrics. This is usually accomplished by rollers or brushes. Spray-up is a partly mechanized version of the hand lay-up process. The thermoset precursor is applied by means of a spray gun to the mold surface simultaneously with the chopped glass-fiber roving. Laminates are left to cure under standard atmospheric conditions.

Both spray-up and hand lay-up cannot achieve a high volume fraction of fibers. Therefore, these techniques are not suitable for high performance applications. They are most suited to large sheetlike components such as boat hulls and furniture. There is virtually no limit to the size of the part that can be made. The molds can be made of wood, metal, neat polymers, or polymer composites with glass fibers. Unlike other processes, they require little or no pressure.

Bag Molding   Bag molding is essentially an extension of the lay-up process. The lay-up structure is covered by a flexible airtight bag and either an external pressure is applied or vacuum is created inside the bag-mold enclosure. This improves the properties of the resultant composite by driving out volatile substances and increasing the volume fraction of reinforcement.

28.4.5.3   Processes for Medium Series

Prepregs   Prepregs are thin sheets of fibers impregnated with formulated thermoset precursors. The thermoset precursor formulation in the prepreg is in the so-called B-stage that characterizes an ungelled liquid of very high viscosity, but with the necessary tack, flexibility, and shelf life to facilitate part production.

There are different ways to impregnate the fabric and reach the B-stage. In a chemical B-stage, the viscosity of the formulated thermoset precursor is reduced by heating. In a physical B-stage, the so-called hot melt process is carried out by impregnating reinforcements at high temperature to reduce viscosity, followed by cooling to reach the initial viscosity at room temperature. A solvent can be also used, followed by its removal by heating. In both cases, chemistry and heating have to be managed to control the beginning of the reaction and to advance the conversion to a point well below gelation.

After its manufacture, the prepreg is backed with release film for storage in a cool dry place or in a refrigerator until its use. Typically prepregs have a guaranteed shelf life of 12 months at $-18\,^{\circ}$C. Tack life at $23\,^{\circ}$C depends on the thermosetting polymer.

Vacuum bag and autoclave processing are the two main methods for the manufacture of final parts from prepregs. Consolidation involves the cutting and stacking of prepreg layers in a predetermined sequence of fiber orientations within a mold containing release agent and absorption layers. An upper plate is laid on top and this assembly is sealed in a vacuum bag. The thermosetting matrix is cured by exposure to a defined combination of temperature and pressure. When the lay-up is heated, the constraint offered by the thermosetting matrix decreases as its viscosity falls. Application of pressure forces the fibers together. Therefore, the temperature and pressure cycle affect not only the fiber volume fraction and void content but also the fiber distribution and alignment.

The constant fiber content allows the production of constant high quality composites. Main applications are in the aerospace sector (mostly using multifunctional epoxy monomers), sporting goods (rackets, skis, bike frames, golf items, baseball bats, etc.), and in the electronic industry (printed circuit boards). Autoclaves usually required for the reaction are expensive, slow to operate, and limited in size.

One application is honeycomb sandwich construction that consists of thin high strength prepreg skins bonded to a thicker honeycomb, foam, or balsa core. The advantages are very low weight, high stiffness, durable, design freedom, and reduced production costs.

Infusion Process   In these transfer molding processes, dry fabrics, core materials, and various inserts are placed manually or robotically in a mold that can be internally heated. The thermosetting matrix is infused under vacuum, either as a semisolid film previously interleaved with the dry fabrics that are wetted when it flows or as a liquid that flows into the fibers with the assistance of vacuum. Just one "lower mold" is necessary; the "upper mold" is a sealed semipermeable vacuum foil (for vacuum-assisted resin transfer molding, VARTM) or an impermeable vacuum bag (for SCRIMP, Seemann composite resin infusion molding). Therefore, no clamping force is required. The assembly is placed into an autoclave. This process is generally performed at both elevated pressure and elevated temperature. The use of elevated pressure facilitates a high fiber volume fraction (typically 50–65% by volume or 60–75% by weight) and low void content for maximum structural efficiency.

These processes are well suited to the production of very large parts ranging from turbine blades and boats to rail cars and bridge decks with relatively low equipment investment. Compared to the conventional composite fabrication methods used in the aeronautical field, these infusion processes are an ideal technique using low cost materials without prepregs and autoclaves.

