POLYESTERS, UNSATURATED

1. Introduction

Low molecular weight polyesters derived from unsaturated dibasic acids (or anhydrides) dissolved in unsaturated vinyl monomers comprise a versatile family of thermosetting materials known generally as *unsaturated polyester resins*. Prototype resins produced in the early 1940s were used in conjunction with glass fiber reinforcements to produce the first composite plastics. The high strength and radiotransparency of this material expanded its role in radome covers employed in large quantities toward the end of World War II.

Markets for the resins have expanded rapidly; the dominant applications are still in conjunction with glass-fiber reinforcement to form laminar composites known generically as *fiber-glass-reinforced plastic* (FRP) in the United States and *glass-fiber-reinforced plastic* (GRP) in Europe and elsewhere. Resins have also evolved for use in casting processes, which usually contain high loadings of fillers or mineral aggregate and are defined as one form of polymer concrete. By 2002, global production of unsaturated polyester resins had exceeded 1,900,000 t, with the United States being the largest market, at over 780,000 t.

2. Raw Materials

The properties of polymers formed by the step-growth esterification (1) of glycols and dibasic acids can be manipulated widely by the choice of coreactant raw materials (Table 1) (2). The reactivity fundamental to the majority of commercial resins is derived from maleic anhydride [108-31-6] (MAN) as the unsaturated component in the polymer, and styrene as the coreactant monomer. Propylene glycol [57-55-6] (PG) is the principal glycol used in most compositions, and *ortho*-phthalic anhydride (PA) is the principal dibasic acid incorporated to moderate the reactivity and performance of the final resins.

Isophthalic (*m*-phthalic) acid [121-91-5] (IPA) is selected to enhance thermal endurance as well as to produce stronger, more resilient cross-linked plastics that demonstrate improved resistance to chemical attack. Terephthalic (p-phthalic) acid [100-21-0] (TA) provides similar properties as isophthalic acid; it is also used in corrosion resinstance and a wide variety of other applications.

Other glycols can be used to impart selective properties to these simple compositions. Ethylene glycol [107-21-1] (EG) is used to a limited degree to reduce cost, whereas diethylene glycol [111-46-6] (DEG) produces a more flexible polymer that can resist cracking when impacted. Neopentyl glycol [126-30-7] (NPG) is used in most commercial products to improve uv and water resistance. Alkoxylated derivatives of bisphenol A (BPA) not only impart a high degree of resistance to strong acidic and alkaline environments, but also provide resistance to deformation and creep at elevated temperatures.

Long-chain aliphatic acids such as adipic acid [124-04-9] are generally used to improve flexibility and enhance impact properties, demonstrating subtle improvements over resins modified with the ether glycols (diethylene glycol) and polyether glycols (polypropylene glycol) (see POLYETHERS).

Novel polyester compositions have also been derived from dicyclopentadiene [77-73-6] (DCPD), which can enter into two distinct reactions with maleic anhydride to modify properties for lower cost. These compositions have effectively displaced *o*-phthalic resins in marine and bathtub laminating applications.

Recycled poly(ethylene terephthalate) (PET), which offers excellent properties at potentially lower cost, is finding wider use as a raw material component and meeting increasing demands for environmentally compatible resins (see POLYESTERS, THERMOPLASTIC; RECYCLING, PLASTICS).

Other minor raw materials are used for specific needs. Fumaric acid [110-17-8], the geometric isomer of maleic acid, is selected to maximize thermal or corrosion performance and is the sole acid esterified with bisphenol A diol derivatives to obtain optimum polymer performance. Cycloaliphatics such as hydrogenated bisphenol A (HBPA) and cyclohexanedimethanol (CHDM) are used in selective formulations for electrical applications. Tetrahydrophthalic anhydride [85-43-8] (THPA) can be used to improve resilience and impart useful air-drying properties to polyester resins intended for coating or lining applications.

Halogenated intermediates, dibromoneopentyl glycol [3296-90-0] (DBNPG), and alkoxylated derivatives of tetrabromobisphenol A are used extensively in flame-retardant applications. Similar properties can be derived from halogenated dibasic acids, chlorendic anhydride [115-27-5] (CAN), and tetrabromophthalic anhydride [632-79-1] (TBPA). Processes can be used to produce brominated products by the *in situ* bromination of polymers derived from tetrahydrophthalic anhydride.

Monomers such as methyl methacrylate [80-62-6] are often used in combination with styrene to modify refractive index and improve uv resistance. Vinyltoluene [25013-15-4] and diallyl phthalate [131-17-9] are employed as monomers in selective molding compositions for thermal improvements.

3. Process Equipment

The polyesterification reaction is normally carried out in stainless steel vessels ranging from 8000–20,000 L, heated and cooled through internal coils (Fig. 1). Blade agitators revolving at 70–200 rpm are effective in stirring the low viscosity mobile reactants, which are maintained under an inert atmosphere of nitrogen or carbon dioxide during the reaction at temperatures up to 240°C.

Weigh tanks or meters measure the liquid glycols into the reactor. Solids are usually added from 25-kg bags or 1000-kg supersacks. Silo and auger are used widely for isophthalic acid, whereas phthalic anhydride [85-44-9] and maleic anhydride are metered in molten form. A packed condenser efficiently separates water from glycol. The glycol is refluxed back into the reactor and the remaining condensate is incinerated on-site using a thermal oxidizer. Once the polymer is formed, it is cooled to below 180°C and drained into a cooled blend tank containing styrene monomer under high agitation.

Glass-lined reactor systems are used occasionally for halogenated resins to prevent corrosion of the reactor components. Copper and brass fitting should be avoided because of the significant influence on resin cure characteristics.

4. Polyesterification

The reaction of glycols with dibasic acid anhydrides, such as phthalic and maleic anhydrides, proceeds at above 100°C, ending with the exothermic formation of the acid half-ester produced by the opening of the anhydride ring. The reaction exotherm effectively raises the temperature of the reactants to over 150°C, at which point the half-esters condense into polymers with the evolution of by-product water. As the reaction proceeds, the viscosity of the reactants increases, restricting the release of water, so that the temperatures must be gradually increased to 220°C to maintain a steady evolution of condensate water. Resins normally lose between 8 and 12% of initial charge weight as condensate.

The polyesterification reaction is reversible because it is influenced by the presence of condensate water in equilibrium with the reactants and the polymer. The removal of water in the latter part of the reaction process is essential for the development of optimum molecular weight, on which the ultimate structural performance depends.

The polyesterification reaction is carried out in the presence of an inert gas, such as nitrogen or carbon dioxide, to prevent discoloration. Usually, the sparge rate of the inert gas is increased in the final stages of polyesterification to assist the removal of residual water. Although the removal of water can be facilitated by processing under vacuum, this is rarely used on a commercial scale.

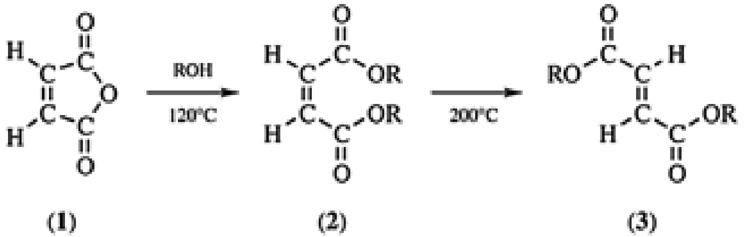
The esterification rate can be accelerated by acid catalysts (3) such as *para*-toluenesulfonic acid and tetrabutyl titanate, but tin salts such as hydrated monobutyl tin oxide are preferred for reasons of product stability during storage. The polyesterification process can be reversed by injecting steam into the reactants; this can be used to control the final molecular weight attained by the polymer. Transesterification during polymer formation also occurs, which leads to changes in the distribution of polymers in the final product. Transesterification is employed on a commercial scale to recycle poly(ethylene terephthalate) waste into useful resins by digesting an equivalent amount of glycol in the presence of catalysts such as tetraisopropyl titanate or zinc acetate. The terephthalate esters subsequently react with maleic anhydride to produce unsaturated terephthalate polymers, which have properties similar to their isophthalic homologues.

The viscosity of the final polymer melt usually limits the progress of molecular weight development, and number-average values (M_n) between 1800 and 2500 are normally observed. Other side reactions also modify molecular weight growth. Side reactions are influenced by the choice of reactants. Ethylene glycol can form cyclic esters with phthalic anhydride; maleic anhydride can produce addition products (4) with lower glycols, forming trifunctional succinate derivatives that lead to high molecular weight branched polymers and the possibility of gelation during esterification. To maintain maximum unsaturation levels during esterification, fumaric acid is often used in place of maleic anhydride. Fumaric acid is also used widely in formulations involving alkoxylated bisphenol A to obtain optimum thermal and corrosion performance.

