1 Unsaturated Polyester Resins

Unsaturated polyester resins consist of two polymers, i.e., a short-chain polyester containing polymerizable double bonds and a vinyl monomer. The curing reaction consists of a copolymerization of the vinyl monomer with the double bonds of the polyester. In the course of curing, a three-dimensional network is formed. Unsaturated polyester resins belong to the group of so-called thermosets. There are several monographs and reviews on unsaturated polyesters and unsaturated polyester resins [1–7].

We will differentiate between unsaturated polyesters and unsaturated polyester resins. Unsaturated polyesters are the polyesters as they emerge from the condensation vessel. They are rarely sold as such, because they are brittle at room temperature and difficult to handle. Instead, whenever a polyester is freshly synthesized in a plant, it is mixed with the vinyl monomer in the molten state. Thus materials that are viscous at room temperature, with a styrene content of ca. 60%, are sold. Such a mixture of an unsaturated polyester with the vinyl polymer is referred to here as an unsaturated polyester resin.

1.1 History

It was realized long ago that some natural oils as well as alkyle resins can be dried by certain additives and used as coatings. This drying results from a polymerization of the unsaturated moieties in the ester molecules. Next it was discovered that the addition of styrene would accelerate the drying. The invention of unsaturated polyester resins is ascribed to Carleton Ellis (1876–1941). The first patents with regard to polyester resins emerged in the 1930s [8–10]. Commercial production started in 1941 already reinforced with glass fibers for radar domes, also referred to as radomes.

1.2 Monomers

According to the composition of an unsaturated polyester resin, the monomers can be grouped in two main classes, i.e., components for the polyester and components for the vinyl monomer.

1.2.1 Monomers for an Unsaturated Polyester

Monomers used for unsaturated polyesters are shown in Table 1.1 and in Figures 1.1 and 1.2. Unsaturated diols are only rarely used.

1.2.1.1 Alcohol Components

The most common alcohol components are 1,2-propylene glycol and ethylene glycol (EG). Ether containing alcohols exhibit better air-drying properties and are used in topcoats. Polyesters based on unsaturated diols can be prepared by the transesterification of diethyl adipate with unsaturated diols, e.g., *cis*-2-butene-1,4-diol and 2-butyne-1,4-diol. The transesterification method is a suitable procedure for the preparation of unsaturated polyesters in comparison to the direct polycondensation [11]. *cis*-2-Butene-1,4-diol, the most available aliphatic unsaturated diol, has been used to produce some valuable polymers such as graftable unsaturated segmented poly(urethane)s and crosslinkable polyesters for medical purposes.

Chemically modified soybean oil is an inexpensive alternative candidate for unsaturated polyester (UP) compositions. In addition, when reinforced with natural fibers, these composites could yield comparable and adequate properties to common products. Acrylated epoxidized soybean oil or maleated acrylated epoxidized soybean oil can be used for the synthesis of a prepolymer that contains vinyl groups. These groups are then copolymerized with styrene, as otherwise usual [15].

1.2.1.2 Acid and Anhydride Components

A general-purpose industrial unsaturated polyester is made from 1,2-propylene glycol, phthalic anhydride, and maleic anhydride. The most commonly used vinyl monomer is styrene. Maleic anhydride without phthalic anhydride would yield a polyester with a high density of double bonds along the polyester chain. This would result in a high crosslinking density of the cured product, thus in a brittle product. Therefore, the unsaturated acid component is always diluted with

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Table 1.1 Monomers for Unsaturated Polyesters

Saturated Alcohols	**Remarks**
1,2-Propylene glycol	Most common glycol
Ethylene glycol	Less compatible with styrene than propylene glycol
Diethylene glycol	Good drying properties
Neopentyl glycol	Good hydrolysis resistance
Glycerol	Trifunctional alcohol, for branched polyesters. Danger of crosslinking during condensation
	Flame retardant
Tetrabromobisphenol A (TBBPA)	
Trimethylol propane	Trifunctional alcohol, cheaper than glycerol
Trimethylol propane mono allyl ether	Weather resistant for coatings [12,13]
Undecanol	Used as chain stopper
Saturated Acids and Anhydrides	**Remarks**
Phthalic anhydride	Most common anhydride
Isophthalic acid	Good hydrolysis resistance
Terephthalic acid	Superior hydrolysis resistance
HET acid	Flame retardant systems. In fact, even when addressed as HET acid, the HET anhydride is used
Tetrabromophthalic anhydride	Flame retardant systems
Adipic acid	Soft resins
Sebacic acid	Soft resins
o-Carboxy phthalanilic acid	[14]
Unsaturated Acids and Anhydrides	**Remarks**
Maleic anhydride	Most common
Fumaric acid	Copolymerizes better with styrene than maleic anhydride
Itaconic acid	

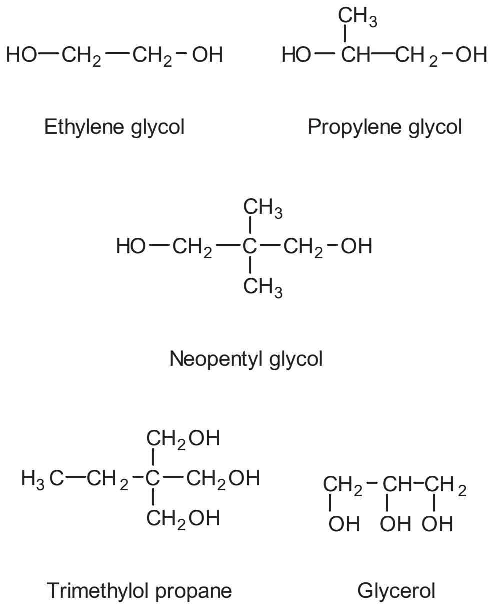
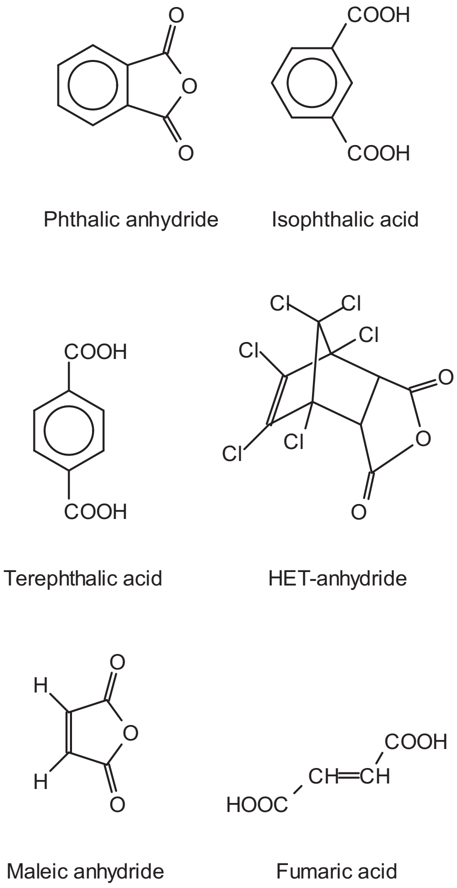


Figure 1.1 Diols and triols used for unsaturated polyester resins.

an acid with non-polymerizable double bonds. Note that aromatic double bonds also will not polymerize with vinyl components. The double bond in HET acid will not polymerize. Fumaric acid copolymerizes well with styrene, but fumaric acid is more costly than maleic anhydride. Therefore, maleic anhydride is the preferred unsaturated acid component. Another aspect is that during the condensation of fumaric acid, 2 mol of water must be removed from the reaction mixtures, whereas in the case of maleic anhydride only 1 mol of water must be removed. Anhydrides are preferred over the corresponding acids because of the higher reactivity.

Isophthalic acid and terephthalic acid cannot form an anhydride. These compounds do not condense as fast as phthalic anhydride. On the other hand, the polyesters from isophthalic acid and terephthalic acid are more stable than those made from phthalic anhydride. That is why these polyesters with neopentyl glycol are used in aggressive environments and as gel coats and top coats. A gel coat is the first layer of a multilayer material; the top coat is the layer on the opposite side. For instance, if a polyester boat is built, the gel coat is first painted into the model. Then a series of glass-fiber-reinforced laminates are applied, and finally the top coat is painted.



Phthalic anhydride Isophthalic acid

Terephthalic acid HET-anhydride

Maleic anhydride Fumaric acid

Figure 1.2 Acids and anhydrides used for unsaturated polyester resins.

Isomerization. During the synthesis of the polyester, maleic anhydride partly isomerizes to fumaric acid. The isomerization follows second-order kinetics because of the catalysis by maleic acid. The activation energy of the isomerization is ca. $63.2\ \mathrm{kJ\,mol^{-1}}$ [16].

2-Methyl-1,3-propanediol offers significant process advantages to resin producers because it is an easily handled liquid, it has a high boiling point, and it has two primary hydroxyl groups for rapid condensations. Polyester resins produced from 2-methyl-1,3-propanediol using conventional condensation polymerization, however, have relatively low fumarate contents (60–70%), and simply increasing the reaction temperature to promote isomerization causes color problems.

The two-step process helps increase the degree of isomerization for such systems. First, the aromatic dicarboxylic acid is allowed to react with 2-methyl-1,3-propanediol at a temperature of up to 225 °C to produce an ester diol intermediate. In the second step, the intermediate reacts with maleic anhydride and with 1,2-propylene glycol. The resulting unsaturated polyester resin has a fumarate content greater than about 85% [17]. The high fumarate content helps the resins to cure quickly and thoroughly with vinyl monomers, giving the resulting thermosets excellent water resistance.

1.2.1.3 Amine Modifiers

The adducts of ethylene oxide or propylene oxide with *N*,*N*′-diphenylethane-1,2-diamine or *N*,*N*-dimethyl-*p*-phenylene diamine and ethylene oxide (EO) with *N*,*N*′-diphenylhexane-1,6-diamine can be used as modifiers. When used in amounts up to 2%, the amines substantially reduce the gelation time of these modified unsaturated polyesters. However, as the reactivity of the resins increases, their stability decreases [18,19].

1.2.1.4 Dicyclopentadiene

Dicyclopentadiene is used in a wide variety of applications, including elastomers, flame retardants, pesticides, and resins for adhesives, coatings, and rubber tackifiers. Approximately 30% of the production is used for unsaturated polyester resins because of their valuable properties [20].

Dicyclopentadiene polyester resins are synthesized from dicyclopentadiene, maleic anhydride, and a glycol. The reaction is performed in the presence of water to generate maleic acid from the maleic anhydride to form dicyclopentadiene maleate. The ene reaction is shown in Figure 1.3.

The maleate is esterified with the glycol to form the unsaturated polyester resin [21,22]. The ene adduct serves to form end capped polyesters. At higher temperatures dicyclopentadiene undergoes a retro Diels-Alder reaction and can add to the unsaturations of fumaric acid and maleic acid (as pointed out in Figure 1.4), to form nadic acid units. When the dicyclopentadiene-modified unsaturated polyester is used for a molding material, the polyester is usually mixed with a radically polymerizable monomer and a polymerization initiator. This allows the viscosity or curing time of the molding material to be suitable for the molding operation.

Dicyclopentadiene-modified unsaturated polyesters yield molded articles with excellent performance. The function of dicyclopentadiene is to impart air-drying characteristics, low-profile properties, high

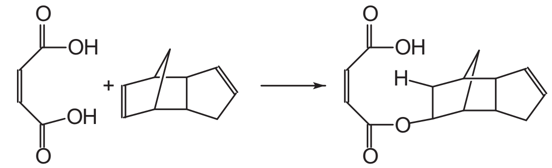


Figure 1.3 Ene reaction between maleic acid and dicyclopentadiene.

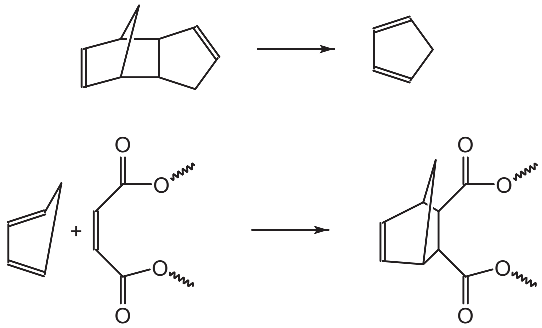


Figure 1.4 Retro Diels-Alder reaction of dicyclopentadiene and Diels-Alder reaction between maleic acid units and cyclopentadiene.

heat distortion, excellent weathering performance, and increased filler dispersibility in the resulting polymer [23].

1.2.2 Vinyl Monomers

The vinyl monomer serves as solvent for the polyester and reduces its viscosity. Further, it is the agent of copolymerization in the course of curing. Vinyl monomers for unsaturated polyester resins are shown in Table 1.2 and in Figure 1.5.

1.2.2.1 Styrenes

Styrene is the most widely used vinyl monomer for unsaturated polyesters. However, styrene has a carcinogenic potential: therefore, replacing styrene by some other vinyl monomer has been discussed for years.

With larger amounts of styrene the rigidity of the material can be increased. α-Methylstyrene forms less reactive radicals, and thus slows down the curing reaction. Therefore, α-methylstyrene is suitable for decreasing the peak temperature during curing.

Polar vinyl monomers, such as vinylpyridine, improve the adhesion of the polyester to glass fibers, which is useful in preventing delamination.

Table 1.2 Vinyl Monomers for Unsaturated Polyester Resins

Monomer	Remarks
Styrene	Most common, but carcinogenic
p-Vinyl toluene	Not really a substitute for styrene
α-Methylstyrene	Slows the curing
Methyl acrylate	
Methyl methacrylate	Good optical properties
Diallyl phthalate	
Triallyl cyanurate	

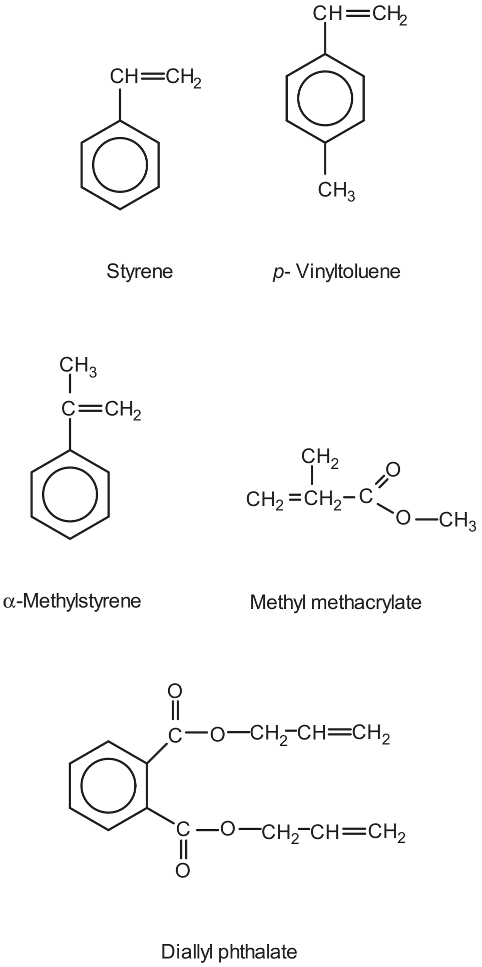


Figure 1.5 Vinyl monomers for unsaturated polyester resins.