Resin Transfer Molding   Resin transfer molding (RTM) is a closed mold infusion process in which reinforcement material is placed between two matching mold surfaces (Fig. 28.7). The matching mold set is then closed and
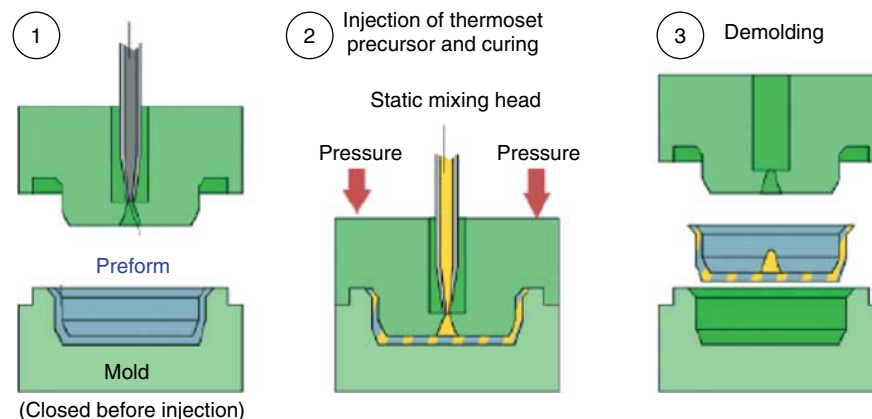
Figure 28.7   Scheme of the RTM process.

clamped and a low viscosity thermoset precursor is injected under moderate pressures (typically, 0.1–0.4 MPa) into the mold cavity through a port (or series of ports). The thermoset precursor fills voids within the mold set and wets the reinforcing materials. Vacuum is sometimes used to enhance flow and reduce void formation. The part is typically cured with heat. In some applications, the exothermic reaction of the thermosetting matrix may be sufficient for proper cure.

RTM is compatible with a variety of thermosetting polymers including polyester, vinyl ester, epoxy, phenolic, modified acrylic, and hybrid polyester–urethane. A convenient typical viscosity of thermoset precursors is in the range of 0.2–0.6 Pa s. The RTM process has the following advantages: (i) emissions are lower than in open-mold processes such as spray-up or hand lay-up; (ii) it can produce parts faster, as much as 5–20 times faster than open-mold techniques; (iii) the mold surface can produce a high quality finish; (iv) complex mold shapes can be achieved; and (v) cabling and other fittings can be incorporated into the design of the mold. However, it has one disadvantage: the contents of reinforcement are limited to allow the flow of thermoset precursors and saturation of the fibers.

28.4.5.4   Processes for Large Series
Compression Molding   Compression molding is the most common method for molding thermosetting materials using processes such as sheet molding compound (SMC) or bulk molding compound (BMC). In these techniques, a compression press is used to apply heat and pressure to a sheet or bulk molding compound. The heated molding compound fills the mold and cures to produce the desired shape. Today, this is the only way to produce thermosetting composite parts in large series (higher than 10,000 parts/year).

SMC is a flat sheetlike compound, produced on a continuous moving belt process. The thermoset precursor is an UP-resin composed of an unsaturated polyester

TABLE 28.1   Typical Formulations for SMC and BMC

Raw Material	SMC Parts by Weight	BMC Parts by Weight
UP-resin	60	60
LPA	20–40	0–40
Initiator	1.5	1.5
Fillers	150	200
Release agent	4	4
Magnesium oxide	~1	~1
Glass fibers	25% on total formulation	15% on total formulation

Abbreviation: LPA, low profile additive.

prepolymer dissolved in a monomer, usually styrene [2]. The UP-resin is premixed with all the components of the formulation to form a paste. A typical formulation is shown in Table 28.1. Calcium carbonate (chalk) is the most commonly used filler. The role of the low profile additive, LPA is to compensate the shrinkage mainly due to the polymerization of styrene.

A scheme of the SMC process is shown in Figure 28.8. The paste is dosed on a polyamide or polyethylene film and glass rovings are cut to lengths of 25–50 mm and sprinkled on the top of the resin paste layer. A second film, on which a resin paste is also applied, is then put on the top of the glass-fiber layer. The thickening agent (MgO) reacts with the free acid groups of the UP prepolymer, producing an enormous increase in the viscosity of the SMC formulation after several days. A leatherlike sheet is formed, which is almost nonsticky and is easy to handle. In this stage, the UP-resin is still not polymerized.