Polyesterification involving insoluble reactants such as isophthalic acid is normally carried out in two-stage reactions, in which isophthalic acid reacts first with the glycol to form a clear melt. The balance of the reactants, including maleic anhydride, is then added to complete the polymer, thus avoiding longer cycle times and some discoloration.

Polyester resins can also be rapidly formed by the reaction of propylene oxide (5) with phthalic and maleic anhydride. The reaction is initiated with a small fraction of glycol initiator containing a basic catalyst such as lithium carbonate. Molecular weight development is controlled by the concentration of initiator, and the highly exothermic reaction proceeds without the evolution of any condensate water. Although this technique provides many process benefits, the low extent of maleate isomerization achieved during the rapid formation of the polymer limits the reactivity and ultimate performance of these resins.

4.1. Maleic Isomerization. Polyesters are formulated using maleic anhydride (**1**) as the common unsaturated moiety. During the course of the polyesterification reaction at 220°C, the *cis*-maleate ester (**2**) isomerizes to the *trans*-fumarate (**3**). The fundamental reactivity of the final polyester with styrene is directly proportional to the degree of isomerization and the level of fumarate polymers formed during the course of esterification. Maleate polymers in the cis form create strain across the double bond, causing some displacement from a planar configuration; fumarate polymers in the trans configuration are influenced less by steric effects and the double bond can assume a planar configuration conducive to addition copolymerization with styrene. Branched asymmetric reactants such as propylene glycol and bulky aromatic dibasic acids such as isophthalic acid create sufficient steric interference to promote isomerization to the *trans*-fumarate polymers, whereas linear glycols such as ethylene and diethylene glycol and linear dibasic acids such as adipic acid produce resins that have higher levels of the maleate polymer.



The temperature of esterification has a significant influence on isomerization rate, which does not proceed above 50% at reaction temperatures below 150°C. In resins produced rapidly by using propylene oxide and mixed phthalic and maleic anhydrides at 150°C, the polyester polymers, which can be formed almost exclusively in the maleate conformation, show low cross-linking reaction rates with styrene.

Isomerization is facilitated by esterification at temperatures above 200°C or by using catalysts, such as piperidine and morpholine (6), which are effective in raising isomerization of fumarate to 95% completion. Resins made by using fumaric acid are exclusively fumarate polymers, demonstrate higher reactivity rates with styrene, and lead to a complete cross-linking reaction.

4.2. End Group Analysis.

The reaction of balanced stoichiometric glycol–dibasic acid ingredients theoretically produces polymers with equivalent acid and hydroxyl end groups. Commercial processes, however, normally include an excess of glycol to offset distillation losses. Depending on column efficiency, the polymer can have a higher relative hydroxyl value and a much lower acid value (Fig. 2), and this controls the ultimate molecular size. Most commercial laminating resins have acid values ranging from 25 to 30, whereas higher molecular weight isophthalic resins have values that fall between 10 and 15.

4.3. Molecular Weight.

Unsaturated polyester resins are relatively low in molecular weight, and are formulated to achieve low working viscosities when dissolved in styrene. The M_n normally falls between 1800 and 2500, although dicyclopentadiene and orthophthalic resins can be useful below this range. The molecular weight follows a Gaussian distribution curve (Fig. 3), the shape of which influences final solution viscosities. In phthalic resins, the presence of a low molecular weight fraction is usually observed, whereas in high maleic resins a high molecular weight shoulder is observed. This indicates significant glycol addition across the double bond to form a trifunctional reactant. Polymers having different chain lengths and compositions exist as a compatible mixture; the ratio of weight-average molecular weight (M_w) and number-average molecular weight (M_n) is defined as the polydispersity D. For o-phthalic and isophthalic resins, D is just over two, but higher molecular weight resins and resins containing high maleic levels are more polydisperse and the distribution curve becomes flatter as the resin viscosity increases.

ortho-Phthalic resins consist of chains having an average of 15 ester groups and a narrow distribution curve. The molecular weight development during the manufacturing process is normally followed by using solution viscosity that tends to increase exponentially in the final stages of the reaction. Arbitrary end points are usually established well before this stage to avoid gelation in the reactor (see Fig. 2).

5. Formulation

5.1. *ortho*-Phtahlic Resins.

Resins based on *ortho*-phthalic anhydride (Table 2) comprise the largest group of polyester resins and are used in a variety of commercially significant applications, including marine craft, translucent glazing, simulated-marble vanity sets, and buttons. Most laminating and casting processes also rely on both colored and clear gel coats to provide some level of surface protection. The glycol generally controls the required performance; the phthalic–maleic anhydride ratio is adjusted to modify the reactivity according to physical properties required for fabrication needs.

The glycol is charged to the reactor and heated to 50°C under an inert-gas sparge. The lower melting maleic anhydride is metered in, allowing the temperature to rise to 100°C, followed by the phthalic anhydride. A clear solution forms and the temperature is increased to 120°C to initiate the exothermic reaction between the glycol and anhydride forming the half-ester. The temperature increases rapidly to 150°C as the exotherm heat is released, at which point the half-ester begins to condense into low molecular weight polymers. The increasing viscosity of the melt tends to restrict the release of water vapor, and the reactants can foam into the condenser unless the reaction is controlled through cooling. The temperature is gradually increased to 220°C to maintain a constant removal of the condensate, but falls off as the reaction nears completion, usually in 12 h. Solid phthalic anhydride sublimes out in the latter stages of the reaction, requiring close control of the inert-gas flow and temperature. Some processors have used xylene as an azeotropic solvent to assist water removal while suppressing the sublimation of the phthalic anhydride, but this is not widely applied.

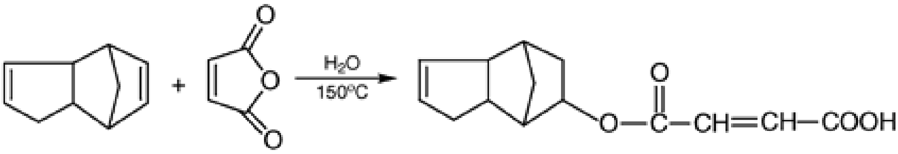
Phthalic resins are usually processed to an acid number of 25–35, yielding a polymer with an average M_n of 1800–2000. The solution viscosity of the polymer is usually followed to ascertain the polymer end point. The resin is cooled to 200°C and hydroquinone stabilizer (150 ppm) is added to prevent premature gelation during the subsequent blending process, with styrene at a maximum temperature of 70°C. The final polymer solution is cooled to 25°C before a final quality check and drumming out for shipment.

5.2. Isophthalic Resins. Isophthalic acid (IPA) can be substituted for phthalic anhydride to enhance mechanical and thermal performance and improve resistance to corrosive environments. Significant products include underground gasoline storage tanks and large diameter sewer and water pipe. Although phthalic resins find wide application in ambient fabrication processes, isophthalic resins (Table 3) are more widely used in products employing high temperature forming processes such as pultruded profile and electrical-grade laminate.

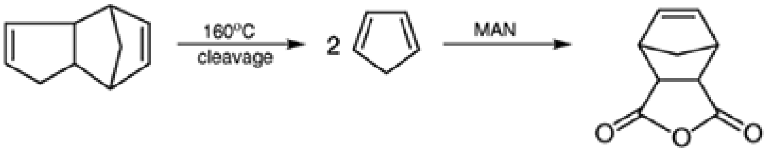
Isophthalic resins are manufactured by two-stage processing to facilitate the dissolution of the isophthalic acid. In the first stage, the glycol and isophthalic acid react under pressure at temperatures of 235°C under an inert atmosphere to produce a clear melt. High pressure processing [207 kPa (30 psi)] and, optionally, esterification catalysts such as hydrated monobutyl tin oxide are also widely employed to reduce the cycle times of two-stage processing. Maleic anhydride is added in the second stage and the final resin completed at 220°C to control color and molecular weight development. Isophthalic resins intended for corrosion application are processed to an M_n of 2200–2500; the reaction cycle is about 24 h.

The melting flow of the higher molecular weight isophthalic polymer is much higher than *ortho*-phthalic resins, and blending temperatures in styrene must be increased to avoid freezing the polymer out. Stabilizers such as toluhydroquinone and benzoquinone are more effective gelation inhibitors for the higher styrene-blending temperatures used for these resins.

5.3. Dicyclopentadiene Resins. Dicyclopentadiene (DCPD) can be used as a reactive component in polyester resins in two distinct reactions with maleic anhydride (7). The addition reaction of maleic anhydride in the presence of an equimolar amount of water produces a dicyclopentadiene acid maleate that can condense with ethylene or diethylene glycol to form low molecular weight, highly reactive resins. These resins, introduced commercially in 1980, have largely displaced *ortho*-phthalic resins in marine applications because of beneficial shrinkage properties that reduce surface profile. The inherent low viscosity of these polymers also allows for the use of high levels of fillers, such as alumina trihydrate, to extend the resin-enhancing, flame-retardant properties for application in bathtub products (Table 4).