1.2.2.2 Acrylates and Methacrylates

Acrylates improve outdoor stability. Methyl methacrylate, in particular, enhances the optical properties. The refractive index can be varied with mixtures of styrene and methyl methacrylate close to that

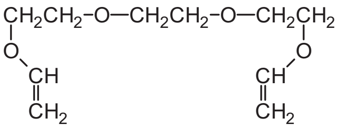

Triethylene glycol divinyl ether

Figure 1.6 Vinyl ethers.

of glass, so that fairly transparent materials can be produced.

1.2.2.3 Vinyl Ethers

Various vinyl and divinyl ethers have been used as substitutes for styrene. Divinyl ethers with unsaturated polyesters are used preferably in radiation curable compositions and coatings. However, special formulations containing no styrene but triethylene glycol divinyl ether (cf. Figure 1.6) are available that can be used for gel coats [24].

Propenyl ethers are generally easier to prepare than their corresponding vinyl ethers. The propenyl ethers are simply prepared by isomerization of the corresponding allyl ethers. Due to the steric effect of the methyl groups in the propenyl ether molecules, they are expected to be much less reactive than their vinyl ether analogs [25]. Examples for propenyl ethers are ethoxylated hexanediol dipropenyl ether and 1,1,1-trimethylol propane dipropenyl ether.

1.2.2.4 Other Vinyl Monomers

Triallyl cyanurate enhances the thermal stability of the final products. Since the compound is trifunctional, it enhances the crosslinking density.

1.2.3 Specialities

1.2.3.1 Monomers for Waterborne Unsaturated Polyesters

Waterborne unsaturated polyesters are used for wood coatings. They have UV-sensitive initiator systems. The basic constituents are selected from ethylene glycol, 1,2-propylene glycol, diethylene glycol, and tetrahydrophthalic anhydride, terephthalic acid, and trimellitic anhydride [26]. The vinyl monomer is trimethylol propane diallyl ether. The UV-sensitive compound is 2-hydroxy-2-methylphenylpropane-1-one. When diluted with water, the resins exhibit a proper viscosity in the range of 2500 cps. The cured products show good tensile properties and weatherability.

Another method used to make unsaturated polyesters water soluble is to introduce polar hydrophilic groups such as carboxylic and sulfonic groups into the resin molecule, which ensures a good dispersibility in water. An example of such a compound is sodium 5-sulfonatoisophthalic acid. Instead of styrene, glycerol monoethers of allyl alcohol and unsaturated fatty alcohols are used as vinyl monomer [27].

Unsaturated polyester resins diluted in water are used for particleboards and fiberboards. They are modified with acrylonitrile and used as mixtures with urea/formaldehyde (UF) resins. A mixture of a UP resin and a UF resin allows the production of boards which have considerably higher mechanical properties than those bonded exclusively with UF resins [28].

1.2.3.2 Low Emission Modifiers

Several methods have been proposed for reducing volatile organic compound emissions:

- adding skin forming materials,
- replacement of the volatile monomer with a less volatile monomer,
- reduction in the amount of the monomer in the compositions, and
- increasing the vinyl monomers by attaching them onto the polyester chain.

The addition of paraffins to unsaturated polyester resins has been shown to reduce emissions by forming a thin film on the resin surface. While suitable for some applications, this solution is unacceptable for other applications due to a decreased interlaminate adhesion [29].

Low Volatile Monomers. Styrene can be partly substituted by low volatile monomers. A number of alternatives have been sought to reduce emissions and as substitutes for styrene. Higher molecular weight derivatives of styrene, such as vinyl toluene and *tert*-butyl styrene, have been utilized as reactive diluents and resulted in decreased emissions [29].

Bivalent metal salts of acrylic acid or methacrylic acid have low vapor pressure. Examples include zinc diacrylate, zinc dimethacrylate, calcium diacrylate, and calcium dimethacrylate [30].

The metal salt monomer is typically a solid, and therefore has much lower vapor pressure than, e.g., styrene. The acrylate functionality copolymerizes readily with styrene. Due to the bivalent metal ions, the acrylates act as crosslinkers of the ionomer type. Therefore, an additional crosslinking occurs in comparison to pure styrene.

Acrylate-modified Unsaturated Polyesters. Acrylate-modified unsaturated polyesters may be used for low-viscosity resins and resins with low emission of volatile monomers. In commercially available unsaturated polyester resin applications, up to 50% of styrene or other vinyl monomers are used. During curing some of the organic monomer is usually lost to the atmosphere, which causes occupational safety hazards and an environmental problem.

Tailoring the polyester by synthesizing branched structures and incorporating additional vinyl unsaturations has been proposed. The diol alcohols used for condensation may be partly replaced by glycidyl compounds in order to obtain low-molecular-weight methacrylate or acrylate-modified or terminated polyesters [31]. Suitable glycidyl compounds include glycidyl methacrylate and glycidyl acrylate. Not more than 60 mol% of the alcohols can be replaced by glycidyl compounds [24,32].

These polyesters have low viscosities because of the branched structures. In addition to the maleic or fumaric units, they bear additional unsaturations resulting from the pending reactive acrylate or methacrylate moieties. For this reason these types need less vinyl monomer (styrene) to increase the crosslinking density of the cured product. The increased unsaturation results in a higher reactivity, which in turn leads to an increase in heat distortion temperature and better corrosion resistance, good pigmentability, and excellent mechanical and physical properties [33]. Such resins are therefore suitable as basic resins in gel coats.

1.2.3.3 Epoxide-Based Unsaturated Polyesters

Epoxide-based unsaturated polyesters are obtained from the reaction of half esters of maleic anhydride of fumaric acid with epoxy groups from epoxide resins. For example, *n*-hexanol reacts easily with maleic anhydride to form acidic hexyl maleate. This half ester is then used for the addition reaction with the epoxy resin [34].

Allyl alcohol in the unsaturated resins enhances their properties. The glass transition temperatures of the epoxy fumarate resins exceed 100 °C. The glass transition temperatures of epoxy maleates are higher than 70 °C. The resins have good chemical resistance [35].

1.2.3.4 Isocyanates

Isocyanates, such as toluene diisocyanate, can be added to a formulated resin, such as polyester plus vinyl monomer. The gelation times increase with the concentration of toluene diisocyanate [36].

During curing, toluene diisocyanate can initially react with the UP moieties and produce poly(urethane) structures. Subsequently, intermolecular crosslinking occurs. Toluene diisocyanate has an obvious effect on the toughness and strength of a UP resin. A ratio of isocyanate to UP of 7.5% exhibited the best mechanical properties [37].

The viscosity increases strongly. Resins with only 3% of toluene diisocyanate are thixotropic [36]. An increase in the viscosity is highly undesirable.

A 1,6-hexane diisocyanate (HDI) trimer can improve the mechanical properties of a hydroxyl terminated UP type. The morphological analysis of the surfaces of fracture reveals the presence of micro phase separated structures. These change from dendritic, to dimple and to cystiform structures when the content of the HDI trimer is increased [38].

To reduce the emissions, styrene-free UP compositions have been developed [29].

These are based on a dicyclopentadiene containing UP, a urethane acrylate or methacrylate, a multifunctional methacrylate monomer, and a hydroxyl functionalized methacrylate monomer.

Hydroxyl functionalized methacrylates may be used in the preparation of the urethane methacrylate monomer component or as a monomeric reactive diluent. These compounds include hydroxyethyl methacrylate, hydroxypropyl methacrylate, hydroxyethyl acrylate, and hydroxypropyl acrylate. The preparation of the base UP and the other monomers has been exemplified in detail [29].

1.2.3.5 *o*-Carboxy Phthalanilic Acid

A new acid monomer, *o*-carboxy phthalanilic acid, cf. Figure 1.7, has been synthesized from *o*-aminobenzoic acid with phthalic anhydride. This monomer was condensed with different acids and glycols to prepare unsaturated polyesters. These polyesters were admixed with styrene and cured. The final materials were extensively characterized [14,39].

It was found that the styrene/poly(1,2-propylene-maleate-*o*-carboxy phthalanilate) polyester resin has the highest compressive strength value and the best chemical resistance and physical properties among the materials under investigation.

1.2.3.6 Modified Plant Oils

Acrylated epoxidized soybean and linseed oils of different characteristics have been incorporated into vinylester resins and UP resins [40,42]. The chemical structure of the modified oils is shown in Figure 1.8.

Blending of UP composition with tung oil results in an improved impact strength, creep resistance, modulus, and hardness [43].

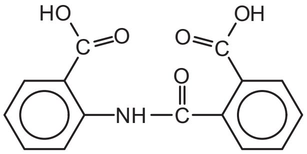


Figure 1.7 *o*-Carboxy phthalanilic acid [14].

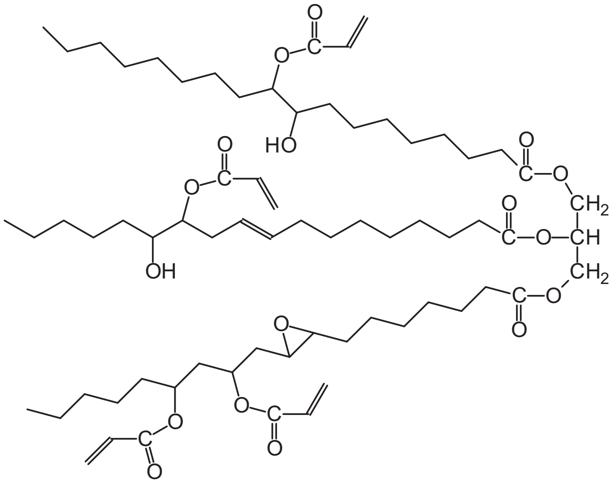


Figure 1.8 Modified natural oil (schematically) [40].

Also polymers from methylene diphenyl isocyanate have been used in the compositions. The influence of the modifications on thermal and mechanical properties has been investigated. With increasing amount of plant oils added, the glass transition temperatures, the elastic modulus, and the Charpy impact strength decrease. In contrast, the static fracture toughness somewhat increases.

The methylene diphenyl isocyanate moieties cause an additional crosslinking. This causes a marked increase of the glass transition temperature, but the elastic modulus in the glassy state markedly decreases. However, the thermal degradation behavior is slightly affected, as the thermal stability decreases [40,42].

Highly adhesive unsaturated polyester resin compositions for fixing or immobilizing coils have been described [41]. These compositions are suitable for electrical insulation and immobilization of electrical equipment such as motors and transformers. Particularly useful isocyanates have a vinyl group attached, e.g., 2-methacryloyloxyethyl isocyanate or 2-[(3,5-dimethylpyrazolyl)carboxyamino]ethyl methacrylate. The latter is a pyrazol blocked isocyanate. These isocyanates do not shorten the pot life of the resulting resin composition and improve the adhesion strength. The structures are shown in Figure 1.9.

1.2.4 Synthesis

The synthesis of unsaturated polyesters occurs either by a bulk condensation or by azeotropic condensation. General-purpose polyesters can be condensed by bulk condensation, whereas more sensitive components need the azeotropic condensation technique, which can be performed at lower temperatures. The synthesis at the laboratory scale does not differ significantly from the commercial procedure.

1.2.4.1 Kinetics of Polyesterification

The kinetics of polyesterification have been modeled. In the models, the asymmetry of 1,2-propylene glycol was taken into account, because it bears a

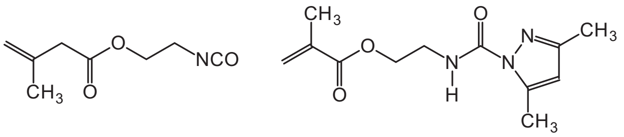


Figure 1.9 Isocyanates for adhesion improvement [41].

primary and secondary hydroxyl group. The reactivities of these hydroxyl groups differ by a factor of 2.6. The relative reactivity of maleic and phthalic anhydrides toward 1,2-propylene glycol, after the ring opening of both anhydrides is complete, increases from ca. 1.7 to 2.3 when the temperature is increased from 160 °C to 220 °C [44].

The rate constants and Arrhenius parameters are estimated by fitting the calculated conversion of the acid with time to the experimental data over the entire range of conversion. For the copolyesterification reactions involving two acids, a cross-catalysis model is used [45]. The agreement between model predictions and experimental data has been proved to be satisfactory. For example, the energy of activation for the condensation reaction of 2-methyl-1,3-propanediol with maleic anhydride was obtained to be 65 kJ mol^{-1}, and with phthalic anhydride a value of 82 kJ mol^{-1} was obtained.

1.2.4.2 Sequence Distribution of Double Bonds

The polycondensate formed by the melt condensation process of maleic anhydride, phthalic anhydride, and 1,2-propylene glycol in the absence of a transesterification catalyst has a non-random structure with a tendency toward blockiness. On the other hand, the distribution of unsaturated units in the unsaturated polyester influences the curing kinetics with the styrene monomer. Segments containing double bonds close together appear to lower the reactivity of the resin due to steric hindrance. This is suggested by the fact that the rate of cure and the final degree of conversion increase as the average sequence length of the maleic units decreases. Due to the influence of the sequence length distribution on the reactivity, the reactivity of unsaturated polyester resins may be tailored by sophisticated condensation methods.

Methods to calculate the distributions have been worked out [46,47]. Monte Carlo methods can be used to investigate the effects of the various rate constants and stoichiometry of the reactants. Also, structural asymmetry of the diol component and the influence of the dynamics of the ring opening of the anhydride are considered.

1.2.5 Manufacture

Unsaturated polyesters are still produced in batch. Continuous processes have been invented, but are not widespread. Most common is a cylindrical batch reactor equipped with stirrer, condenser, and a jacket heater. Thus the synthesis in the laboratory and in industry is very similar. The typical size of such reactors is between 2 and 10 m^3.

We now illustrate a typical synthesis of an unsaturated polyester. The reactor is filled at room temperature with the glycol, in slight excess to compensate the losses during the condensation. Losses occur because of the volatility of the glycol, but also due to side reactions. The glycol may eliminate water at elevated temperatures. Then maleic anhydride and phthalic anhydride are charged to the reactor. Typical for a general-purpose unsaturated polyester resin is a ratio of 1 mol maleic anhydride, 1 mol phthalic anhydride, and 1.1 mol 1,2-propylene glycol. Further, other components, such as adhesion promoters, can be added.