For the production of complex parts, BMC may be used instead of SMC. The starting formulation for BMC has the aspect of a doughlike material made by mixing all ingredients together. A typical formulation is shown in Table 28.1. Depending on the requirements for the finished
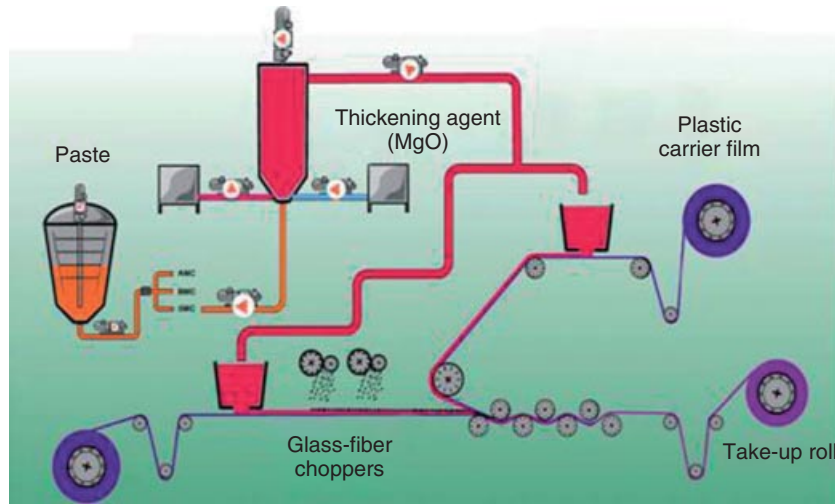
Figure 28.8   Scheme of the SMC process.

product, a wide variety of formulations is nowadays available. Products are made that possess high corrosion resistance, excellent surface finish, and high mechanical properties.

Injection Molding   The processing and equipment for injection molding of thermosetting polymers differs slightly from the conventional injection machines used for thermoplastics. Reasons are (i) the thermosetting formulation must have a short residence time in the barrel or nozzle and (ii) the injection pressure is reduced after the mold is filled.

Free flowing molding powders are used in the production of electrical and electronic parts, such as connectors and switches. The powders consist of mixtures of thermoset precursors (phenolic, epoxy, silicone, or diallyl phthalate), fillers, short glass fibers, pigments, initiators or catalysts, etc. They are produced in high shear mixing and extruding equipment. Powders are fed into the mold and cured under high pressure at temperatures up to $180\,^{\circ}\text{C}$.

BMC formulations can also be processed by injection molding. A typical product made of a BMC formulation is a headlamp reflector produced by a fully automatic injection molding process in very short cycle times. Modern installations produce several thousands of these products per day.

RRIM and SRIM are also injection molding processes, described in Section 28.4.4.

28.4.5.5   Processes for Unfilled Parts
Filament Winding   The filament winding process is used in the fabrication of tubular composite parts. Typical examples are composite pipe, electrical conduit, containers, and composite tanks. Fiber-glass roving strands are impregnated by passing through a bath containing the liquid thermoset precursors. Then, they are wound onto a mandrel in a variety
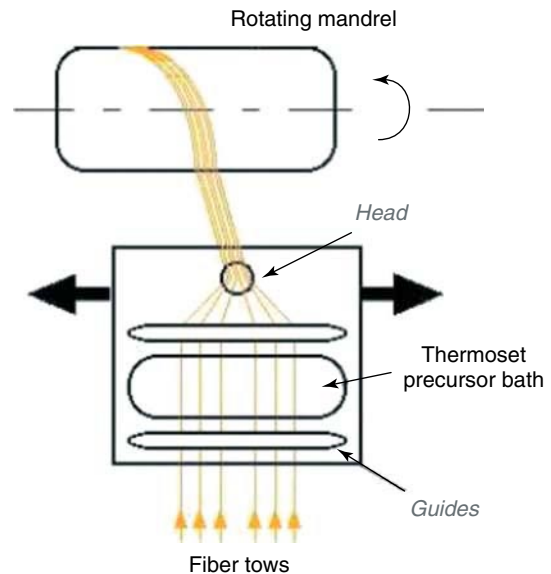

Figure 28.9   Scheme of the filament winding process. *Source*: Adapted from http://www.polymerprocessing.com/operations/filwind/index.html, with permission.

of orientations that are controlled by the fiber feeding mechanism and the rate of rotation of the mandrel (Fig. 28.9). Usually epoxy (mainly epoxy-anhydride systems), unsaturated polyester, or vinyl ester systems are used because of their long pot-life at ambient atmosphere during the impregnation step. When the winding operation is completed, the thermosetting matrix is polymerized and the composite part is removed from the mandrel.