The cleavage of dicyclopentadiene into cyclopentadiene can be accomplished at temperatures above 160°C, producing the heterocyclic Diels–Alder maleic addition product, which opens to the diacid. This product can be esterified with propylene glycol to produce resins that demonstrate enhanced resilience and thermooxidative resistance suitable for molded electrical components.



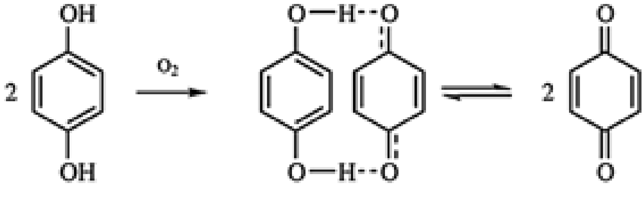
5.4. Flame-Retardant Resins. This type of resins are formulated to conform to fire safety specifications developed for construction as well as marine and electrical applications. Resins produced from halogenated intermediates (Table 5) are usually processed at lower temperatures (180°C) to prevent excessive discoloration. Dibromoneopentyl glycol requires glass-lined equipment because of its corrosive nature due to some elimination of bromine during the process at high tempretaures. Tetrabromophthalic anhydride and chlorendic anhydride (8) are formulated with ethylene glycols to maximize flame-retardant properties; reaction cycle times are about 12 h. Resins are also produced commercially by the *in situ* bromination of polyester resins derived from tetrahydrophthalic anhydride (9).

Methyl methacrylate (MMA) is often used in combination with styrene to improve light transmission and uv stability in flame-retardant glazing applications. Recently, MMA is used to a limited extent because of new environmental regulations. Phosphate ester (triethyl phosphate) additives are also included to supplement flame-retardant efficiency; benzophenone uv stabilizers are required to prevent yellowing of these uv-sensitive resins.

5.5. Bisphenol Resins. Ethoxylated and propoxylated derivatives of bisphenol A form the basis for two distinct resin groups that demonstrate superior thermal and corrosion resistance. The addition product of propylene oxide [75-56-9] and bisphenol A, reacted with fumaric acid and dissolved in styrene monomer, has established commercial significance in applications involving extreme corrosive environments. The resins known generically as bisphenol fumarates (10) have been used since 1955 in the fabrication of tanks and piping used in the chloralkali and pulp and papermaking industries. This resin is unique among polyester compositions in resisting strong alkaline solutions that readily decompose *ortho*-phthalic and isophthalic resins.

5.6. Stabilizers.

Hydroquinone [123-31-9] (**4**) is widely used in commercial resins to provide stability during the dissolution of the hot polyester resin in styrene during the manufacturing process. Incorporation of oxygen (air) into the styrene containing the resin inhibitor is required to activate them, which is converted to an equilibrium mixture of quinone and the quinhydrone (**5**) (11). At levels of 150 ppm, a shelf life of over 6 months can be expected at ambient temperatures.



(**4**) (**5**)

Toluhydroquinone and methyl *tert*-butylhydroquinone provide improved resin color retention; 2,5-di-t-butylhydroquinone also moderates the cure rate of the resin. Quaternary ammonium compounds, such as alkyl trimethylammonium chloride, are effective stabilizers in combination with hydroquinones and also produce beneficial improvements in color when promoted with cobalt octoate. Copper naphthenate is an active stabilizer at levels of 10 ppm; at higher levels (150 ppm) it influences the reactivity preventing the resin from curing. Tertiary butylcatechol (TBC) is a popular stabilizer used by fabricators to adjust room temperature gelation characteristics.

6. Cross-Linking Mechanism

The reaction rate of fumarate polyesters with styrene is 20 times that of similar maleate polymers. Commercial phthalic and isophthalic resins usually have fumarate levels in excess of 95% and demonstrate full hardness and property development when catalyzed and cured. The addition polymerization reaction between the fumarate polyester and styrene monomer is initiated by free-radical polymerization. Commercially, benzoyl peroxide (BPO) and methyl ethyl ketone peroxide (MEKP) are the most common initiators used to cross-link unsaturated polyester and styrene. The initiators can be dissociated by heat or redox metal activators into peroxy and hydroperoxy free radicals.

The free radicals initially formed are neutralized by the quinone stabilizers, temporarily delaying the cross-linking reaction between the styrene and the fumarate sites in the polyester. This temporary induction period between catalysis and the change to a semisolid gelatinous mass is referred to as *gelation time* and can be controlled precisely between 1 and 60 min by varying stabilizer and catalyst levels.

As the quinone stabilizer is consumed, the peroxy radicals initiate the addition chain propagation reactions through the formation of styryl radicals. In dilute solutions, the reaction between styrene and fumarate ester follows an alternating sequence. However, in concentrated resin solutions, the alternating addition reaction is impeded at the onset of the physical gel. The liquid resin forms an intractable gel when only 2% of the fumarate unsaturation is cross-linked with styrene. The gel is initiated through small micelles (12) that form the nuclei for the expansion of the cross-linked network. The free styrene monomer is restrained within the gel and further reaction with fumarate groups is determined by the spacial arrangement; the styrene polymerizes in homopolymer blocks as it intercepts fumarate reaction sites. As individual micelles expand and deplete available fumarate sites in the short polymer chains, the remaining styrene forms homopolymer blocks that terminate at the boundaries between overlapping micelles (Fig. 4). Styryl free radicals simultaneously initiate micelle nuclei at points of high fumarate concentration. The micelles continue to expand, interacting with free styrene until the fumarate groups are depleted. The micelles eventually overlap at the boundaries that contain higher levels of terminal styrene homopolymer blocks.

As the micelles expand, the soft gel is transformed into a hard, rubbery transition stage that demonstrates low physical strength before the onset of the exotherm of polymerization. The temperature increases exponentially as the micelle expands. As the temperature subsides, the resulting cross-linked thermoset solid develops superior properties characteristic of the polymer. Generally, optimum strength characteristics are obtained in resins having a styrene/fumarate molar ratio of 2:1. Most resins are formulated with a styrene content consistent with this relationship (Tables 2–5). In resins having equivalent molar ratios of dibasic and unsaturated acid, this equates to resin polymer solutions containing around 40% styrene. However, this imposes some limitation on viscosity and most commercial resins contain between 40 and 45% styrene to achieve lower application viscosities.

In resins having low isomerization levels (80%), the fumarate–styrene reactions run to completion, leaving many unreacted maleate groups within the cross-linked structure. This results in an excess of styrene that inevitably forms larger homopolymer blocks between the intersecting micelles. The performance of such resins is characterized by lower softening temperatures and lower physical properties because of the additional plasticizing effects of the maleate ester group.

The cross-linking reaction mechanism is also influenced by the presence of other monomers. Methyl methacrylate is often used to improve the uv resistance of styrene-based resins. However, the disparate reaction rates of styrene and methacrylate monomer with the fumarate unsaturation not only preclude the use of more than 8% of the methacrylate monomer because of the significant slowing of the cross-linking reaction but also result in undercured products.

6.1. Catalyst Selection. The low resin viscosity and ambient temperature cure systems developed from peroxides have facilitated the expansion of polyester resins on a commercial scale, using relatively simple fabrication techniques in open molds at ambient temperatures. The dominant catalyst systems used for ambient fabrication processes are based on metal (redox) promoters used in combination with hydroperoxides and peroxides commonly found in commercial MEKP and related perketones (13). Promoters such as styrene-soluble cobalt octoate undergo controlled reduction–oxidation (redox) reactions with MEKP that generate peroxy free radicals to initiate a controlled cross-linking reaction.

$$\mathrm{ROOH} + \mathrm{CO}^{+2} \rightarrow \mathrm{RO}^{\bullet} + \mathrm{OH}^{-} + \mathrm{CO}^{+3}$$
$$\mathrm{ROOH} + \mathrm{CO}^{+3} \rightarrow \mathrm{ROO}^{\bullet} + \mathrm{CO}^{+2}$$

This catalyst system is temperature-sensitive and does not function effectively at temperatures below 10°C; but at temperatures over 35°C the generation of free radicals can be too prolific, giving rise to incomplete cross-linking formation. Redox systems are preferred for fabrication at temperatures ranging from 20 to 30°C (Fig. 5).