The reactor is sparged with nitrogen and slowly heated. At ca. 90 °C the anhydrides react with the glycol in an exothermic reaction. This is the initial step of the polyreaction, shown in Figure 1.10. At the end of the exothermic reaction a condensation catalyst may be added.

Catalysts such as lead dioxide, *p*-toluenesulfonic acid, and zinc acetate [48] affect the final color of the polyester and the kinetics of curing. Temperature is raised carefully up to 200 °C, so that the temperature of the distillate never exceeds ca. 102–105 °C. Otherwise the glycol distills out. The reaction continues under nitrogen or carbon dioxide atmosphere. The sparging is helpful for removing the water. Traces of oxygen can cause coloration. The coloration emerges due to multiple conjugated double bonds. Maleic anhydride is helpful in preventing coloration, because the series of conjugated double bonds are interrupted by a Diels-Alder reaction. In the case of sensitive components, e.g., diethylene glycol, even small amounts of oxygen can cause gelling during the condensation reaction.

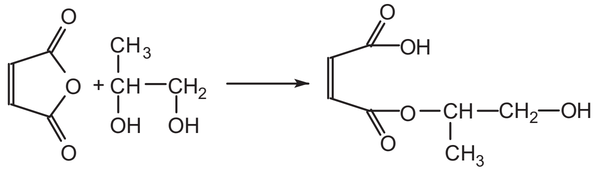


Figure 1.10 Reaction of maleic anhydride with 1,2-propanediol.

There are certain variations of water removal. Simply sparging with inert gas is referred to as the melt condensation technique. In the case of thermal sensitive polyesters, the water may be removed by the azeotrope technique. Toluene or xylene is added to the reaction mixture. Both compounds form an azeotrope with water. During reflux, water separates from the aromatic solvent and can be collected. In the final stage, the aromatic solvent must be removed either by enhanced sparging or under vacuum. The azeotrope technique is in general preferred, because condensation proceeds faster than in the case of melt condensation.

Vacuum also can be used to remove the water, although this technique is used only rarely for unsaturated polyesters because of the risk of removal of the glycol.

At early stages, the progress of the condensation reaction can be controlled via the amount of water removed. In the final stage, this method is not sufficiently accurate and the progress is monitored via the acid number. Samples are withdrawn from the reactor and are titrated with alcoholic potassium hydroxide (KOH) solution. The acid number is expressed in milligrams KOH per gram of resin. Even though other methods for the determination of the molecular weight are common in other fields, the control of the acid number is the quickest method to follow the reaction.

The kinetics of self-catalyzed polyesterification reactions follows a third-order kinetic law. Acid-catalyzed esterification reactions follow second-order kinetics. In the final stage of the reaction, the reciprocal of the acid number is linear with time.

General-purpose unsaturated polyester resins are condensed down to an acid number of around 50 mg KOH/g resin. This corresponds to a molecular weight of approximately 1000 Da. After this acid number has been reached, some additives are added, in particular polymerization inhibitors , e.g., hydroquinone, and the polyester is cooled down, to initiate the mixing with styrene. The polyester should be cooled down to the lowest possible temperature. In any case the temperature of the polyester should be below the boiling point of the vinyl monomer. There are two limiting issues:

1. If the polyester is too hot, after mixing with the vinyl monomer a preliminary curing may take place. In the worst case the resin may gel.
2. If the polyester is too cold, its viscosity becomes too high, which jeopardizes the mixing process.

Mixing can occur in several ways: either the polyester is poured into styrene under vigorous stirring, or under continuous mixing, or the styrene is poured into the polyester. The last method is preferred in the laboratory. After mixing, the polyester resin is then cooled down to room temperature as quickly as possible. Finally some special additives are added, such as promoter for preaccelerated resin composition. An unsaturated polyester resin is not miscible in all ratios with styrene. If an excess of styrene is added, a two-phase system will emerge.

The resins have a slightly yellow color, mainly due to the inhibitor. The final product is filtered, if necessary, and poured into vats or cans.

1.3 Special Additives

1.3.1 Inhibitors

The double bonds in an unsaturated polyester resin are very easily affected by impurities or the ambient temperature at the stage of storing. The higher the ambient storage temperature or the longer the storage time, the more is the danger of preliminary self-polymerization.

In this way an undesired gelation of the resin occurs which makes the resin unusable. A monetary loss due to deterioration of the workability of the resin occurs [49].

There is a difference between inhibitors and retarders. Inhibitors stop the polymerization completely, whereas retarders slow down the polymerization rate. Inhibitors influence the polymerization characteristics. They act in two ways:

1. increasing the storage time,
2. decreasing the exothermic peak during curing.

Common inhibitors are listed in Table 1.3.

Inhibitors are used to increase the storage time and to increase the pot life time. Sometimes a combination of two or more inhibitors is used, since some types of inhibitors act more specifically on the storage time and others influence the pot life time.

The storage time of an unsaturated polyester resin increases with the amount of inhibitor. Storage at high temperatures decreases the possible shelf life. On the

Table 1.3 Inhibitors and Retarders for Unsaturated Polyester Resins [50]

Compounds
2-Methoxyphenol
4-Methoxyphenol
2,6-Di-*tert*-butyl-4-methylphenol
2,6-Di-*tert*-butylphenol
2,4,6-Trimethylphenol
2,4,6-*tris*-Dimethylaminomethylphenol
4,4′-Thio-bis (3-methyl-6-*tert*-butylphenol)
4,4′-Isopropylidene diphenol
2,4-Di-*tert*-butylphenol
6,6′-Di-*tert*-butyl-2,2′-methylene di-*p*-cresol
Hydroquinone
2-Methylhydroquinone
2-*tert*-Butylhydroquinone
2,5-Di-*tert*-butylhydroquinone
2,6-Di-*tert*-butylhydroquinone
2,6-Dimethylhydroquinone
2,3,5-Trimethylhydroquinone
Catechol
4-*tert*-Butyl catechol
4,6-Di-*tert*-butyl catechol
p-Benzoquinone
2,3,5,6-Tetrachloro-1,4-benzoquinone
Methylbenzoquinone
2,6-Dimethylbenzoquinone
1,4-Naphthoquinone
Chloranil
Picric acid
1-Oxyl-2,2,6,6-tetramethylpiperidine
1-Oxyl-2,2,6,6-tetramethylpiperidine-4-ol (TEMPOL)
1-Oxyl-2,2,6,6-tetramethylpiperidine-4-one (TEMPON)
1-Oxyl-2,2,6,6-tetramethyl-4-carboxylpiperidine
1-Oxyl-2,2,5,5-tetramethylpyrrolidine (4-carboxy-TEMPO)
1-Oxyl-2,2,5,5-tetramethyl-3-carboxylpyrrolidine (3-carboxy-PROXYL)

other hand, high doses of inhibitor detrimentally influence the curing of the resin. Higher amounts of radical initiators are required in the presence of high doses of inhibitors. The exothermic peak during curing is reduced. This influences the degree of monomer conversion. A high degree of conversion is needed to have optimal properties.

Further, if the additive amount of the inhibitor is excessive, the color of cured vinylester resin or cured unsaturated polyester resin becomes darkened, thus undesirably degrading the appearance of the product [49].

Alternatively, the resin can be stored in a freezer during transportation or general storage to reduce the preliminary polymerization reactions. However, the costs of performing this method are high, thus undesirably increasing the price of the product.

1.3.1.1 Shelf Life Extension

The shelf life can be extended by enhancing the oxygen content of the resin [49]. In this way, the self-polymerization reaction of the reactive functional groups can be minimized.

The oxygen content may be enhanced by introducing a gas containing oxygen. The oxygen-containing gas should contain 92% oxygen.

Alternatively, the oxygen content may be enhanced by a chemical reaction that can produce oxygen. Chemical substances that produce oxygen may be deposited in a first vessel that is connected to a second vessel in which the resin is stored. Therefore, the oxygen produced from a chemical reaction may diffuse into resin.

Suitable chemical substances for the production of oxygen are calcium peroxide, hydrogen peroxide, or manganese dioxide [49].

This method for extending the shelf life not only prevents formation of a product with a darkened color, but can also prevent the reduction of the reactivity of the unsaturated polyester resin caused by the addition of excessive inhibitor. Further, in comparison to the conventional method, in which the unsaturated polyester resin is stored in a freezer or is stored using an inhibitor, this method may effectively reduce the cost.

1.3.2 Thickeners

1.3.2.1 Multivalent Salts

For sheet molding compounds and bulk molding compounds, the resins are thickened. This can be achieved particularly with MgO, at a concentration of about 5%.

It is believed that it first interacts with the carboxylic acid group on chains. Then a complex is formed with the salt formed and the carboxylic acid groups of other chains, leading to an increase in viscosity. The maximum hardness is achieved at 2% MgO with an increase from 190 MPa to 340 MPa for the specimen cured at room temperature. High-temperature curing decreases the hardness.

1.3.2.2 Thixotropic Additives

For gel coat applications, fumed silica, precipitated silica, or an inorganic clay can be used. Hectorite and other clays can be modified by alkyl quaternary ammonium salts such as di(hydrogenated tallow) ammonium chloride. These organoclays are used in thixotropic unsaturated polyester resin systems [51].

1.3.3 Emission Suppressants

If a polyester is exposed to open air during curing, the vinyl monomer can easily evaporate. This leads to a change in the composition and thus to a change in the glass transition temperature of the final product [52]. Still more undesirable is the emission of potentially toxic compounds. There are several approaches to achieving products with low emission rates.

The earliest approach has been the use of a suppressant which reduces the loss of volatile organic compounds. The suppressants are often waxes. The wax-based products are of a limited comparability with the polyester resin. The wax-based suppressants separate from the system during polymerization or curing, forming a surface layer which serves as a barrier to volatile emissions.

For example, a paraffin wax having a melting point of about 60 °C significantly improves the styrene emission results. Waxes with a different melting point from this temperature will not perform adequately at the low concentrations necessary to maintain good bonding and physical properties while inhibiting the styrene emissions [53]. The waxy surface layer must be removed before the next layer can be applied, because waxes are likely to cause a reduction in the interlaminar adhesion bond strength of laminating layers.

Suppressants selected from polyethers, polyether block copolymers, alkoxylated alcohols, alkoxylated fatty acids, or polysiloxanes show a suppression of the emission as well and better bonding properties [54–56]. Unsaturated polyesters that contain α,β-unsaturated dicarboxylic acid residues and allyl ether or polyalkylene glycol residues (so-called gloss polyesters) require no paraffin for curing the surface of a coating, because the ether groups initiate an autoxidative drying process [66].

1.3.4 Fillers

Examples of fillers include calcium carbonate powder, clay, alumina powder, silica sand powder, talc, barium sulfate, silica powder, glass powder, glass beads, mica, aluminum hydroxide, cellulose yarn, silica sand, river sand, white marble, marble scrap, and crushed stone. In the case of glass powder, aluminum hydroxide, and barium sulfate the translucency is imparted on curing [67]. Common fillers are listed in Table 1.4. Fillers reduce the cost and change certain mechanical properties of the cured materials.

Table 1.4 Fillers for Unsaturated Polyester Resins

Filler	Reference
Bentonite	[57]
Calcium carbonate	[58]
Clay	[59]
Glass beads	
Fly ash	[60]
Wood flour	[61]
Rubber particles	[62]
Nanocomposites	[63–65]

1.3.4.1 Inorganic Fillers

Bentonite. Ca-bentonite is used in the formulation of unsaturated polyester-based composite materials. Increasing the filler content, at a constant styrene/polyester ratio, improves the properties of composites. Maximum values of compressive strength, hardness, and thermal conductivity of composites are observed at about 22.7% of styrene, whereas the water absorption capacity was a minimum at a styrene content of 32.8% [57].

Montmorillonite. Sodium montmorillonite and organically modifiedmontmorillonite (MMT) were tested as reinforcing agents. Montmorillonite increases the glass transition temperatures. At 3–5% modified montmorillonite content, the tensile modulus, tensile strength, flexural modulus, and flexural strength values showed a maximum, whereas the impact strength exhibited a minimum. Adding only 3% of organically modified montmorillonite improved the flexural modulus of an unsaturated polyester by 35%. The tensile modulus of unsaturated polyester was also improved by 17% at 5% of montmorillonite [59].

Instead of styrene, 2-hydroxypropyl acrylate as a reactive diluent has been examined in preparing an unsaturated polyester/montmorillonite nanocomposite [68]. The functionalization of MMT can be achieved with polymerizable cationic surfactants, e.g., with vinylbenzyldodecyldimethyl ammonium chloride or vinylbenzyloctadecyldimethyl ammonium chloride (VOAC). Polymerizable organophilic clays have been prepared by exchanging the sodium ions of MMT with these polymerizable cationic surfactants [69]. With an unsaturated polyester, nanocomposites consisting of UP and clay were prepared. The dispersion of organoclays in UP caused gel formation. In the UP/VDAC/MMT system, intercalated nanocomposites were found, while in the UP/VOAC/MMT system partially exfoliated nanocomposites were observed.

When the content of organophilic montmorillonite is between 25% and 5%, the mechanical properties, such as the tensile strength, the impact strength, the heat resistance, and the swelling resistance of the hybrid, are enhanced. The properties are better than those of composites prepared with pristine or non-polymerizable quaternary ammonium-modified montmorillonite [70].

Rectorite. Rectorite is a layered silicate. Organically modified layered silicate clay composites, which are glass fiber reinforced, are suitable to tailor the properties of the composite. The addition of organically modified rectorite increases the gel time and the viscosity [71].

Fly Ash. Fly ash is an inexpensive material that can reduce the overall cost of the composite if used as filler for unsaturated polyester resin. A fly ash-filled resin was found to have a higher flexural modulus than those of a calcium carbonate-filled polyester resin and an unfilled resin. Fly ash was found to have poor chemical resistances but good saltwater, alkali, weathering, and freeze–thaw resistances [60].

An enhancement of the tensile strength, flexural strength, and impact strength is observed when the fly ash is surface-treated with silane coupling agents [72].

Fly ash-filled composites with high damping behavior were developed. Fly ash-filled polymer composites do not show very high damping and this limits their fields of application. However, the presence of latex particles significantly enhances the damping properties. A very high damping can be achieved with a UP and 10% SBR latex with 50% fly ash [73].

Marble. For a gray composite material, powdered marble was used as filler [74]. The optimum amount of marble powder that was added was 2 g per g of UP resin. This composite material proved to be smooth and equally distributed. No aggregation of the particles of the marble powder was observed.

Silica. In contrast, UP resins can be used for the consolidation of marble-based natural rocks that are used in the sculptural art [75]. A nanosilica filler, i.e., Aerosil® 2000, has been proposed to improve the performance of the composite resin used in the experiments.