Capital investment is relatively high compared to open-mold processes mainly due to the cost of the winding mandrel for a specific application.

Rotomolding Rotomolding or centrifugal casting is an industrial process for the production of pipes, masts, rollers, and containers. The casting equipment consists of a cylinder (often made of steel), which lies on the top of a series of roller bearings. It can be rotated at variable speed. A mixture of glass fibers and thermoset precursors is dosed simultaneously into the rotating cylinder. As a result of the centrifugal forces, the glass fibers are impregnated and deaerated. The resulting product is a tube with a good inner surface quality and mechanical properties determined by the amount of reinforcing fibers and the turning speed of the cylinder.

28.4.5.6 *Continuous Processes*

Pultrusion is a continuous and highly automated molding process used in the fabrication of composite parts that have a constant cross-sectional profile. Dry glass-fiber rovings are pulled through a thermoset precursor bath in which they are impregnated with epoxy, unsaturated polyester, or vinyl ester systems. The impregnated fibers are pulled through a heated metal die in which the thermosetting precursors polymerize at temperatures of $110-160\,°C$. The flow through the die completes the impregnation of the fibers and controls the fiber content. Polymerization produces the material into its final shape. The cured profiles with a constant cross-section and very straight fibers are cooled down and cut to the desired length. The process is fast and the fiber content can be very high and accurately controlled.

The high glass fibers content gives very high mechanical properties to the profiles obtained. This is a particular advantage for civil engineering applications such as bridges and large structures. Compared to steel profiles, pultruded profiles based on glass-reinforced thermosets show a much better corrosion resistance and electrical insulating properties.

28.5 CONCLUSIONS

The large number of manufacturing processes reflects the variety of applications of thermosetting polymers in structural and functional materials. They can be deposited on substrates for adhesives, paintings, and coating, and they can be used as foams or as matrices for composites. In all these applications, chemistry and processing are strongly interrelated.

The thermosetting polymer field is continuously changing. Different precursors, combinations of materials, and modifications of existing manufacturing methods are introduced for new applications. The sustainable development is the major trend for the future. LCA is a new tool for the choice of a reactive system coupled with a processing technique. Efforts are made to decrease the energy consumption by the use of solvent-free and nontoxic chemistries enabling to produce the cure at low temperatures and reduce the number of steps to obtain the final material.

Concerning advanced composite materials, optimal ways to impregnate the reinforcement material with the thermoset formulation and shape and cure the part as fast as possible and with low energy consumption are continuously searched. The density-related performance of these advanced composites is the key to their penetration as lightweight structural components. As reinforcement materials, carbon fibers are extending their use from high tech to more traditional applications.

Functional materials with applications in electronic, optical and magnetic devices, sensors, and catalysts can be produced by dispersing liquid crystals, organic crystals, metallic or inorganic oxide nanoparticles (NPs) in thermosetting polymers. BCPs with a variety of morphologies can be stabilized in thermosetting polymers [20–22]. To keep the dispersion of micelles in the final material, it is necessary that one of the blocks remains miscible with the reactive thermosetting polymer at least up to the gel point. The remaining blocks may be initial immiscible with the thermoset precursors or become phase separated at low conversions. Nanocomposites produced by a dispersion of micelles of BCP in a thermosetting polymer exhibit a significant increase in toughness, much higher than the one obtained by dispersing conventional rubbers or thermoplastics [23, 24]. Detailed mechanistic investigations revealed that the dominant toughening mechanism is BCP micelle cavitation-induced matrix shear banding [25, 26]. Also important is the fact that the glass transition temperature and the Young modulus of the thermosetting polymer are not affected by this modification.

The thermosetting polymer may also be the host of a variety of NPs such as POSS, CNTs, and nanoclays [21]. Self-healing thermosetting polymers with potential applications in paints and coatings have been developed [27, 28]. Thermosetting polymers also have a great potential as shape-memory actuators [29, 30].

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