Some fabrication processes, such as continuous panel processes, are run at elevated temperatures to improve productivity. Dual-catalyst systems are commonly used to initiate a controlled rapid gel and then a fast cure to complete the cross-linking reaction. Cumene hydroperoxide initiated at 50°C with benzyl trimethylammonium hydroxide and copper naphthenate in combination with *tert*-butyl octoate are preferred for panel products. Other heat-initiated catalysts, such as lauroyl peroxide and *tert*-butyl perbenzoate, are optional systems. For higher temperature molding processes such as pultrusion or matched metal die molding at temperatures of 150°C, dual-catalyst systems are usually employed based on *tert*-butyl perbenzoate and 2,5-dimethyl-2,5-di-2-ethylhexanoylperoxy-hexane (Table 6).

The action of redox metal promoters with MEKP appears to be highly specific. Cobalt salts appear to be a unique component of commercial redox systems, although vanadium appears to provide similar activity with MEKP. Cobalt activity can be supplemented by potassium and zinc naphthenates in systems requiring low cured resin color; lithium and lead naphthenates also act in a similar role. Quaternary ammonium salts (14) and tertiary amines accelerate the reaction rate of redox catalyst systems. The tertiary amines form beneficial complexes with the cobalt promoters, facilitating the transition to the lower oxidation state. Copper naphthenate exerts a unique influence over cure rate in redox systems and is widely used to delay cure and reduce exotherm development during the cross-linking reaction.

Another unique redox system used for extending gel times consists of cumene hydroperoxide and manganese naphthenate, which provides consistent gel times of between two and four hours over a temperature range of 25–50°C.

For application temperatures below 10°C or for acceleration of cure rates at room temperature, nonredox systems such as benzoyl peroxide initiated by tertiary amines such as dimethylaniline (DMA) have been applied widely. Even more efficient cures can be achieved using dimethyl-*p*-toluidine (DMPT), whereas moderated cures can be achieved with diethylaniline (DEA).

Tertiary amines are also effective as accelerators in cobalt redox systems to advance the cure rate (Fig. 6). Hardness development measured by Shore D or Barcol D634-1 penetrometer can be used to demonstrate this benefit, which is useful in increasing mold turnover at ambient temperatures.

6.2. Cure Exotherm. The cross-linking reaction between the unsaturated polymer and styrene results in a spontaneous change from liquid to a solid state with the onset of the exotherm. The exothermic heat generated is proportional to the fumarate level in the polymer, but increasing styrene levels can enhance it further. Although some exotherms can be tolerated in molding processes, these can lead to excessive shrinkage, warpage, and cracking in large moldings or GFR laminations thicker than 9 mm. The cure exotherm can be suppressed in a number of ways to afford a more controllable fabrication system, without adversely affecting the final cure or structural performance.

Copper naphthenate added to the resin at levels between 5 and 20 ppm effectively extends gel and cure characteristics, resulting in a reduction in exothermic heat (Fig. 7). Copper additives are widely used in commercial laminating resins to modify process exothermic effects. α-Methylstyrene [98-83-9] substituted for styrene at levels of 5–8% has also been used effectively in resins cured at above ambient temperatures. The inhibitor 2,5-di-*t*-butylhydroquinone exerts significant exotherm suppression at levels of 200–400 ppm and is useful in high temperature molding processes.

6.3. Shrinkage. Polyester resins that undergo cross-linking reactions have as a result a net contraction in volume. Resins dissolved in styrene demonstrate a volumetric shrinkage of 17%. Such high shrinkage can lead to cracking or warping of castings or laminates. Monomers such as vinyltoluene or diallyl phthalate reduce shrinkage; these monomers are often used in high temperature molding compositions to avert warpage or internal voids. With vinyltoluene, volumetric shrinkage during cure is 12.6% and with diallyl phthalate, 11.8%. The effects of shrinkage can also be modified by incorporating soluble poly(vinyl acetate) and related thermoplastic additives into the liquid resins, which phase out during the cross-linking reaction, thus significantly reducing shrinkage. Additional benefits can be obtained by incorporating high filler loadings into resins used in casting or high temperature molding processes.

6.4. Air Inhibition. Polyester resins are widely used in open-mold lamination or casting and quite often develop a tacky surface feel after curing. The free-radical polymerization process is sensitive to oxygen, which interferes with the surface cross-linking mechanism and impedes the cure. Lower molecular weight phthalic resins display a pronounced effect, but higher molecular weight isophthalic resins have less tack. Low molecular weight resins normally produce small fractions of unreactive portions that can migrate to the surface of the resin during the curing process. The lower reactivity of those fractions produce surfaces with high tackiness. Resins based on dicyclopentadiene react with oxygen through an air-drying mechanism and give rise to tack-free surfaces; resins derived from tetrahydrophthalic anhydride have similar air-drying qualities useful for polyester coatings and linings.

Paraffin wax additives are effective in overcoming surface inhibition by forming a monomolecular wax layer at the curing surface. Although effective in excluding oxygen, this waxy layer must be removed for subsequent lamination or bonding processes (see WAXES).

6.5. Performance Characteristics. Polyester resins undergo a rapid transformation from a viscous liquid to a solid plastic state that comprises a three-dimensional cross-linked polymer structure. The level of polyester unsaturation determines essential performance characteristics (Table 7), although polymer components can influence subtle features that affect thermal, electrical, and mechanical performance as defined by ASTM procedures.

The cross-linked polymers form a thermoset plastic which cannot be changed or returned to its original condition by heating, as it can with thermoplastics. This thermoset characteristic is beneficial in providing high temperature properties, good solvent and chemical resistance, and high flexural modulus. Cross-linked polyester resins are rigid materials and are highly sensitive to brittle fracture. Reinforcing with glass fiber produces a composite plastic, which has exceptional strength characteristics suitable for replacing conventional fabricating materials such as wood, steel, and concrete. Aggregates and fillers such as ground limestone also improve the strength characteristics of polyester resins and are used widely in cast objects such as bathroom vanity sets and building components. Polyester resins are used in an unfilled condition in cast objects such as bowling balls and buttons, in thin films for gel coats, and, to a lesser extent, as clear wood coatings.

6.6. Mechanical Properties. The performance of various polyester resin compositions can be distinguished by comparing the mechanical properties of thin castings (3 mm) of the neat resin defined in ASTM testing procedures (15). This technique is used widely to characterize subtle changes in flexural, tensile, and compressive properties that are generally overshadowed in highly filled or reinforced laminates.

Resins of higher molecular weight demonstrate higher tensile strength, whereas high fumarate resins have higher flexural modulus. Formulations containing diethylene glycol and adipic acid produce resins that have higher resilience reflected in enhanced tensile and flexural strength but lower flexural modulus. Isophthalic resins provide better mechanical properties than *ortho*-phthalic resins and are consequently preferred in laminate applications requiring higher structural performance. The strength of all polyester resins is enhanced significantly by glass and other fibrous reinforcements. Laminates are usually fabricated from glass fiber mat, having individual fibers 5 cm in length. The structural properties increase in proportion to the glass fiber content, which can be varied from 25 to 40%. Increased reinforcement levels can be achieved by using woven glass roving in alternating plies with chopped strand glass mat. Higher strength can be realized from continuous glass-fiber rovings used in filament-wound structures in the form of pipes or tanks. Helical wind angles are varied to achieve design requirements in hoop or axial directions; a wind angle of 55° can generate twice the strength in the hoop direction. Continuous glass-fiber roving used at reinforcement levels of 65% in pultruded products provides composites that have the highest flexural and tensile properties. Carbon fiber can be useful in developing composites that have higher modulus characteristics, but economics have reduced their wider attractiveness in combinations with polyester resins. Kevlar cloth can be used in combination with unsaturated polyester urethanes to produce light weight, high strength composite plastics for sporting equipment such as kayaks, skis, and bulletproof composites.

Resins filled with ground limestone to levels of 80% by weight are useful in solid-cast products. The fillers reduce sensitivity to brittle fracture and improve modulus, but have little effect on general strength properties (Table 8).

6.7. Thermomechanical Properties. The highly cross-linked structure of cured unsaturated polyester resins produces thermoset characteristics in which the resistance to softening and deformation is greatly enhanced at elevated temperatures. The cross-linked network undergoes a structural transition during heating, in which the rigid crystalline state transforms to a softer amorphous condition at the glass-transition temperature T_g, accompanied by a small expansion in volume, thus facilitating some relaxation along the amorphous micellular boundaries and allowing deformation to take place. Aromatic constituents enhance the T_g, as do high fumarate and high styrene levels, whereas aliphatic derivatives (adipic) and reduced fumarate levels lower T_g values. Resins containing high adipic acid levels display rubbery or elastomeric properties at below ambient temperatures. Glass-reinforced products using these resins have exceptional impact properties and demonstrate high tolerance to low temperature cryogenic applications. Deformation at higher temperatures is moderated by fibrous reinforcements. However, as the temperature exceeds the T_g of the cross-linked polymer, laminate properties fall off considerably (Fig. 8).