The experiments revealed an increase in the impact resistance of UP-coated marble pieces. The improvement is traced back to the formation of a network between the nanosilica and the resin matrix which results in an increased stiffness and toughness of the cured UP composite [75].

To improve the performance of a silica containing UP, the surface of the silica particles was modified with vinyltrimethoxysilane and methacrylic acid. Further the compatibility between silica and the polyester resin can be improved by the addition of a block copolymer [76].

1.3.4.2 Wood Flour

Plant-based fillers like sawdust, wood flour, and others are utilized because of their low density, and their relatively good mechanical properties and reactive surface. The main disadvantage is the hygroscopicity [77] and the difficulties in achieving acceptable dispersion in a polymeric matrix.

Surface modification of these materials can help reduce these problems. Wood flour can be chemically modified with maleic anhydride to improve the dispersion properties and adhesion to the matrix resin. This treatment decreases the hygroscopicity, but excessive esterification has to be avoided, because it leads to the deterioration of the wood flour, adversely affecting its mechanical properties [61].

The incorporation of wood flour into the resin increases the compression modulus and the yield stress but decreases the ultimate deformation and toughness in all cases.

Thermogravimetric analysis of wood flour indicates changes in the wood structure occur as a consequence of chemical modifications. Alkaline treatment reduces the thermal stability of the wood flour and produces a large char yield. In composites a thermal interaction between fillers and matrix is observed. Thermal degradation of the composites begins at higher temperature than the neat wood flours [78].

1.3.4.3 Rubber

Rubber particles toughen the materials [62,79]. They act also as low-profile additives. A low-profile additive, in general, diminishes shrinking in the course of curing.

Toughening. Rubbers with functional groups have been tested in blends of unsaturated polyesters with respect to improving the mechanical properties. In particular, functional rubbers such as hydroxy-terminated poly(butadiene), epoxidized natural rubber, hydroxy-terminated natural rubber, and maleated nitrile rubber were tested. The performance of a maleic anhydride grafted nitrile rubber is superior to those of all other rubbers studied. The improvement in toughness, impact resistance, and tensile strength is achieved without jeopardizing other properties [80].

Rubber as Low-profile Additive. A low-profile additive consisting of a styrene butadiene rubber solution is prepared by heating styrene with hydroquinone up to 50 °C. Into this liquid a styrene butadiene rubber is dissolved to obtain a resin solution having a solid content of 35%. This solution is taken as a low-profile additive [81].

Rubber Core-shell Structured Particles. Structural composite latex particles have been prepared in a two-stage emulsion polymerization. Initially, partially crosslinked poly(*n*-butyl acrylate) cores were prepared, and afterwards, a poly(vinyl acetate-*co*-methyl methacrylate) shell has been grafted onto the rubber cores [82].

These structural rubber particles with various shell structures have been used to toughen UP resins. The incorporation of these structured particles can improve considerably the impact fracture energy of the material. The toughening efficiency of the rubber particles is highly dependent on their content of MMA moieties [82].

1.3.4.4 Nanocomposites

Nanocomposite materials are increasingly commercially available but these materials are still very expensive. In order to make a successful nanocomposite, it is very important to be able to disperse the filler material thoroughly throughout the matrix to maximize the interaction between the intermixed phases.

Titanium Dioxide. Titanium dioxide nanoparticles with 36 nm average diameter have been investigated. The nanoparticles have to be dispersed by direct ultrasonification [63]. The presence of the nanoparticles has a significant effect on the quasi-static fracture toughness. Even at small volume fractions an increase in toughness is observed. The changes in quasi-static material properties in tension and compression with increasing volume fraction of the nanoparticles are small due to the weak interfacial bonding between the matrix and the filler. The dynamic fracture toughness is higher than quasi-static fracture toughness. Quite similar experimental results have been presented by another group [83]. Titanium dioxide nanoparticles can also be bound by chemical reaction to the polyester itself [84].

Aluminum Oxide. It was observed that the addition of untreated Al_2O_3 particles does not result in an enhanced fracture toughness. Instead, the fracture toughness decreases [64,65]. However, adding an appropriate amount of (3-methacryloxypropyl)-trimethoxysilane to the liquid polyester resin during particle dispersion process leads to a significant enhancement of the fracture toughness due to the crack trapping mechanism being promoted by strong particle-matrix adhesion.

For example, the addition of 4.5% volume fraction of treated Al_2O_3 particles results in a nearly 100% increase in the fracture toughness of the unsaturated polyester.

Halloysite. This substance is an aluminosilicate clay mineral with the formula $Al_2Si_2O_5(OH)_4$. It is related to kaolin minerals but it has a different morphology. Halloysite is formed by the hydrothermal alteration of aluminosilicates. Halloysite nanotubes can be used as fillers in polymers, both in thermoplastic polymers [85,86] and in thermosets [87,88]. For a complete list of references cf. Ref. [89].

In the natural state, halloysite is highly hydrophilic. Therefore it has a low compatibility with hydrophobic polymers. Layered silicates, such as montmorillonite, can be compatibilized by cationic exchange using quaternary ammonium salts [90]. However, this compatibilization method is not effective for halloysite since it is not a good cation exchanger.

More promising is to modify the surface of halloysite with certain coupling agents. Silane-based chemicals, such as triethoxyvinylsilane and aminopropyltriethoxysilane, have been proposed as coupling agents [89]. These chemicals are shown in Figure 1.11.

The thus treated halloysite has been used as fillers in UP resins. The compositions have been characterized in several ways. It has been shown that the modification by halloysite does not result in a change of the curing behavior.

On the other hand, the glass transition temperature of the final materials changes significantly. Halloysite modified with triethoxyvinylsilane effects an increase of the glass transition temperature, whereas aminopropyltriethoxysilane-modified halloysite acts as a plasticizer, thus decreasing the glass transition temperature [89].

1.3.4.5 Nanoclays

The addition of a nanoclay in amounts of 0.5–1% increases the viscosity of resin. Also the gel time and the degree of shrinking are decreased. In the cured composites, improved thermal properties are achieved. On the other hand, the glass transition temperature is not affected. Furthermore, the impact strength is improved and a good adhesion to the surface of natural stone is observed [91].

1.3.4.6 Carbon Nanotubes

A detailed investigation of the effects of single-walled carbon nanotubes in UP composed from isophthalic acid has been reported. The growth of the nanotube network was shown to be dependent on the concentration and crossover parameters could be established which provided an empirical basis for master curve scaling. From these master curves, the rheological percolation was found to occur at around 0.1% content of nanotubes [92].

1.3.5 Reinforcing Materials

Suitable reinforcing materials are shown in Table 1.5. The application of reinforcement fibers is strongly governed by the relation of the price of matrix resin and fiber. Therefore, expensive fibers, such as carbon fiber, are usually used with epoxide resins, not with unsaturated polyester resins. If the fiber is expensive and has superior properties, then the matrix resin should have superior properties.

Table 1.5 Reinforcing Materials for Unsaturated Polyesters

Fiber	Reference
Glass fibers	
Jute	[93]
Sisal	[94]
Hemp	[95]
Wollastonite	[94]
Barium titanate	[96]

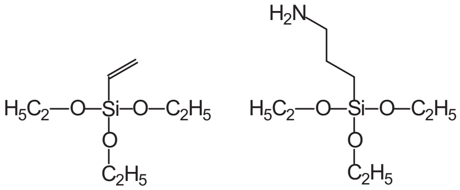


Figure 1.11 Triethoxyvinylsilane (left) and aminopropyltriethoxysilane.

1.3.5.1 Glass Fibers

The most common “fillers” are reinforcing materials, like glass fibers. Because of the unavoidable shrinking during curing, interfacial stresses between resin and glass fiber arise that lower the adhesion forces.

To enhance the adhesion, glass fibers are surface modified. Silane coupling agents such as (3-methacryloxypropyl)trimethoxysilane and (3-aminopropyl)triethoxysilane are preferably used.

In the case of (3-methacryloxypropyl)trimethoxysilane the pendant double bonds may take part in the curing reaction; thus chemical linkages between resin and glass surface are established.

The surface free energy and the mechanical interfacial properties especially showed the maximum value for 0.4% silane coupling agent [97,98].

In an E-glass/vinylester composite it was observed that the fibers significantly inhibit the final conversion [99].

1.3.5.2 Wollastonite

A suitable coupling agent for wollastonite is (3-methacryloxypropyl)trimethoxysilane. In such a treated wollastonite-unsaturated polyester composite, the tensile and flexural strength increase initially with the wollastonite content and then decrease. The flexural strength reaches an optimum value at 30% wollastonite content, whereas the tensile strength reaches an optimum point at 50% wollastonite content [94].

1.3.5.3 Carbon Fibers

Reports on carbon fiber-reinforced polyester are rare [100]. Carbon fibers have mainly been used in aerospace with epoxide resins or high-temperature thermoplastics, whereas polyesters have found application in large-volume and low-cost applications with primarily glass fibers as reinforcement. The combination of carbon fibers and polyester matrix is becoming more attractive as the cost of carbon fibers decreases. In comparison to epoxide resins, unsaturated polyester exhibits a relatively low viscosity. This property makes them well suited for the manufacture of large structures [101].

The interfacial shear strength with untreated carbon fibers increases with increasing degree of unsaturation of the polyester. The unsaturation is adjusted by the amount of maleic anhydride in the feed. This is explained by a contribution of chemical bonding of the double bonds in the polymer to the functional groups of the carbon fiber surface [101].

1.3.5.4 Natural Fibers

Agrowastes and biomass materials, e.g., sawdust, wood fibers, sisal, bagasse, etc., are slowly penetrating the reinforced plastics market, presently dominated by glass fibers and other mineral reinforcements. These fillers have very good mechanical properties and low density, and are loaded into polymeric resin matrices to make useful structural composite materials [77].

Jute. Jute as reinforcing fiber is particularly significant from an economic point of view. On a weight and cost basis, bleached jute fibers are claimed to have better reinforcement properties than other fibers [93].

Sisal. Sisal fiber is a vegetable fiber having specific strength and stiffness that compare well with those of glass fiber. Most synthetic resins are, however, more expensive than the sisal fiber, making these composites less attractive for low-technology applications. Therefore, for sisal fibers naturally occurring resol-type resins, cashew nut shell liquid is an attractive alternative [103].

For unsaturated polyester composites the surface treatment of sisal fibers is done with neopentyl (diallyl)oxy tri(dioctyl) pyrophosphatotitanate as the coupling agent [94,104]. In a sisal/wollastonite reinforcing system for unsaturated polyester resins, the tensile strength and the flexural strength drop with increasing sisal content.

Sisal composites with unsaturated polyesters can be formulated to be flame retarded using decabromodiphenyloxide and antimony trioxide to reach a satisfactory high state of flame retardancy [105].

Kenaf Bast. Kenaf is related to jute and has similar properties. The plant occurs in southern Asia. Nowadays, Kenaf is cultivated for the sake of its fiber in southern Asia, e.g., India, Bangladesh, Indonesia, Malaysia, but also in the USA and South Africa.

The density of Kenaf fiber in comparison to other fibers is shown in Table 1.6.

Table 1.6 Density of Fibers [102]

Fiber Material	Density ($\mathrm{g\ cm^{-1}}$)
Kenaf fiber	0.15
Glass fiber	2.55
Carbon fiber	1.77
Hemp fiber	1.48

In nanocomposite-based UP formulations, Kenaf bast fiber and montmorillonite were used as reinforcing agents. The sodium ions in montmorillonite were modified to ammonium ions by ion exchange with cetyltrimethylammonium bromide. The composites prepared in this way showed higher mechanical properties than those prepared without montmorillonite and fiber [102].

Base UP resins based on palm oil have been prepared from the monoglyceride and maleic anhydride (MA) using 2-methylimidazole as catalyst. The monoglyceride monomer is prepared by the treatment of palm oil with gylcerol, to result in an intermolecular transesterification [106]. The reaction is shown in Figure 1.12.

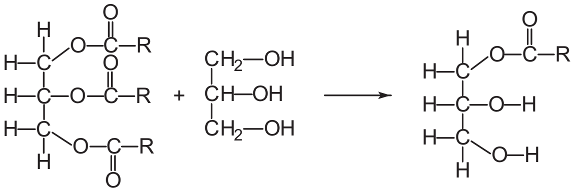


Figure 1.12 Transesterification of palm oil [106].

To these bio-based resins, Kenaf fibers are added as reinforcing agent. For fabrication an ultraviolet curing technique was used with Irgacure® 1800 as photoinitiator [107].

Scanning electron micrograph techniques reveal that the fibers are tightly embedded in the matrix and there is evidence that the fiber breaks when a mechanical failure occurs. This indicates good wetting between the fiber and matrix [107].

Sesam Husks. Sesame husks were used as reinforcing filler materials. The sesame husk particles are subjected to treatment with 5% aqueous NaOH. The flexural strength, flexural modulus, and impact strength increase in the alkali-treated sesame husk composites in comparison to the untreated composites. Moreover, the increase in flexural strength properties is accompanied by an increased impact strength, which is usually not observed [108].

1.3.6 Additives for Molding Applications

Molding compositions based on UP resin systems are widely used in the form of [109]:

- SMC: sheet molding compounds,
- BMC: bulk molding compounds,
- DMC: dough molding compounds,
- TMC: thick molding compounds, or
- LDMC: low-density molding compounds.

For such formulations, the resins are treated with inert fillers and with fibrous reinforcing materials. When the moldings are compressed, the resin cures by a polymerization reaction.

Table 1.7 Monomers for Mixture Stabilizing Additives [109]

Monomer
N,*N*-Dimethylaminoethyl acrylate
N,*N*-Dimethylaminoethyl methacrylate
N,*N*-Dimethylaminopropyl acrylate
N,*N*-Dimethylaminopropyl methacrylate
2-Butylaminoethyl methacrylate
2-Vinylpyridine
4-Vinylpyridine
Vinylimidazole

1.3.6.1 Mixture Stabilizing Additives

For certain applications, such as sheet molding, resin mixtures should be stabilized with respect to demixing.

The mixture stabilizing additives should not reduce the viscosity of the resin mixture, because a viscosity reduction promotes the demixing. So, for this purpose, block copolymers based on ethylenically unsaturated monomers are added to UP resin mixtures [109].

Examples of monomers suitable for such additives are shown in Table 1.7.

The block polymers are prepared by radical polymerization using 2,2′-azobisisobutyronitrile as initiator. Poly(propylene glycol) is used as a solvent [109].

1.3.6.2 Mold Release Agents

Mold release agents are needed for the molding processes, i.e., for the manufacture of bulk molding compounds and sheet molding compounds. There are two classes of mold release agents:

1. external mold release agents,
2. internal mold release agents.

External mold release agents are applied directly to the mold. This procedure increases the manufacturing time and must be repeated every one to five parts. In addition, the mold release agent builds up on the mold, so the mold must be cleaned periodically with a solvent or washing agent. This is costly and time consuming.

Internal mold release agents are added directly into the molding compound. Since they do not have to be continuously reapplied to the mold, internal mold release agents increase productivity and reduce cost.

There are mostly internal mold release agents, e.g., metal soaps, amine carboxylates, amides, etc. Zinc stearate acts by exuding to the surface of the molding compound, thereby contacting the mold and providing lubrication at the mold surface to permit release. Liquid mold release agents are liquid zinc salts and phosphate esters and higher fatty acid amines [110]. The amine salts are obtained simply by neutralizing the acids with appropriate amines.

1.3.7 Low-profile Additives

A high surface finish quality is highly desirable in the automotive industry for exterior body panel applications [111]. The surface quality is influenced mostly by dimensional changes in the process of curing. UP resins are notorious for the shrinkage during curing which goes up to 9% of volume shrinkage. This effect results in a poor surface finish.

The shrinkage of the resin can be measured by both volumetric and non-volumetric methods. Volumetric methods use a dilatometer design. In contrast, non-volumetric methods measure simply the linear amount of shrinkage. A simple method has been developed to estimate the surface finish quality of panels caused by both thermal expansion and shrinking during curing [111].

Low-profile additives (LPA) reduce the shrinking of the cured products. Shrinking causes internal voids and reduced surface quality. Thermoplastic resins are added to reduce shrinking, e.g., poly(vinyl acetate). This additive absorbs some styrene in the early stages of curing. When the temperature is increased in the course of curing, the styrene eventually evaporates and consequently a counter pressure is formed which counterbalances the shrinking.

The successful performance of low-profile additives depends essentially on the phase separation phenomena in the course of curing, cf. Section 1.4.4.3.

The effects of poly(vinyl acetate), poly(vinyl chloride-*co*-vinyl acetate), and poly(vinyl chloride-*co*-vinyl acetate-*co*-maleic anhydride) have been studied [112,113]. The curing rate decreases with an increase of the molecular weight of the low-profile additive which causes the chain entanglement effect. The plasticizing effect is reduced with an increase in the molecular weight of the low-profile additive [114].

Low-profile additives with higher molecular weight and lower content of additive seem to work better under low-temperature curing conditions [115].

Polymers from the acrylic group have been tested as low-profile additives. In particular, binary copolymers from methyl methacrylate and *n*-butyl acrylate, and ternary copolymers from methyl methacrylate, *n*-butyl acrylate, and maleic anhydride have been studied [116,117]. The volume fraction of microvoids generated during the curing process is governed by the stiffness of the UP resin, the compatibility of the uncured ST/UP/LPA systems, and the glass transition temperature of the low-profile additive. A good volume shrinkage control can be achieved by raising the curing temperature slowly to allow sufficient time for phase separation, and going to a high final temperature to allow the formation of microvoids [118].

Dilatometric studies in the course of curing of a low-profile resin containing poly(vinyl acetate) [119] have revealed that there are two transition points in both volume and morphological changes in the course of curing. The thermoplastics start to be effective on shrinkage control at the first transition point when the low-profile additive-rich phase and the unsaturated polyester resin-rich phase become co-continuous. At the second transition point when the fusion among the particulate structures is severe, the shrinkage control effect vanishes.

The relative rate of polymerization in the two phases plays an important role in shrinkage control. Instead of poly(vinyl acetate) a copolymer with acrylic acid or itaconic acid should have better properties as a low-profile additive. This is based on the assumption that the presence of acid groups on the copolymer chain changes the selectivity of the cobalt promoter, and therefore the relative reaction rate in the thermoplastic-rich and the unsaturated polyester resin-rich phases during polymerization.

Itaconic acid is about twice as acidic as acrylic acid and more reactive than maleic acid or fumaric acid. The two carboxyl groups allow the introduction of larger amounts of acidity into the copolymer even at rather low comonomer concentrations in comparison to acrylic acid. The monoester of 2-hydroxyethyl acrylate and tetrachlorophthalic anhydride also has been proposed as a comonomer. The acidity of tetrachlorophthalic anhydride is much stronger than that of itaconic acid because of the four chloro substituents in its structure.

Samples with an acid-modified low-profile additive showed an earlier volume expansion during curing, as a result of faster reaction in the low-profile additive-rich phase [120].

The relative reaction rate in the two phases can be controlled in addition to the selectivity control by the low-profile additive in a reverse manner, i.e., by the addition of secondary vinylic comonomers and special promoters. Secondary monomers, such as divinylbenzene and trimethylol propane trimethacrylate, were added to the formulation. 2,4-Pentandione was chosen as co-promoter [121]. In fact, the combination of trimethylol propane trimethacrylate and 2,4-pentandione increased the reaction rate in the low-profile rich phase.

Methyl methacrylate was tested as a secondary monomer [122]. At a low ratio of methyl methacrylate to styrene, the amount of residual styrene decreases and the volume shrinkage of the resin system remains unchanged. However, at a high ratio of methyl methacrylate to styrene, the amount of residual styrene can be substantially reduced. This advantageous behavior occurs because of the monomer reactivity ratios. However, the study of shrinkage shows that methyl methacrylate has a negative effect on the shrinkage control.

Styrene has a polymerization shrinkage of 15% and methyl methacrylate has a shrinkage of 20%. Therefore, the addition of methyl methacrylate contributes to a larger volume shrinkage. The performance of a low-profile additive becomes less effective when the molar ratio of methyl methacrylate to styrene exceeds 0.1.

A dual initiator system, i.e., methylethylketone peroxide/*tert*-butylperoxybenzoate, was used in combination with cobalt octoate as promoter. *tert*-Butylperoxybenzoate cannot be considered as a low-temperature initiator because the reaction temperature needs to reach almost 90 °C to ensure the proper progress of the reaction. On the other hand, *tert*-butylperoxybenzoate is more active compared to methylethylketone peroxide at high temperatures, because the latter completely decomposes. *tert*-Butylperoxybenzoate is therefore a good initiator to finish the reaction.

Volume shrinkage measurements of the resin system initiated with dual initiators revealed that a good performance of the low-profile additive was achieved at low temperatures (e.g., 35 °C) and high temperatures (100 °C) but not at intermediate temperatures [123].

It was found that in bulk molding compounds calcium stearate, which is primarily used as an internal mold release agent, is active as a low-profile additive [124]. Even when added in small quantities, some internal mold release agents may provoke the formation of a polyester-rich phase in the form of spherical globules ca. 60 μm.

Organically modified clay nanocomposites have been tested as low-profile additives [125]. The shrinkage of resins of such compositions revealed that the addition of 3% nanoclay does not result in a superior reduction of volume shrinkage. On the other hand, some other mechanical properties are improved significantly.

1.3.8 Interpenetrating Polymer Networks

An interpenetrating polymer network is a mixture of two or more polymers that are not necessarily independently crosslinked. If another polymer that is capable of crosslinking separately is added to an unsaturated polyester resin, the physical properties can be enhanced dramatically. Other special types of such systems are also addressed as hybrid systems.

1.3.8.1 Poly(urethane)s

For example, besides the unsaturated polyester resin, compounds that simultaneously form a crosslinkable poly(urethane) are added, such as polyglycols and diisocyanates [126].

The rate of reaction of one component might be expected to be reduced due to the dilutional effects of the other components [127]. However, during free-radical polymerization, the reaction may become diffusion controlled and a Trommsdorff effect emerges. The Trommsdorff effect consists of a self-acceleration of the overall rate of polymerization. When the polymerizing bulk becomes more viscous as the concentration of polymer increases, the mutual deactivation of the growing radicals is hindered, whereas the other elementary reaction rates, such as initiation and propagation, remain constant.

For an unsaturated polyester resin-poly(urethane) system, the rate of the curing process increased substantially in comparison to the pure homopolymers. Collateral reactions between the poly(urethane) isocyanate groups and the terminal unsaturated polyester carboxyl groups were suggested that may lead to the formation of amines, cf. Eq. (1.1)

$$\begin{aligned} &\mathrm{R-N=C=O+R'COOH} \\ &\rightarrow \mathrm{R-NHCO-O-CO-R'} \\ &\rightarrow \mathrm{R-NHCO-R'+CO_2} \end{aligned} \tag{1.1}$$

These amines may act as promoters of the curing process. Moisture, which does not influence the curing reaction of the unsaturated polyester resin, would also lead to the formation of amines by the reaction of water with the isocyanate groups [128].

A tricomponent interpenetrating network system consisting of castor oil-based poly(urethane) components, acrylonitrile, and an unsaturated polyester resin(the main component) was synthesized in order to toughen the unsaturated polyester resin. By incorporating the urethane and acrylonitrile structures, the tensile strength of the matrix(unsaturated polyester resin) decreased and flexural and impact strengths were increased [129].

Maleated castor oil has been used as a biomodifier in composites from UP resins and fly ash [130]. The maleated castor oil is polymerized and crosslinked with the UP in situ during the formation of the composites. For this reason, an IPN is formed. This causes a significant enhancement in the properties. The addition of only 5% of maleated castor oil is highly effective as an increase of the impact strength by 52% is observed without any loss in the modulus. Also, the glass transition temperature shifts to a higher temperature.

1.3.8.2 Epoxides

Mixtures of unsaturated polyester resin systems and epoxy resins also form interpenetrating polymer networks. Since a single glass transition temperature for each interpenetrating polymer network is observed, it is suggested that both materials are compatible. On the other hand, an interlock between the two growing networks was suggested, because in the course of curing, a retarded viscosity increase was observed [131]. A network interlock is indicated by a lower total exothermic reaction during simultaneous polymerization in comparison to the reaction of the homopolymers [132].

The thermal and dynamic mechanical properties of interpenetrating networks formed from unsaturated polyester resin and epoxy resins were investigated.

The epoxies were cured with acid anhydrides: Tetrahydrophthalic anhydride and maleic anhydride. It was shown that both the content of epoxy resin and the curing system influence the properties.

When the content of epoxy resin is increased, the glass transition temperature is also increased. The thermal and viscoelastic properties of the blends cured with dibenzoyl peroxide (BPO) and maleic anhydride are better than from those cured with the systems cumene hydroperoxide and tetrahydrophthalic anhydride, or BPO and tetrahydrophthalic anhydride [133].

In bismaleimide-modified unsaturated polyester-epoxy resins, the reaction between unsaturated polyester and epoxy resin could be confirmed by IR spectral studies [134]. The incorporation of bismaleimide into epoxy resin improved both mechanical strength and thermal behavior of the epoxy resin.

1.3.8.3 Vinylester Resins

Unsaturated polyesters modified with up to 30% of vinylester oligomer are tougheners for the unsaturated polyester matrix. The introduction of vinylester oligomer and bismaleimide into an unsaturated polyester resin improves thermomechanical properties [135].

1.3.8.4 Phenolic Resins

An interpenetrating network consisting of an unsaturated polyester resin and a resol type of phenolic resin not only improves heat resistance but also helps to suppress the smoke, toxic gas, and heat release during combustion in comparison to a pure unsaturated polyester resin [136].

1.3.8.5 Organic-inorganic Hybrids

Organic-inorganic polymer hybrid materials can be prepared using an unsaturated polyester and silica gel. First an unsaturated polyester is prepared. To this polyester the silica gel precursor is added, i.e., tetramethoxysilane, methyltrimethoxysilane, or phenyltrimethoxysilane.

Gelling of the alkoxysilanes was achieved at 60 °C using HCl catalyst in the presence of the unsaturated polyester resin. It was confirmed by nuclear magnetic resonance spectroscopy that the polyester did hydrolyze during the acid treatment. Finally, the interpenetrating network was formed by photopolymerization of the unsaturated polyester resin [137]. It is assumed that between the phenyltrimethoxysilane and the aromatic groups in the unsaturated polyester resin π-interactions arise.

1.3.9 Poly(urethane) Hybrid Networks

The mechanical properties of the unsaturated polyester resin can be greatly improved by incorporating a poly(urethane) linkage into the polymer network. The mechanical properties can also be altered by the techniques used in segmented poly(urethane)s. The basic concept is to use soft segments and hard segments.

The polyester is prepared with an excess of diol and diluted with styrene as usual. Additional diols as chain extenders are blended into the resin solution. 4,4′-Diphenylmethane diisocyanate dissolved in styrene is added to form the hybrid linkages. Suitable peroxides are added to initiate the radical curing.

The curing starts with the reaction between the isocyanates and the hydroxyl groups, thus forming the poly(urethane) linkage. Then the crosslinking reaction takes place [139].

The mechanical properties of the hybrid networks were generally improved by the incorporation of a chain extender at room temperature. 1,6-Hexanediol (HD) increased the flexibility of the polymer chains, resulting in a higher deformation and impact resistance of the hybrid networks. Hybrid networks with EG as the chain extender are stiffer.

1.3.9.1 UV Stabilizers

UP compositions with improved weathering characteristics have been developed [138]. The compositions exhibit both an improved hydrolytic stability and enhanced UV light resistance in comparison to conventional materials. Further, the compositions meet the US EPA limits for MACT compliance for hazardous air pollutants.

The UV stability is improved by the addition of light stabilizers and UV absorbers. A special class of light stabilizers are hindered amine light stabilizers (HALS). These stabilizers oxidize and scavenge radicals that are formed by the radiation. On the other hand, UV absorbers shield the polymer by absorbing UV and dissipating the energy as heat. Combinations of these classes of compounds can be readily used. Conventional light stabilizers that are advantageously used as additives are summarized in Table 1.8. [138].

Table 1.8 Light Stabilizers and UV Absorbers [138]

Light Stabilizers	**Type**	**Manufacturer**
TINUVIN® 123	HALS	Ciba
Lowilite® 92	HALS	Great Lakes
UV Absorbers	**Type**	**Manufacturer**
TINUVIN® 400	Triazine	Ciba
Lowilite® 20	Benzophenone	Great Lakes
Lowilite® 27	Benzotriazole	Great Lakes
Titanium dioxide	Inorganic	
Fumed silica	Inorganic	

1.3.10 Flame Retardants

The major drawback of UP resins is their flammability. For example, a general grade UP made with styrene has a low limiting oxygen index (LOI) of 19% [140].

Flame retardant compositions can be achieved by flame retardant additives, by flame retardant polyester components, and by flame retardant vinyl monomers. Halogenated compounds are still common, but there is a trend toward substituting these compounds with halogen-free compositions. In halogenated systems, bromine atoms mostly are responsible for the activity of the retardant. On the other hand, a disposal problem arises when a pyrolytic recycling method is intended at the end of the service times of such articles. Flame retardants are summarized in Table 1.9.