Although reinforcements can improve the structural behavior of the composite at elevated temperature, the polymer, irrespective of its composition, begins to disassociate chemically in the presence of oxygen. *ortho*-Phthalic resins having the weaker ester bonds depolymerize readily at temperatures over 200°C and form low molecular weight fractions disintegrating the polymer network. Determination of laminate weight loss or flexural property retention indicates that alicyclic diols, including hydrogenated bisphenol A and cyclohexanedimethanol, perform better than lower glycols such as propylene, and neopentyl glycol imparts exceptional thermal stability at temperatures up to 200°C. However, all resins depolymerize spontaneously at around 300°C as the ester groups disassociates from the polymer network, producing by-products that include lactones, dimer esters, and glycols. Vinyltoluene provides enhanced thermal performance on account of the increased bond strength resulting from the inductive influence of the methyl group para to the vinyl unsaturation. Oxidative disassociation at elevated temperature can be suppressed with antioxidants, but these eventually interfere with the catalyst's activity, thus reducing cure rate.

Halogenated intermediates based on chlorendic anhydride and alkoxylated brominated bisphenol A are quite stable and are used extensively in flame-retarded high temperature compositions, but brominated alicyclics, such as dibromotetrahydrophthalic resin, are rapidly dehydrohalogenated at lower temperatures.

Cross-linked polyester composites have a relatively low coefficient of thermal conductivity, which can provide beneficial property retention in thick laminates at high temperatures as well as remove the need for secondary insulation. The coefficient of thermal expansion of glass-reinforced composites is similar to aluminum but higher than most common metals.

6.8. Dielectric Properties. Polyester resins are nonconductors, have relatively low dipolar characteristics, and provide high dielectric strength and surface resistivity. At high voltage or high current, however, the cross-linked plastics fail due to carbon arcing or tracking caused by the charring of the polymer surface into a conductive carbonaceous residue. Hydrated fillers such as alumina trihydrate (16) suppress surface char formation and are used extensively with glass reinforcement in molding compounds intended for electrical applications. High temperature electrical applications usually specify bisphenol fumarate resins or high molecular weight isophthalic resins having high fumarate reactivity. Dicyclopentadiene resins provide enhanced oxidative resistance, whereas vinyltoluene monomer is used for superior thermal properties. Specialized granulated molding compounds are also formulated by using diallyl phthalate monomers, and are used for injection molding smaller electrical components.

6.9. Chemical Properties. The three-dimensional cross-linked network resists penetration and attack by most corrosive chemicals and nonpolar solvents, although weak alkalies and especially polar solvents such as lower ketones, chlorinated aliphatics, and aromatics readily attack *ortho*-phthalic, isophthalic, and dicyclopentadiene resins. Water has wide-ranging effects on different resin compositions as it penetrates into the plastic network. Cross-linking density and the presence of steric constituents local to the ester groups can enhance water resistance. Isophthalic resins have better water absorption characteristics than corresponding *ortho*-phthalic resins. Neopentyl glycol and alkoxylated bisphenol constituents provide maximum performance in aqueous media. Ethylene and diethylene glycols demonstrate high water absorption that leads to the loss of mechanical strength. The presence of glass reinforcements within the cross-linked plastic is also affected by chemical attack. Water absorbed onto surface fibers is carried into the plastic matrix, decoupling the resin−glass fiber interfacial bond in the process. Alkalies compliment this attack on the glass reinforcement and lead to surface blistering and rapid loss of laminate strength. Chemical attack is usually minimized by incorporating surface protection in the form of corrosion-resistant (C glass) surface veils and high surface resin content in laminates intended for chemical service. Reinforced polyester composites or FRPs perform well in concentrated hydrochloric and phosphoric acids; concentrated sulfuric and nitric acid oxidize and degrade the polymer rapidly. High performance resins based on bisphenol A fumarate and their brominated homologues have featured prominently in FRP piping, tanks, chemical ducting, and scrubbers used to handle corrosive chemicals and emissions in pulp and paper plants, mining and ore classification, and the chloralkali industries. FRP has also emerged as a strategic solution for designing equipment intended for high temperature applications in fossil fuel electric power generating utilities such as chimney stack liners and scrubbers for the control of sulfur dioxide emissions.

Corrosion attack on the polymer is influenced by permeation rate, as well as internal stresses or fatigue, which distorts or fractures the resin glass fiber interface. Localized corrosion failure in large tanks or piping systems can sometimes be explained by stress-induced corrosion failure. FRP composites normally contain air voids that distort into elliptical voids adjacent to the reinforcing fiber. Water and chemicals penetrating these voids set up osmotic cells that plasticize and soften the surrounding polymer, initiating brittle fracture along the fibers and progressively opening up new surface area for corrosion attack in areas under high stress. Nonpolar solvents have little effect on polyester resins and have been used extensively for underground storage of gasoline. However, with the reformulation to unleaded gasoline, the higher aromatic fuels require resins that have higher cross-linking density. This is provided by high fumarate isophthalic or terephthalic derivatives.

6.10. Flammability. Polyester resin products ignite and burn by emitting sooty smoke. Flammability can be reduced significantly through halogen-modified components either formulated into the polyester polymer as chlorendic anhydride, tetrabromophthalic anhydride, or dibromoneopentyl glycol, or as part of the monomer system, ie, dibromostyrene. Additives such as phosphate esters are frequently used to enhance flame retardance, whereas antimony trioxide at levels of 5% or less on resin provides optimum retardance in combination with halogenated intermediates. The flame-retardant mechanism depends on the thermal disassociation of the organohalogen component, which, upon exposure to the heat of the flame, releases hydrogen chloride or hydrogen bromide gases that become active as radical transfer agents in suppressing the oxidation–combustion process (17). The activity of the halogen gases is synergized through the formation of antimony oxy halides and trihalides; arsenic and molybdenum salts offer comparable activity. Organophosphorus compounds behave in a supplementary role by forming polyphosphoric acids that induce char at the burning surface. However, phosphates plasticize the polymer and reduce performance at levels exceeding 5%, thus offering marginal benefits. Organoferrous compounds such as ferrocene demonstrate unique synergism with halogenated resins, reducing both flame spread and smoke generation. Also, ferrous oxide (18) is active in chlorendic resins in a similar capacity. The formation of ferric chloride promotes aromatization and enhances char formation and the subsequent reduction of smoke emissions. The exothermic nature of the combustion process can provide sufficient energy for sustained burning, unless halogen modification is used. Nonhalogenated resin systems, based on hydrated fillers such as alumina trihydrate, have emerged. Alumina trihydrate undergoes endothermic disassociation at above 300°C, and can offset the combustion heat and reduce surface temperatures sufficiently to interrupt the high energy oxidation mechanism. Resins incorporating over 40% by weight of aluminum trihydrate not only qualify for most construction and electrical flammability specifications but also provide significant reduction in smoke emissions. Useful bench-scale tests, such as ASTM E162 and ASTM D2863, have been developed for characterizing flammability and smoke emissions, but the dynamic nature of the combustion process requires large-or full-scale fire testing, such as ASTM E84, to be performed for applications intended for confined areas. Halogenated resins are sensitive to heat and ultraviolet radiation; resins based on tetrabromophthalic anhydride yellow after a few days in direct sunlight. Benzophenone and benzotriazole stabilizers used at levels of 1% are highly effective with chlorendic, dibromoneopentyl, and dibromotetrahydrophthalic derivatives, but resins based on brominated aromatics such as tetrabromophthalic anhydride and tetrabromobisphenol eventually discolor in exterior applications.

6.11. Weathering. Polyester resins in the form of laminates, coatings (gel coats), and castings perform well in outdoor exposures; marine craft, tanks, pipes, and architectural facia produced in the 1960s are still in service. Polyesters undergo some change in their surface features in direct sunlight, discoloration or yellowing being most obvious. Dulling and microcrazing occur only in products not appropriately formulated for the exposure. Long-term surface erosion of laminates exposes the glass fibers, which, unless corrected, can lead to rapid loss of structural integrity. Absorption of water influences the interfacial bond between the resin matrix and either the fibrous or aggregate reinforcement, leading to some loss of mechanical properties over 30 years. However, observations indicate that most applications reach this equilibrium after three to five years and do not show much significant change thereafter. Most FRP products are designed with protective and decorative gel coats (19) formulated from neopentyl glycol, which, in combination with some methyl methacrylate monomer and benzophenone uv stabilizers, provides improved weather resistance. Platelet fillers such as talcs and clays, as well as high pigment levels, are incorporated into gel coats to obscure the underlying laminate from the effects of direct sunlight. Surface oxidation and discoloration can also be controlled by using uv-resistant lacquers based on polymethacrylate resins or by cladding with poly(vinyl fluoride) (PVF) or acrylic and poly(ethylene terephthalate) (PET) films.