Table 1.9 Flame Retardants for Unsaturated Polyester Resins

Flame Retardant	**Remarks**	**Reference**
Aluminum hydroxide		
Melamine diphosphate		
Melamine cyanurate		[141]
Ammonium polyphosphate		[142]
Nanoclays		[143]
Antimony trioxide	Synergist	
Zinc hydroxystannate		[144–146]
2-Methyl-2,5-dioxo-1-oxa-2-phospholane	Reactive	[147]
Decabromodiphenyloxide		[148]
HET acid	Reactive	
TBBPA	Reactive	[149]
Tetrachlorophthalic anhydride	Reactive	
Tetrabromophthalic anhydride	Reactive	

In general, bromine compounds are more effective than chlorine compounds. Suitable additives are chlorinated alkanes, brominated bisphenols, and diphenyls. Antimony trioxide is synergistic to halogenated flame retardants. It acts also as a smoke suppressant in various systems [150].

1.3.10.1 Flame Retardant Additives

Decabromodiphenyloxide. Decabromodiphenyloxide with 2% of antimony trioxide increases the oxygen index values linearly with the bromine content. Some improvement of the mechanical properties can be achieved by adding acrylonitrile to the polyester [151]. Decabromodiphenyloxide with antimony trioxide increases the activation energy of the decomposition of the unsaturated polyester [148].

Aluminum Hydroxide. Fillers, such as aluminum hydroxide, yield crystallization water at higher temperatures, thus achieving a certain flame retardancy. At high degrees of filling in the range of 150–200 parts of aluminum hydroxide per 100 parts of unsaturated polyester resin, it is possible to achieve self-extinguishing and a low smoke density. A disadvantage of such systems is that the entire material has a high density. The density can be reduced if hollow filler is used for reinforcement [152].

Lower amounts of aluminum hydroxide are sufficient if red phosphorus and melamine or melamine cyanurate are admixed [141]. Magnesium hydroxide acts in a similar way to aluminum hydroxide.

Ammonium Polyphosphate. Ammonium polyphosphate is a halogen-free flame retardant for unsaturated polyester resin composites [142]. Commonly used are ammonium polyphosphates having the general formula $(NH_4)_{n+2}P_nO_{3n+1}$.

A significant reduction of the flame spread index is achieved by a combination of a polyhydroxy compound, a polyphosphate, melamine, cyanuric acid, melamine salts, e.g., melamine cyanurate, and a polyacrylate monomer [153].

The effect of aluminum trihydroxide in combination with ammonium polyphosphate has been investigated. Thermogravimetric experiments revealed an improved thermal stability in the range of 200–600 °C. Obviously, aluminum trihydroxide is more efficient than calcium carbonate in delaying the time of ignition and lowering the yield of carbon monoxide. However, no significant synergistic effect in reducing the peak heat release was observed [155].

The fire retardant polyacrylate component should be distinguished from the unsaturated monomers that may be included as crosslinkers in the resin systems. It cannot be ruled out that the polyacrylate may become involved in the crosslinking reactions of such systems. However, it has been observed that the fire retardant effect of the polyacrylates is also effective in those resin systems that do not involve curing by way of unsaturated groups. Preferred polyacrylates are those having backbones of a type that is known to contribute to char formation, for example those having alkylene or oxyalkylene backbones [156].

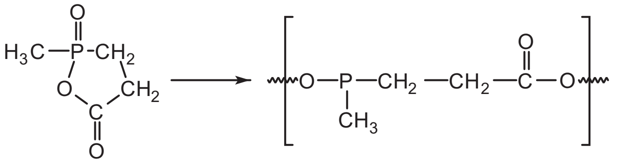


Figure 1.13 Ring opening of 2-methyl-2,5-dioxo-1-oxa-2-phospholane [147].

Reactive Phosphor Compound. Oxaphospholanes are heterocyclic compounds. Certain derivatives are reactive to alcohols and can be incorporated in a polyester backbone. Due to their phosphor content they also act as flame retardants, with the advantage that they are chemically bound to the backbone [147]. The ring opening reaction of 2-methyl-2,5-dioxo-1-oxa-2-phospholane is shown in Figure 1.13. As a side effect, phosphoric compounds increase the adhesion of the final products, without toughening too much.

A transparent flame retardant unsaturated polyester resin was obtained by the reaction of PG with MA, phthalic anhydride, and 9,10-dihydro-10[2,3-di (hydroxy carbonyl) propyl]-10-phosphaphenanthrene-10-oxide [154]. This compound can be synthesized from 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide and IA. The synthesis is shown in Figure 1.14.

Thermal stability of the composition was studied by thermogravimetric analysis both in air and in nitrogen [154]. In comparison to an unsaturated polyester resin without the phosphorus flame retardant, which reaches an LOI of 19%, by the addition of the reactive flame retardant an LOI of up to 29% could be reached.

Expandable Graphite. The flammability of cross linked unsaturated polyester resins is reduced by the addition of EG even at levels as low as 7 phr. Expandable graphite is particularly useful when used in combination with ammonium polyphosphate or with a halogenated flame retardant [157].

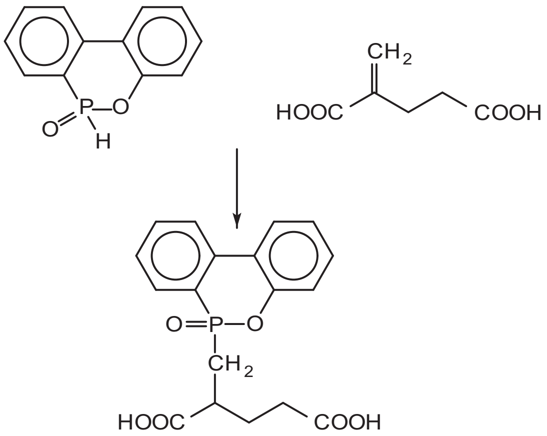


Figure 1.14 Synthesis of 9,10-dihydro-10[2,3di-(hydroxycarbonyl)propyl]-10-phosphaphenanthrene-10-oxide [154].

Nanoclays. Polymer-layered silicate nanoclays have been investigated as potential flame retardants in unsaturated polyester resins [143].

While the incorporation of condensed-phase flame retardants, such as ammonium polyphosphate, melamine phosphate, and alumina trihydrate, reduces the peak heat release rate and the total heat release values, the inclusion of small amounts of nanoclay in combination with the above char promoting flame retardants causes the total reduction of the peak heat release rates by some 60–70% [143]. The best results are observed with ammonium polyphosphate and polyester-nanoclay hybrids.

1.3.10.2 Flame Retardant Polyester Components

The flame retardant polyester component can be also built in the polymer backbone. Examples are HET acid, tetrachlorophthalic anhydride, and tetrabromophthalic anhydride. The mechanical properties decrease with increasing halogen content in the backbone [158]. HET acid is used for fireproof applications, e.g., for panels in subways, etc.

1.3.10.3 Flame Retardant Vinyl Monomers

Dibromostyrene is a suitable brominated vinyl monomer [159]. However, it is not commonly used. Dibromoneopentylglycol and diallyl ether of bromobutenediol have been used as curing agents for unsaturated polyester resins in paint coatings. Both monomers act effectively against inhibition by oxygen. The bromine content decreases the flammability of the final products. The monomers can be obtained in a direct allylation by the use of allyl bromide. The resins can be photocured in a system consisting of mono- or diazide and hydroxy alkylphenone [160].

Flame retardant polyester resin polymers wherein the ability of the polyester resin to transmit light is not significantly affected can be formulated using, instead of antimony trioxide, organic antimony compounds together with halogen flame retardants. Antimony ethylene glycoxide (i.e., ethylene glycol antimonite) can be incorporated in the polyester backbone. Antimony tri-alloxide and antimony methacrylate are vinyl monomers [161]. The antimony alkoxides can be prepared by dissolving antimony trichloride in a slight excess of the corresponding alcohol in an inert solvent, e.g., carbon tetrachloride or toluene, and sparging with anhydrous ammonia. The antimony acylates are prepared by mixing stoichiometric amounts of saturated or unsaturated acid and antimony alkoxide.

In addition to good light transmission, polyester resins may contain a smaller proportion of combined antimony than those produced using antimony trioxide and still retain their self-extinguishing properties. Moreover, a smaller proportion of chlorine than for formulations using antimony trioxide is sufficient to retain the self-extinguishing properties.

1.3.11 Production Data

Global production data of the most important monomers used for unsaturated polyester resins are shown in Table 1.10.

1.4 Curing

Curing is achieved in general with a radical initiator and a promoter. A promoter assists the decomposition of the initiator delivering radicals, even at low temperatures at which the initiator alone does not decompose at a sufficient rate. Promoters are also addressed as accelerators.

1.4.1 Initiator Systems

Even when a wide variety of initiators are available, common peroxides are used for cold curing and hot curing. Coatings of unsaturated polyester resins are cured with light-sensitive materials.

Table 1.10 Global Production/Consumption Data of Important Monomers and Polymers [162]

Monomer	Mill. Metric Tons	Year	Reference
Methyl methacrylate	2	2002	[163]
Styrene	21	2001	[164]
Phthalic anhydride	3.2	2000	[165]
Isophthalic acid	0.270	2002	[166]
Dimethyl terephthalate (DMT) and terephthalic acid (TPA)	75	2004	[167]
Adipic acid	2	2001	[168]
Bisphenol A	2	1999	[169]
Maleic anhydride	1.3	2001	[170]
1,4-Butanediol	1	2003	[171]
Dicyclopentadiene	0.290	2002	[172]
Unsaturated polyester resins	1.6	2001	[173]

Table 1.11 Peroxide Initiators

Peroxide Type	Example
Ketone peroxides	Methylethylketone peroxide Acetyl acetone peroxide
Hydroperoxides	Cumene hydroperoxide
Diacyl peroxides	Dibenzoyl peroxide
Dialkyl peroxides	Dicumyl peroxide *tert*-Butylcumyl peroxide
Alkyl peresters	*tert*-Butylperoxy-2-ethylhexanoate *tert*-Butylperoxybenzoate *tert*-Amylperoxybenzoate *tert*-Hexylperoxybenzoate
Percarbonates	Bis(4-*tert*-butylcyclohexyl)-peroxydicarbonate

Peroxide initiators include ketone peroxides, hydroperoxides, diacyl peroxides, dialkyl peroxides, alkyl peresters, and percarbonates. Azo compounds, such as 2,2′-azobis(isobutyronitrile) and 2,2′-azobis (2-methylbutyronitrile), are also suitable. These curing agents can be used alone, or two or more can be used in combination. Some peroxide initiators are shown in Table 1.11.

1.4.1.1 In Situ Generated Peroxides

Allyl alcohol propoxylate can generate a peroxide in situ in the presence of metal salt promoter. This peroxide cures the unsaturated polyester resin. The curing proceeds with a very low exothermic reaction and low product shrinkage [177].

1.4.1.2 Functional Peroxides

Peroxides can be functionalized. Functional peroxides based on pyromellitic dianhydride, PEG, and *tert*-butyl hydroperoxide contain two types of functional groups:

1. Carboxylic groups that can participate in ionic reactions.
2. Peroxide groups that can initiate certain radical reactions.

The oligoesters are able to form three-dimensional networks when heated to 130 °C [178].

1.4.1.3 Photoinitiators

Photoinitiators are mostly used for coating applications. Some common photoinitiators are listed in Table 1.12. A common problem is yellowing during curing. α-Aminoacetophenones and thioxanthone derivatives impart yellowness. Such derivatives are used in thin layers.

Although suitable initiators for clear systems have become available only in the last few years, photoinitiators for pigmented systems have been developed for some time. Problems with regard to the absorption of ultraviolet light, needed for curing, arise when the coating is pigmented or when it is UV stabilized for outdoor applications. Ultraviolet stabilizers consist of ultraviolet absorbers or hindered amine light stabilizers. The curing performance depends on the pigment absorption and particle size.

The adsorption of bisacylphosphine oxides is in the near UV-visible range, and thus at much lower energy than other common photoinitiators. Those photoinitiators therefore allow the curing of thick pigmented layers. Acylphosphine oxides were originally used in dental applications.

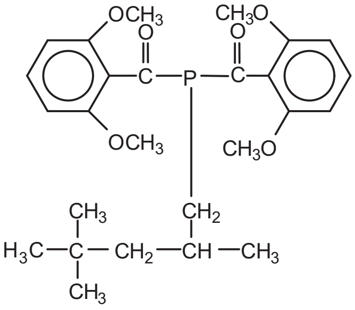
Acylphosphine oxides and bisacylphosphine oxides are prone to solvolysis attack; that is why the carbon phosphor bond is shielded by bulky groups.

Earlier investigations on acylphosphine oxides, in particular 2,4,6-trimethylbenzoyldiphenylphosphine oxide, did not show any advantage over 2,2-dimethoxy-2-phenylacetophenone. It was even concluded that acylphosphonates cannot be considered as useful photoinitiators [179,180].

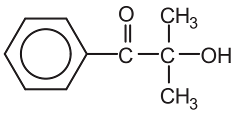
A mixture of bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide and 2-hydroxy-2-

Table 1.12 Common Photoinitiators

Photoinitiator	Reference
Benzoin methyl ether	[174]
2,2-Dimethoxy-2-phenylacetophenone	
2-Hydroxy-2-methylphenylpropane-1-one	
α-Hydroxy-acetophenone	[175]
Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine oxide	[176]
2-Hydroxy-2-methyl-1-phenyl-propan-1-one	
2,4,6-Trimethylbenzoyldiphenylphosphine oxide	
Bis(2,6-dichlorobenzoyl)-(4-propylphenyl)-phosphine oxide	



Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine

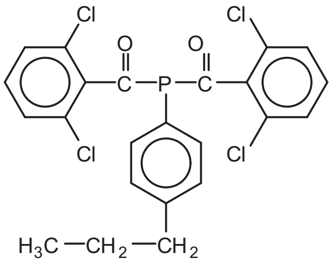


2-Hydroxy-2-methyl-1-phenyl-propan-1-one

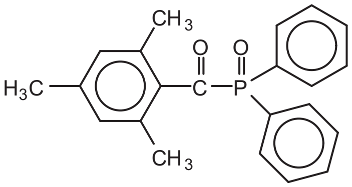
Figure 1.15 Bis(2,6-dimethoxybenzoyl)-2,4,4-trimethylpentylphosphine and 2-hydroxy-2-methyl-1-phenyl-propan-1-one.

methyl-1-phenyl-propan-1-one is suitable for curing thick pigmented furniture coatings [176]. The structures of these compounds are shown in Figure 1.15. Further, a combination of a bis-acylphosphine oxide and an α-hydroxy-acetophenone photoinitiator overcomes the limitations imposed by filtering of UV radiation by the pigments and provides a balanced cure [175].

The chloro compounds, e.g., bis(2,6-dichlorobenzoyl)-(4-propylphenyl)phosphine oxide, are less satisfactory, cf. Figure 1.16.



Bis(2,6-dichlorobenzoyl)-(4-propylphenyl)phosphine oxide



2,4,6-Trimethylbenzoyl-diphenylphosphine oxide

Figure 1.16 2,4,6-Trimethylbenzoyldiphenylphosphine oxide and bis(2,6-dichlorobenzoyl)-(4-propylphenyl)-phosphine oxide.

1.4.2 Promoters

There is a difference between hydroperoxides such as methylethylketone peroxide and peroxides such as dibenzoyl peroxide. Redox promoters, e.g., cobalt naphthenate, can stimulate the decomposition of hydroperoxides catalytically, whereas they cannot stimulate the decomposition of diperoxides. Therefore, for hydroperoxides only catalytic amounts of metal salts are necessary, whereas the salts do not act readily on diperoxides. The mechanism of catalytic action of metal salts is shown in Eq. (1.2):

$$\begin{aligned} \mathrm{ROOH} + \mathrm{Co}^{2+} &\rightarrow \mathrm{RO}^{\bullet} + \mathrm{OH}^{-} + \mathrm{Co}^{3+}, \\ \mathrm{ROOH} + \mathrm{Co}^{3+} &\rightarrow \mathrm{ROO}^{\bullet} + \mathrm{H}^{+} + \mathrm{Co}^{2+}. \end{aligned} \tag{1.2}$$

The cobalt ion is either oxidized or reduced by the peroxides depending on its value. If too much promoter is added, then the exotherm can be very high. Since the thermal conductivity of polymers is small, the heat of reaction cannot be transported out of the resin. The material would overheat and gas bubbles would form.

Promoters can be metal soaps, e.g., cobalt octoate or manganese octoate, or further metal chelates such as cobalt acetylacetonate and vanadium acetylacetonate. These promoters are redox promoters and amine compounds such as *N*,*N*-dimethylaniline. These

Table 1.13 Promoters

Promoter Type	Example
Metal soaps	Cobalt octoate Manganese octoate
Metal chelates	Cobalt acetylacetonate Vanadium acetylacetonate
Amine compounds	*N*,*N*-Dimethylaniline

accelerators can be used alone, or two or more kinds of them can be used in combination.

Examples of promoters are shown in Table 1.13. The auxiliary accelerator is used for enhancing the potency of the accelerator and includes, for example, acetyl acetone, ethyl acetoacetate, and anilide acetoacetate. These auxiliary accelerators can be used alone, or two or more of them can be combined.

Cobalt naphthenate and cobalt octoate are the most widely used. However, for environmental reasons and for health protection, there arose a demand to replace these cobalt-based catalysts with safer alternatives [181,182].

Alternatives to cobalt compounds are iron complexes of pyridine-containing compounds, such as dimethyl-2,4-di-(2-pyridyl)-3-methyl-7-(pyridine-2-yl-methyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate. This compound is shown in Figure 1.17.

NPy2 is synthesized from 2-pyridinecarboxaldehyde and dimethyl-1,3-acetonedicarboxylate. From NPy2, N2Py3O is synthesized with formaldehyde and 2-picolyamine. Eventually, the iron complex is formed with $FeCl_2$.

Curing experiments showed that iron complexes with N2Py3O (cf. Figure 1.17) are highly effective as promoters, whereas manganese complexes are not effective [181]. Also NPy2 is not an effective ligand.

1.4.3 Initiator Promoter Systems

Some common initiator promoter systems and the preferred temperature range to use are shown in Table 1.14. Methylpropylketone peroxide offers some advantage over methylethylketone peroxide, as the curing times are shorter [183].

Diperoxyketal initiators are often used for high-temperature molding processes. Dichloroacetic acid is a suitable promoter. It does not negatively influence the pot life and the cure cycle [184].

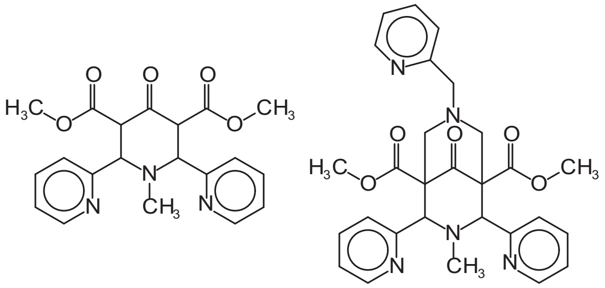


Figure 1.17 2,6-Di-(2-pyridyl)-1-methyl-piperid-4-one-3,5-dicarboxylate (NPy2) (left) and dimethyl-2,4-di-(2-pyridyl)-3-methyl-7-(pyridine-2-yl-methyl)-3,7-diaza-bicyclo[3.3.1]nonan-9-one-1,5-dicarboxylate (N2Py3O) (right) [181].

Table 1.14 Initiator Promoter Systems

Initiator	Promoter	Temperature (°C)
Methylethylketone peroxide	Cobalt naphthenate	20
Dibenzoyl peroxide	*N*,*N*-Dimethylaniline	60
Di-*tert*-butyl peroxide		130
tert-Butylperoxybenzoate		130

1.4.4 Polymerization

The initiators together with the accelerator initiate a crosslinking copolymerization. The monomer reactivity ratios for the system styrene/fumarate indicate an alternating system, i.e., a styrene radical reacts with a fumarate unit, and vice versa. On the other hand, the system styrene/maleate will tend to form blocks. Therefore, the fumarate system yields final products with better properties. Fortunately the maleate unit isomerizes during the condensation reaction.

If a nonazeotropic composition is used, then the ratio of styrene to polymerizable double bonds in the polyester varies in the course of curing. Such systems show a decrease in network density in the course of conversion [185].

1.4.4.1 Kinetics of Curing

The kinetics of curing can be conveniently investigated by differential scanning calorimetry and IR. Both methods have been compared [186]. The overall conversion measured by differential scanning calorimetry is in between the styrene consumption and the consumption of the pending double bonds in the polyester obtained by infrared spectroscopy.

The curing of laminates containing 50–70% glass fiber mat can be monitored by Raman spectroscopy [187]. Also, white and lightly colored gel coats can easily be monitored by Raman spectroscopy, but fluorescent problems are encountered with heavily colored pigments.

Using differential scanning calorimetry, both isothermal runs and temperature programmed runs can be used. Usually a complete conversion is not achieved during ordinary curing.

There are two portions of reaction enthalpy that can be investigated under laboratory conditions:

1. The enthalpy characterizing the styrene homopolymerization and copolymerization during curing.
2. A residual enthalpy that can be determined by heating up to near the degradation point of the resin.

In isothermal curing experiments, it was found that the sum of the enthalpy of polymerization and residual enthalpy depends on the curing (isothermal) temperature [188].

An unsaturated polyester resin initiated with a curing system of methylethylketone peroxide and a cobalt salt as promoter was studied by dynamic scans from −100 °C to 250 °C at heating rates from 2 °C/min to 25 °C/min. The amount of heat generated by a curing reaction decreases with increasing heating rate. The energy of activation of the overall reaction is around 90 kJ mol^{-1}. The traces can be fitted by either an empiric model or a model based on the theory of free-radical polymerization [189].

The rate of curing depends on the amount of initiator added to the mixture. A universal isoconversional relationship of the type

$$t = d - b \ln[I]_0 + \frac{E_a}{RT} \tag{1.3}$$

was established that expresses the dependency of the curing time t on the temperature, T, and the initial concentration of the initiator $[I]_0$ and the energy of activation E_a [190].

The differential isoconversional method has been used to yield the dependency of the apparent activation energy on the conversion. Thereby it was concluded that the gelling stage of the curing process is mainly controlled chemically and can be described by a two-parameter autocatalytic model [191].

Gel Point. At a certain conversion the reacting mixture rather suddenly changes its appearance: it gels. The gel point is an important parameter for the pot life time. The gel point can be determined most simply by stirring from time to time, although there are other more sophisticated methods available.

A well-known phenomenon in radical polymerization is the acceleration at moderate conversion which is addressed as the Trommsdorff effect. This effect can also be observed in crosslinking polymerization. The increase in rate causes a temperature rise in the bulk material. It was found that the gel time corresponds closely to the initial rise of the temperature [192].

The same is true when inhibitors are added or when the curing system is changed. For example, the addition of a *tert*-butyl catechol inhibitor increases the gel time in a linear fashion and the exothermic reaction is similarly delayed. An increase in the concentrations of initiator (either methylethylketone peroxide or acetyl acetone peroxide) or cobalt octoate promoter decreases the gel time.

The gel point has been extrapolated by thermal mechanical analysis, as the point at which the shrinkage rate drops to zero and the dimensions of the material show no appreciable change [193].

The curing characteristics can also be measured by the change of ultrasonic properties in the course of curing [194]. The sound velocity is constant until the gel point is reached. Afterwards the sound velocity increases to a plateau. Reaching the plateau indicates the end of the chemical reaction. The attenuation reaches a maximum which is attributed to the vitrification. The transition into the vitreous state causes a strong change of the acoustic properties.

The glass transition temperature increases continuously with conversion. When the glass transition temperature reaches the polymerization temperature, then vitrification occurs. Vitrification strongly hinders the mobility of the reactive groups. For this reason, the polymerization reaction slows down or stops before complete conversion is reached.

The increase of the longitudinal sound velocity with curing time can be associated with the increase of longitudinal modulus L', while the irreversible viscous losses are responsible for the increase of sound attenuation.

Kinetic Model. To describe the curing behavior of sheet molding compounds, a kinetic model based on radical polymerization mechanisms was developed [195]. In the model, three radical reaction steps are involved:

$$\begin{array}{llcl} \text{Initiation:} & I_0 & \rightarrow & 2R^{\bullet} \\ \text{Propagation:} & R_n^{\bullet} + M & \rightarrow & R_{n+1}^{\bullet} \\ \text{Inhibition:} & R^{\bullet} & \rightarrow & \text{Products} \end{array} \tag{1.4}$$

Here I_0 is the (initial) initiator concentration, $R_n^{\bullet}$ a growing radical with chain length n, and M a monomer unit. $R^{\bullet}$ refers to the total concentration of growing radicals. The kinetic constants were experimentally obtained by DSC measurements in model unsaturated polyester resins.

DSC measures the rate heat produced in a certain process. Thus DSC is highly suitable to characterize the kinetics of curing.

The conversion α can be expressed in terms of the heat H_t generated until a certain time t and the heat generated when the full conversion is reached H_{tot} [196]:

$$\alpha = \frac{H_t}{H_{\text{tot}}}. \tag{1.5}$$

Differentiation of Eq. (1.5) with respect to time results in

$$\frac{d\alpha}{dt} = \frac{1}{H_{\text{tot}}}\frac{dH_t}{dt}. \tag{1.6}$$

Further, from Eq. (1.6) the terms can be modeled, e.g., by the introduction of the Arrhenius equation and the order of reaction, as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp(-E/RT)\alpha^m(1-\alpha)^n. \tag{1.7}$$

In the case of methylethylketone and cobalt octoate, a two modal curing mode has been observed. It has been proposed that two independent cure reactions are taking place [196]. Therefore, the kinetic model has been modified as

$$\alpha = y\alpha_1 + (1-y)\alpha_2.$$

Here, subscripts 1 and 2 refer to the first and the second reactions. A computer program has been developed to calculate the degrees of freedom to evaluate the kinetic parameters [196].

The prediction of the gel time using a dual initiator system at low temperatures has been achieved [197]. The curing reaction was examined by gel time and pseudo-adiabatic exotherm measurements.

Another kinetic model has been presented that is based on the irreversible thermodynamic fluctuation theory. Because the glass transition temperature is related to molecular relaxation processes, the chemical kinetics also can be explained in terms of fluctuation theory [198].

The physical or mechanical properties of polymers during curing can be expressed by Eq. (1.8)

$$\frac{P(\infty) - P(t)}{P(\infty) - P(0)} = \exp\left(-(t/\tau)^{\beta}\right). \tag{1.8}$$

$P(t), P(\infty)$, and $P(0)$ are some property at times t, ∞, and $0, \beta$ is a constant, and τ is the curing relaxation time, $\tau \propto \exp(H/RT)$, where H is the activation energy of the curing reaction. If the property P is addressed as the monomer concentration, then the left-hand term in Eq. (1.8) is the fraction of unreacted monomer $1-\alpha$. Thus the conversion α is a function of the curing relaxation time, reaction time, and the reaction temperature [198,199].

Gel Time Drift. All polyester resins, by their nature, undergo some changes over time from their production till their actual curing. One of the characteristics where such changes become visible is the gel time drift [50].

It has been found that UP resins with good curing properties can be formulated by providing a two-component composition [50]. The first component is a non-aqueous resin composition, a transition metal compound selected from a copper, iron, manganese, or titanium compound, and a potassium compound. Further the resin composition contains less than 0.01 m mol cobalt per kg and less than 0.01 m mol vanadium per kg primary resin system. The second component contains a peroxide compound. Such compositions have a short gel time, a short peak time, and a high peak temperature. Further, resins can be obtained that exhibit a reduced gel time drift.

Gel time drifts for various two-component formulations are shown in Table 1.15. The drifts are exceptionally low. For comparison, the drifts of the corresponding cobalt-based system (to Formulations B and C in Table 1.15) based on 180 g Palatal P 6-01 and Palatal P 4-01, 20 g styrene, 0.4 g Co ethylhexanoate, and 0.016 g *tert*-butyl catechol are 158% and 384% after 171 days, respectively [50].

Table 1.15 Gel Time Drifts [50]

Formulation	Cured After (days)	Gel Time (min)	Drift (%)	Peak Time (min)	Peak Temperature (°C)
A	0	82		96	152
A	95	83	1	99	149
B	0	57		67	168
B	95	54	−6	61	165
C	0	132		159	126
C	186	125	−6	150	126

A, first component: 200 g Daron XP45, 0.289 Fe naphthenate, 2 g K-octanoate (in PEG), 0.016 g *tert*-butyl catechol, and 2 g acetyl acetone. Second component: 3% Butanox M50, relative to the primary resin system.

B, first component: 180 g Palatal P 6–01, 20 g styrene, 0.48 g Cu naphthenate, 0.4 g KOH (50% solution in water), and 0.016 g *tert*-butyl catechol. Second component: 3% Butanox, M50 relative to the primary resin system.