7. Application Processes

7.1. Open-Mold Process. Polyester resins are fabricated easily in open molds at room temperature. Such processes account for over 80% of production volume, the remaining being fabricated using matched metal dies in high temperature semiautomated processes.

The hand lay-up or spray-up process, used universally for the production of laminar composites incorporating glass-fiber reinforcement, is most efficient for the manufacture of large parts, such as boats, bathtubs, tanks, architectural shapes, and recreational accessories. Resins intended for spray-up processes are usually modified with thixotropic additives, such as fumed silica (1%), to reduce the risk of drainage when applied over large vertical mold surfaces. Molds are also made from FRP for short-run products usually surfaced with a tooling gel coat to provide consistent surface quality and appearance.

Gel coats are pigmented polyester coatings applied to the mold surface and are an integral part of the finished laminate. Gel coats are used widely on hand lay-up and spray-up parts to enhance surface esthetics and coloration, as well as to provide an abrasion-resistant waterproof surface that protects the underlying glass-reinforced structure.

Thermoformed acrylic sheet is displacing gel coats in some bathtub applications; spas have converted almost exclusively to formed acrylic sheet reinforced with glass-reinforced polyester laminations because of higher temperatures and higher structural requirements.

Products of axial symmetry such as pipes and tanks can be produced by filament-winding resin-impregnated glass rovings over a rotating mandrel. This process provides for some versatility in adjusting the winding angle to meet design cost considerations. A winding angle of 55° to the axis produces pipes that have twice the strength in the hoop direction, suitable for conveying high pressure liquids that may be corrosive to metals. Large-diameter piping systems (1–3 m) are also produced by centrifugal casting techniques, by which high levels of silica sand can be used to improve pipe stiffness. FRP pipes have been used extensively as slip linings for deteriorated concrete sewer pipes that avoid costly excavation.

Resins containing fillers and aggregates can be usefully cast into attractive components that simulate marble and granite. Bathroom vanity sets and kitchen countertop components have emerged as a significant commercial outlet for filled resins cast in open molds that often employ gel coats having superior hydrolytic properties to enhance resistance to thermal shock and crazing. Specially formulated isophthalic resins in admixture with sand have been developed for surfacing worn concrete roads and bridges. Polyester resins are also emerging in filled pigmented coatings used as permanent road marking, as some U.S. states displace solvent-based alkyd marking materials. Other products such as buttons and bowling balls are cast from resins containing low filler levels.

7.2. Closed-Mold Processes. In an effort to improve the productivity of the hand lay-up process, closed-mold systems containing two mating dies have evolved. In resin-transfer molding (RTM), glass reinforcement is placed in the open mold; once the molds are in place, precatalyzed resin is injected into the cavity under pressure. The process has been further modified to use a vacuum that ensures complete air removal and faster mold filling. The process is adaptable to large components and can be used to encapsulate foam, aluminum, and wood components into the structure. The process is also beneficial in reducing styrene emissions that are regulated under Title III of the U.S. Clean Air Act passed in 1990.

High temperature compression molding has grown rapidly since 1985 as applications for glass-reinforced composites have expanded in the automotive body panel market. Molding compounds incorporating resins, catalysts, fillers, pigments, and glass fiber reinforcements have evolved as bulk molding compounds (BMC) and sheet molding compounds (SMC) to meet requirements in the electrical, business machine, as well as structural automotive markets.

Matched die molding is the most efficient process to produce high volumes of relatively large parts. The mold cycle is under two minutes at 150°C and the process can be incorporated into an automated manufacturing system, reducing labor and scrap while improving quality. Resins have been uniquely formulated to reduce shrinkage and provide composite surfaces that can be primed and coated by using conventional baked enamels. The polyester technology providing these low profile, low shrink resins is based on the action of thermoplastic additives (20) incorporated into unique polyester resin formulations based on propylene glycol fumarate.

Poly(methyl methacrylate) and poly(vinyl acetate) precipitate from the resin solution as it cures. This mechanism offsets the contraction in volume as the polyester resin cross-links, resulting in a nonshrinking thermoset. Other polymer additives such as poly(butylene adipate) provide similar shrinkage control. The change in volume and compatibility of the polymer produces a whitening of the composite and results in nonuniform coloration in pigmented products. Polystyrene additives used in BMC can be formulated into nonshrinking, pigmentable compounds suitable for colored electrical products and kitchen utensils.

Injection molding of BMC and thick molding compounding (TMC) is expanding to improve the efficiency of the matched die process. TMC is a compound intermediate between BMC and SMC in which the glass-fiber strand integrity is retained in the molded product, thus greatly enhancing strength and impact properties.

High strength composites with linear symmetry can be produced by the pultrusion process (21) using continuous glass-fiber reinforcements in the form of rovings. Special continuous glass mats have also evolved to meet the process requirements of this technology. Glass fiber levels of 65% can be formed into polyester composites that demonstrate exceptional flexural performance characteristics required in such applications as flag poles and automotive springs. The process can also form hollow structures and profiles compatible with extruded aluminum and PVC useful in window and portal construction.

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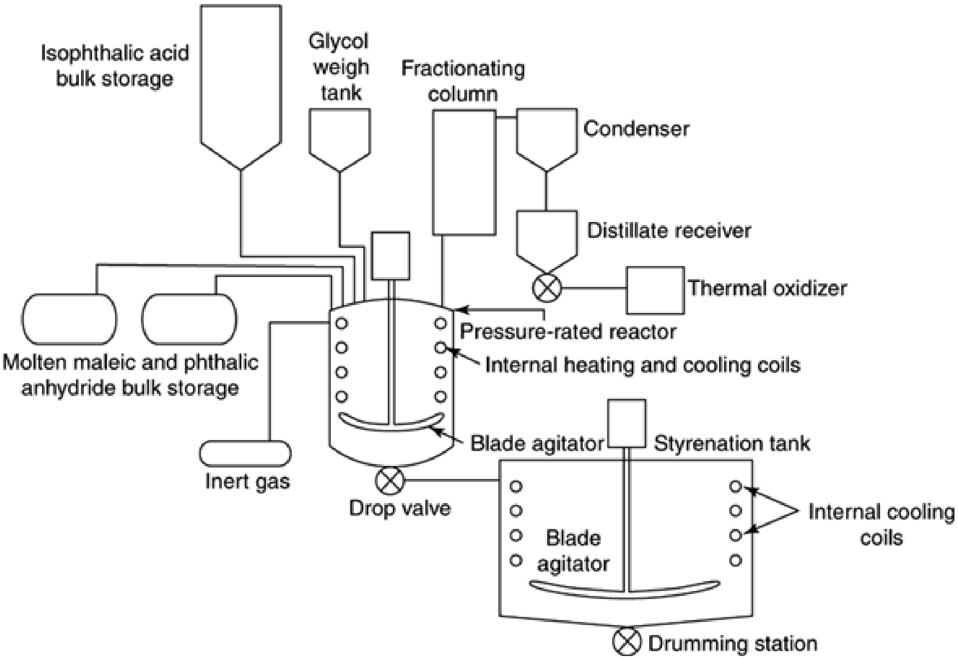

Fig. 1. Reactor system for the manufacture of polyester resins.

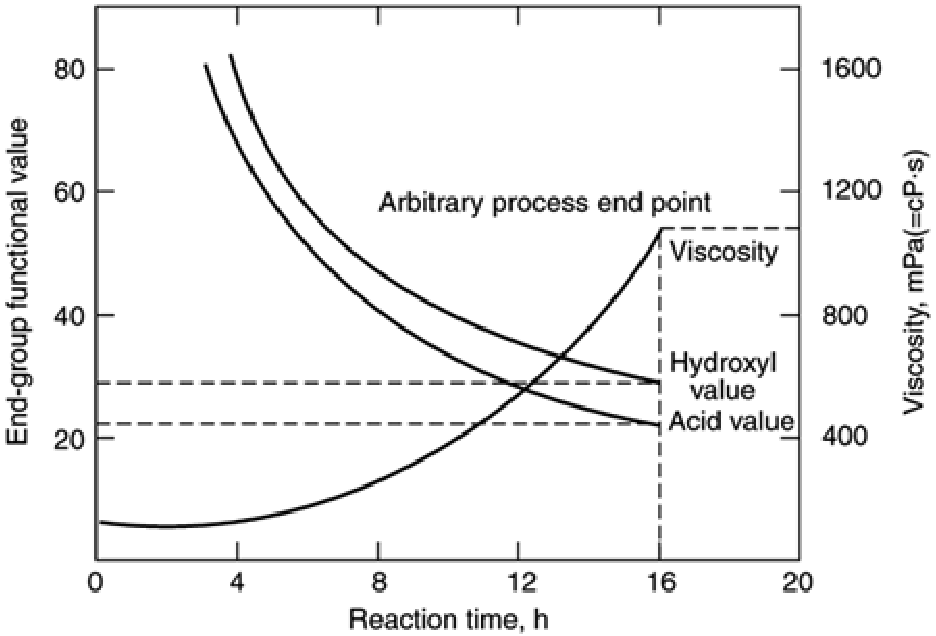

Fig. 2. Functional end groups and solution viscosity during polyester resin manufacture. Acid value is defined as the milligrams of KOH required to neutralize 1 g of polymer; hydroxyl value is defined as the milligrams of acid equivalent required to neutralize 1 g of polymer. Solution viscosities are determined at 60 wt% in styrene.

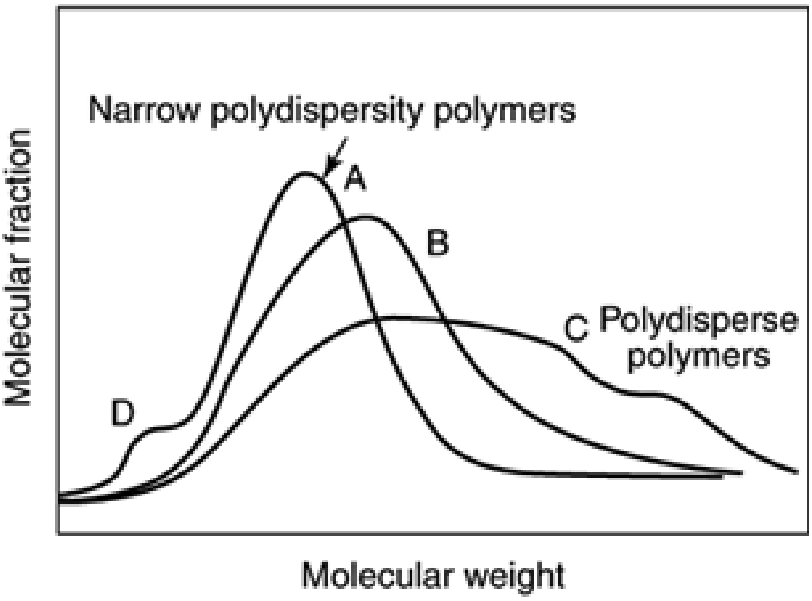

Fig. 3. Molecular weight distribution curves as determined by gel-permeation chromatography. A represents *ortho*-phthalic resins; B, highest molecular weight isophthalic resins; C, high molecular weight polydisperse polymers having high maleic addition reactions; and D, low molecular weight fraction seen in most phthalic resins.

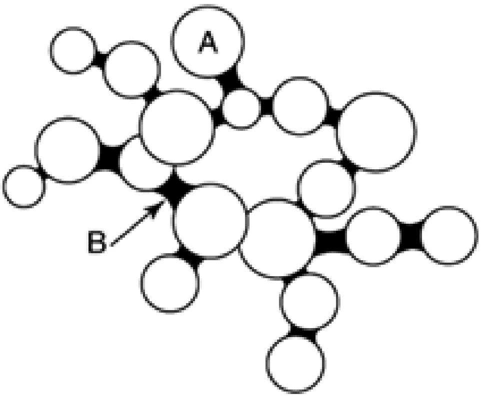

Fig. 4. Micellular gelation mechanism. A shows micelle nuclei, highly cross-linked; B, boundary where micelle growth terminates in styrene block polymers. Styryl free radicals simultaneously initiate micelle nuclei at points of high fumarate concentration. The micelles continue to expand, interacting with free styrene until the fumarate groups are depleted. The micelles eventually overlap at the boundaries that contain higher levels of terminal styrene homopolymer blocks.

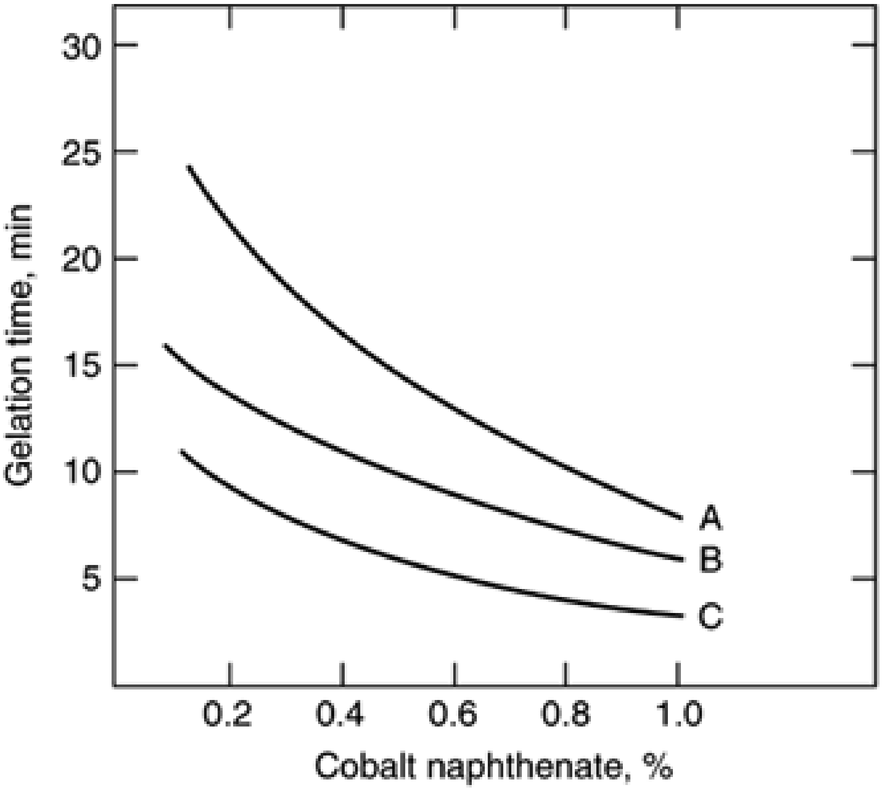

Fig. 5. Influence of catalyst systems on cure rate; gelation time is at 25°C as a function of the initiator concentration. A represents MEKP (1.0%); B, MEKP (1.0%) and dimethylaniline (DMA) (0.05%); and C, MEKP (2.0%).

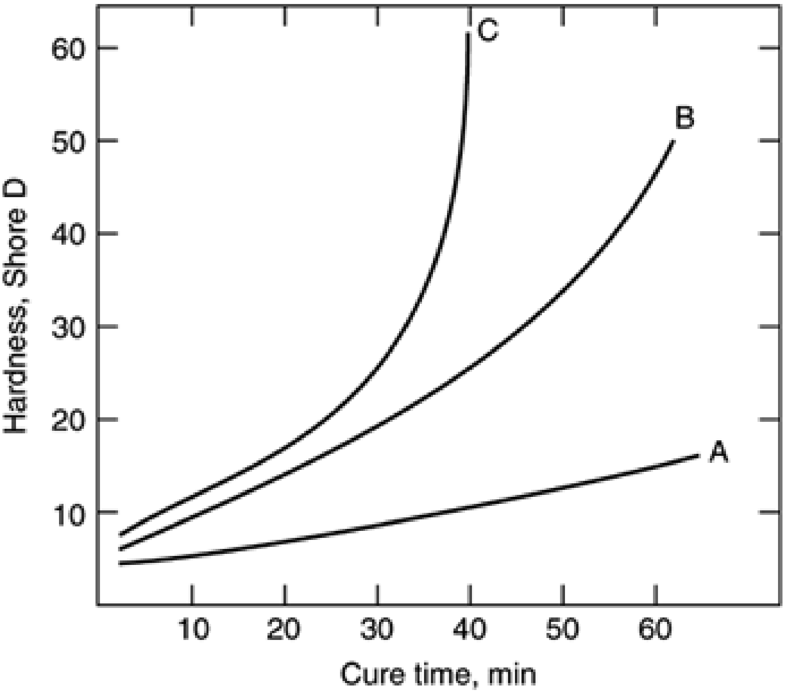

Fig. 6. Influence of catalyst systems on cure rate; effect of dimethylaniline (DMA) on cure rate of cast polymer resin at 25°C. Initiator system contains cobalt naphthenate (0.5%), MEKP (1.0%), and one of the following: A, DMA (0.0%); B, DMA (0.05%); or C, DMA (0.1%).

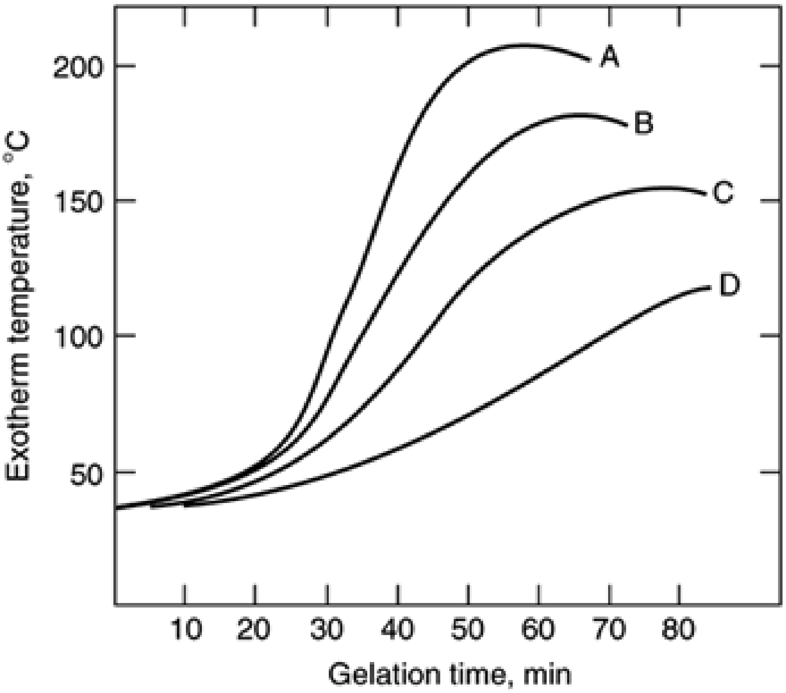

Fig. 7. Influence of copper naphthenate on exotherm temperature. Composition in pph; isophthalic laminating resin is cobalt naphthenate (0.20), dimethylaniline (0.05), and copper naphthenate: A (0.00); B (0.01); C (0.015); or D (0.02).

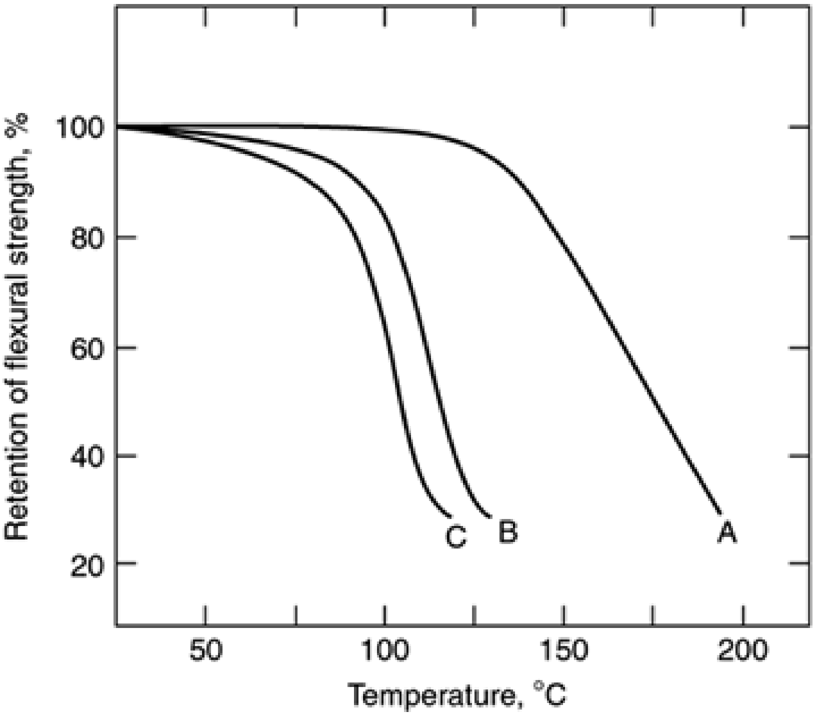

Fig. 8. Flexural properties at elevated temperatures. Laminates constructed from alternating plies of 46.7-g (1.5-az) mat and 746-g/m^2 (24-oz(yd^2) woven roving at a nominal glass content of 45%. A represents bisphenol fumarate (T_g = 130°C); B, isophthalic resin (T_g = 100°C); and C, *ortho*-phthalic resin (T_g = 80°C).

Table 1. **Ingredients of Polyester Resin Formulations in Descending Order of Commercial Significance**

Glycol	Dibasic acid or anhydride	Unsaturated acid or anhydride	Unsaturated monomer
propylene glycol	phthalic anhydride	maleic anhydride	styrene
diethylene glycol	dicyclopentadiene–	fumaric acid	vinyltoluene
ethylene glycol	maleic anhydrideaAcid addition product, formed *in situ*.	methacrylic acid	methyl methacrylate
neopentyl glycol	isophthalic acid	acrylic acid	diallyl phthalate
dipropylene glycol	adipic acid	itaconic acid	α-Methylstyrene
dibromoneopentyl glycol	chlorendic anhydrideb1,4,5,6,7,7-Hexachlorobicyclo(2,2,1)-5-heptene-2,3-dicarboxylic anhydride [115-27-5].		triallyl cyanurate divinylbenzene
bisphenol A diglycidyl ether	tetrabromophthalic anhydride		
bisphenol A dipropoxy ether	tetrahydrophthalic anhydride		
tetrabromobisphenol diethoxy ether	terephthalic acid		
propylene oxide	tetrachlorophthalic anhydride		
1,4-Butanediol			

Table 2. **Molar Component Ratio Used in *ortho*-Phthalic Formulations**

	Glycol			Acid		
Resin	PG	DEG	NPG	PA	MAN	Styrene monomer
marine	1.0			0.5	0.5	1.0
marble	0.8	0.2		0.65	0.35	1.0
gel-coat	0.5		0.5	0.5	0.5	1.0
button	0.85	0.15		0.60	0.4	1.0

Table 3. **Molar Component Ratio Used in Isophthalic Formulations**

	Glycol		Acid		
Resin	PG	DEG	IPA	MAN	Styrene monomer
tank	1.0		0.5	0.5	1.2
pipe	0.5	0.5	0.4	0.6	1.2
pultrusion	0.3	0.7	0.4	0.6	1.0
electrical	1.0		0.3	0.7	1.0

Table 4. **Molar Component Ratio Used in Dicyclopentadiene Formulations**

	Glycol					
Resin	PG	EG	DEG	DCPD	MAN	Styrene monomer
marine		1.0		2.0	2.0	3.0
molding	1.0			0.5	1.0	1.0
bathtub			1.0	2.0	2.0	3.0

Table 5. **Molar Component Ratio Used in Flame-Retardant Formulations**

	Glycol		Acid				
Resin	EG	DBNPG	TBPA	PA	CAN	MAN	Styrene monomer
building	1.0				0.6	0.4	1.5
glazing		1.0		0.5		0.5	2.0
marine	1.0		0.15	0.35		0.5	1.0

Table 6. **Optimal Temperature Range of Conventional Catalyst Systems for Unsaturated Polyesters**

Catalyst	CAS Registry Number	Activator	Processing temperature, °C
benzoyl peroxide	[94-36-0]	dimethylaniline	0–25
methyl ethyl ketone peroxides (MEKP)	[1338-23-4]	cobalt octoate	20–25
cumene hydroperoxide	[80-15-9]	manganese naphthenate	25–50
lauroyl peroxide	[105-74-8]	heat	50–80
tert-butyl peroctoate	[13467-82-8]	heat	80-120
benzoyl peroxide	[94-36-0]	heat	80–140
2,5-dimethyl-2,5-di-2-ethylhexanoylperoxyhexane	[13052-09-0]	heat	93–150
tert-butyl perbenzoate	[614-45-9]	heat	105–150

Table 7. **Standard Test Methods for Polyester Resins and Compounds**

Properties	ASTM designation
specific gravity	D792
Barcol hardness	D2583
heat distortion	D648
flexural strength modulus	D790
tensile strength modulus, elongation	D638
tensile impact	D1822
compressive strength modulus	D695
Izod impact	D256
shear	D732
Taber abrasion	D1044
flammability	E84, E162
dielectric strength	D149
dissipation factor	D150
arc resistance	D495
water absorption	D570
water vapor transmission	C355
chemical resistance	C581

Table 8. **Strength Characteristics of Isophthalic Resin and Composite Derivatives**

Characteristic	Cast resin	Filled resin	Glass-reinforced laminate	Filament-wound laminate	Pultruded profile
glass fiber content, %	0	0	30	50	60
flexural strength, MPa[a]	110	82	193	296	448
flexural modulus, GPa[b]	3.44	4.68	5.86	13.7	20.6
tensile strength, MPa[a]	68.9	44.8	110	193	241
tensile modulus, GPa[b]	3.1	2.6	5.51	12.4	15.1
tensile elongation, %	2.5	0.5	1.6	1.6	1.5
compressive strength, MPa[a]	103	110	137	193	200

[a] To convert MPa to psi, multiply by 145.

[b] To convert GPa to psi, multiply by 145,000.