C, first component: 180 g Palatal P 4–01, 20 g styrene, 0.09 g Mn ethylhexanoate, 2 g K-octanoate (in PEG), 0.016 g *tert*-butyl catechol, and 2 g acetyl acetone. Second component: 3% Butanox, M50 relative to the primary resin system.

1.4.4.2 Catalysis by Nanoparticles

Nanoparticle additives are widely used in various fields of application. It has been found that the addition of nanoparticles to UP compositions has a catalytic effect on the curing ration of a UP resin [200]. This is of importance in practice for the choice of proper manufacturing conditions since the gel time is a critical parameter.

It was observed that the extent of exfoliation of nanoclay platelets has an important impact on the viscosity of polymers in the molten state [201].

A systematic study used different mixing techniques for the dispersion of nanoclays in UP resins. The following mixing techniques are used in this study [200]: Manual mixing, sonication, and high shear mixing.

The state of dispersion of the nanoparticles in the UP is evaluated by rheologic experiments and by scanning electron microscopy (SEM). As a result, dependence of the catalytic effect of the nanoclays on the kinetics of curing has been assessed by the measurement of the gel time. In this way, it was intended to find out the most efficient dispersion technique and its impact on the kinetics of curing.

After the addition of the nanoparticles, the viscosity of the resin increases dramatically. However, the experiments revealed that the various mixing techniques do not influence the increase of viscosity of the resin.

In contrast, the gel time is reduced by the addition of the nanoclays, as much as the state of dispersion increases. This is explained due to an enhanced exfoliation, which increases the surface between the polymer matrix and the clays. It is assumed that the interfacial region acts as a catalyst and thus accelerates the curing reaction [200].

The effects are rather dramatic. It was reported that the resin without nanoparticles showed a gel time of some 45 min, but a blend with nanoparticles manufactured by 10 passes of high shear mixing showed a gel time of 3 min [200].

Other studies using methylethyl ketone peroxide as initiator and cobalt naphthenate accelerator have been targeted to assess the energy of activation of the processes in the presence of nanoclays [202]. The dynamic DSC curing curves show a bimodal exothermic peak, as already observed by other researchers [196].

Therefore, two independent curing mechanisms, redox and thermal copolymerization, have been postulated [202]. The evaluation of the energies of activation suggests that the nanoclay effects a decrease of the activation energy of the redox reaction in comparison to the neat UP resin. Also, the pre-exponential factor of the first reaction for UP/OMC was less than that of the neat UP.

The decrease of the activation energy and the decrease of the number of collisions of components caused by the nanoclay result in an increase of the reaction rate of the redox copolymerization mechanism. Further, the kinetic analysis discloses that the thermal decomposition reaction of the initiator is not affected by the nanoclay. So, the addition of nanoclay results in an increase of the total reaction [202].

The addition of carbon nanofibers effects a delay in the kinetics of curing. A shift of the exothermal peak is observed to higher times. Also rheological experiments exhibit a shift. However, the extent of conversion is not affected by the addition of carbon nanofibers [203].

Carbon nanofibers can be used as a filler in a glass-fiber-reinforced UP. Because of the high aspect ratio of the nanofibers, a small amount is sufficient to modify the electrical properties of the composites. The measurement of the electrical resistance can be used to detect damage in the course of mechanical stress [204].

1.4.4.3 Phase Separation

A phase separation may occur in the course of curing, when styrene is in excess. In this case a crosslinked phase and a poly(styrene)-rich phase appear.

In the case of unsaturated polyester systems, the phase separation occurs mainly by chemical changes of the system, in contrast to the more common thermally induced phase separation. The phase separation is therefore addressed as a chemically induced phase separation. Thermodynamic models have been established to understand this phenomenon [205].

The final morphology of the resin is primarily determined by the phase separation process and the gelation resulting from the polymerization [206]. The cured polymer of a single-phase resin shows a flake-like structure, while spherical particles form in the two-phase system [207].

The phase behavior can be observed by measuring the glass transition temperatures where shoulders are observed in the presence of a two-phase system. The shoulders become more evident utilizing dynamic mechanical analysis by plotting $\log \tan \delta$ vs. temperature [208].

Phase separation is an important feature in low-profile resin systems. Here the system separates in a thermoplastic-rich phase and in an unsaturated polyester-rich phase. This two-phase structure provides a weak interface where microcracking can initiate and microvoids can form to compensate the shrinkage [120].

In such systems an optical microscope equipped with a heating chamber is employed to observe the phase separation process during curing. At the same time, conversion is monitored by IR. The results show that the copolymerization routes locate between the azeotropic and the alternating copolymerization line, and shift gradually toward the azeotropic line.

1.5 Properties

1.5.1 Structure-properties Relationships

The properties can be widely influenced by the choice of the components, since there is a wide variety of compounds. Some aspects are briefly indicated in Table 1.1.

Aliphatic chains, both in the acid moiety and in the diol moiety, will result in comparatively soft materials. Therefore, 1,2-butanediol and diethylene glycol and adipic acid will make the resin softer than phthalic anhydride. The rigidity decreases in the following order: 1,2-propanediol, 2,3-butanediol, 1,4-butanediol, dipropylene glycol, diethylene glycol. For acids the rigidity decreases in the order orthophthalic acid, isophthalic acid, succinic acid, adipic acid, glutaric acid, isosebacic acid, and pimelic acid [1].

More rigid materials do not absorb water as much as flexible materials. Therefore, because there is less water available, the rigid materials show better resistance to hydrolysis. Bisphenol A and neopentyl glycol-containing resins shield the access of small molecules to the ester group and therefore they exhibit a better chemical resistance.

The crosslink density grows with the amount of maleic anhydride feed. The rigidity can be controlled with the content of maleic anhydride in the polyester. The glass transition temperature also increases with increasing crosslinking density.

The resistance against hydrolysis increases, as the ester linkages are more stable. Bulky alcohol molecules, like neopentyl glycol, cyclohexanediol, or hydrogenated bisphenol A, are used for hydrolytic resistant materials. The alcohols are used in combination with isophthalic acid and terephthalic acid.

1.5.2 Hydrolytic Stability

The ester group is a weak link with regard to hydrolysis. Hydrolysis occurs in aqueous media and is enhanced at elevated temperatures and in particular in alkaline media.

The long-term behavior of glass fiber-reinforced plastic pipes was tested in an aqueous environment at 20 °C. The strength of the wet pipes after a 1000 h loading reduced to about 60% of the dry strength in short-term loading [209].

1.5.3 Recycling

In recent years, disposal of waste matter of polyesters has become a problem, and various methods to recover and reuse the waste matter have been studied. One of the methods, so-called feedstock recycling, comprising depolymerizing a waste matter of a polyester or the like to convert it into monomers and performing polymerization reaction using the monomers as raw materials to form a polyester such as PET again has been studied. Feedstock recycling is expected as a means capable of realizing the reuse of resources, because separation of impurities is feasible and the qualities of the raw materials do not differ so much from those of virgin materials.

Methods for depolymerizing a polyester into monomers are broadly divided into three methods [210]:

1. a hydrolysis method using water as a solvent,
2. an alcoholysis method using an alcohol as a solvent, and
3. a glycolysis method using a glycol as a solvent.

The hydrolysis method is, for example, a method wherein a PET melt is allowed to react with water vapors and then allowed to react with ammonium hydroxide to decompose the PET into terephthalic acid and ethylene glycol.

Although this method has the advantage that a glycol or an alcohol does not need to be used for the reaction, it is necessary to use a pressure resistant special apparatus, because the reaction is carried out under the conditions of high pressure.

The alcoholysis method is a method wherein a polyester is heated in an alcohol solvent to depolymerize the polyester.

This method has an advantage that when PET is depolymerized with methanol as solvent, dimethyl terephthalate is obtained. This monomer is directly formed by the depolymerization reaction and the depolymerization reaction proceeds relatively rapidly. On the other hand, the alcohol used as a solvent is low-boiling, and in order to promote the reaction, application of pressure is necessary.

The glycolysis method is a method wherein a polyester is heated together with a depolymerization catalyst such as sodium carbonate in an excess alkylene glycol solvent to depolymerize the polyester and thereby form a bis(β-hydroxy alkyl) terephthalate and ethylene glycol. When ethylene glycol is used as a solvent, bis(β-hydroxyethyl) terephthalate is formed by the depolymerization reaction, and by further adding methanol in the presence of a transesterification catalyst and performing transesterification reaction, dimethyl terephthalate can be recovered.

Using glycolysis, the reaction can be carried out at atmospheric pressure. However, the reaction time is relatively long, around 4 h. Here emerges still another problem as the glycol solvent can deteriorate because it is heated for a long period of time. Therefore, shortening of the reaction time is desirable.

A depolymerization method has been described where unsaturated polyester waste is allowed to react with a glycol at a relatively high temperature of 150–300 °C. In the presence of a radical initiator to cut even a part of styrene crosslink that is hardly decomposed by the usual glycolysis method.

1.5.3.1 Microwave Radiation

It has been suggested that microwaves not only increase the temperature of the reactant in the polymerization reaction or the depolymerization reaction but also exert a great effect on the reaction itself.

A method for depolymerizing a polyester has been described that uses microwaves in the presence of a given reaction solvent. A monohydric alcohol or polyhydric alcohol containing an alkali metal or an alkaline earth metal is used [210].

1.5.3.2 Poly(ethylene terephthalate) Waste Products

Oligomers obtained from depolymerization of poly(ethylene terephthalate) waste products can be reused. The glycolysis products can be used for the synthesis of polyester polyols for rigid poly(urethane) foams and for the synthesis of unsaturated maleic or fumaric polyester resins. Bis(2-hydroxyethyl) terephthalate is the main product from the glycolysis of poly(ethylene terephthalate). A mixture of maleic anhydride and sebacic acid is added and a condensation is performed [211].

The glycolysis reaction is conducted by heating poly(ethylene terephthalate) and the glycol in a nitrogen atmosphere at a temperature preferably within the range from 200 °C to 260 °C to obtain a terephthalate oligomer [67] containing two to three terephthalate units. Zinc acetate is a suitable transesterification catalyst [212].

Unsaturated polyesters based on the glycolyzed poly(ethylene terephthalate) with propylene glycol or diethylene glycol and mixtures of both glycols show a broad bimodal molecular weight distribution. Larger molecular weight oligomers were obtained with increasing diethylene glycol contents in the glycol mixtures. The tensile modulus decreased and the toughness of cured products increased with increasing diethylene glycol content [213].

A study of the glycolysis of waste bottles made from poly(ethylene terephthalate) and back condensation with maleic anhydride indicated that the type of glycol used in glycolysis had a significant effect on the characteristics of the uncured and cured resins [214]. Unlike hydrolysis under acidic or basic conditions, glycolysis does not cause any problems related to corrosion and pollution [215].

On the other hand, it was also found that no separation of the type of bottles was needed before glycolysis, since the resins prepared from either water bottles, soft drink bottles, or a mixture of both bottles showed all the same characteristics. The properties of materials recycled in this way have been presented in detail [216]. Similarly, residues from the manufacture of DMT have been tried as feedstock for the aromatic acid component and condensed with maleic anhydride [217]. The complete process of how to come from a poly(ethylene terephthalate) to a suitable unsaturated polyester resin composition is described in detail in the literature [218].

The glycolysis products can be directly incorporated in an unsaturated polyester resin composition. However, toluene diisocyanate as an intermediate agent must be added. The isocyanate accelerates the curing significantly [219]. It is proposed that at the beginning of the curing, the isocyanate reacts with the oligo glycols to form chain extended products.

The glycolysis product acts as a modifier that improves the mechanical properties of the resulting composites. The procedure allows an effective utilization of the waste products. It is reasonable to use only partly glycolyzed products, when the molecular mass of the degradation products is still higher.

In another study, PET from bottle wastes was recycled by glycolysis process with ethylene glycol as usual. Then, a UP was prepared by the reaction MA. Liquid natural rubber was blended into the compositions. A blend of 2.5% liquid natural rubber in the UP-based recycled PET wastes achieved the highest strength in the mechanical properties with well-dispersed elastomer particles. The glass transition temperature of such recycled materials is higher than that of comparable compositions. This arises due to the degree of crystallinity.

Liquid natural rubber is an effective impact modifier. The compatibility of the recycled products to liquid natural rubber is better than those of commercial products [220].

1.5.3.3 Cured Unsaturated Polyester Resin Waste

Cured unsaturated polyester resin waste can be decomposed with a decomposition component such as a dicarboxylic acid or a diamine to obtain resin raw material. The unsaturated polyester resin is resynthesized with this resin raw material [221]. It is also possible to synthesize poly(urethane) resin by reacting the glycolic raw material with a diisocyanate compound [222].

1.6 Applications and Uses

The properties can be adjusted in a wide range, since a wide variety of basic materials can be used. Consequently, unsaturated polyesters have a very wide area of application. They can be used either as pure resin or with fillers, or reinforced, respectively.

One of the early uses of unsaturated polyesters was to produce cast items such as knife and umbrella handles, encapsulation of decorative articles, and electronic assemblies.

1.6.1 Decorative Specimens

Pure resins can be used for embedding of decorative specimens. Together with a photosensitive curing formulation, furniture coatings are on the market. The most important casting application is the manufacture of buttons.

1.6.2 Polyester Concrete

Polymer concrete is usually composed of silica sand and a binder consisting of a thermoset resin, such as unsaturated polyester. Polyester concrete is more resistant to chemicals than conventional concrete. An unsaturated polyester concrete is developed by adding the methyl methacrylate monomer to the resin to improve the early-age strength and the workability of the UP polymer concrete [223]. The study revealed that the workability is remarkably improved as the methyl methacrylate content is increased. The ratio of filler to binder is an important parameter for the workability.

1.6.3 Reinforced Materials

Bulk and sheet molding compounds are used in a wide variety of areas such as transportation, electrical applications, building, and construction.

Reinforced unsaturated polyester resins are used for the manufacture of articles for sanitary furniture, panels, pipes, boats, etc.

There are several techniques for manufacturing the final products, i.e.,

- hand lay-up process,
- fiber spray-up process,
- cold press molding, hot press molding,
- sheet molding, bulk molding,
- wet-mat molding,
- pultrusion.

In the hand lay-up process, parts in an open, glass-reinforced, mold are produced. First the mold surface is treated with release wax and then coated with a special polyester resin, the so-called gel coat. Then glass fibers are placed into the mold and impregnated with the formulated resin which cures after a short time. This procedure is repeated several times, until the desired thickness is reached. Finally a top coat is placed. In this way, for example, glass-fiber-reinforced boats can be fabricated.

The fiber spray-up process is an improvement of the hand lay-up process. A spray system is used to apply both chopped glass strands and the polyester resin. The spray system places simultaneously resin, catalyst, and glass strands by means of air pressure. The fiber spray-up process is much faster than hand lay-up process and can be automated.

In cold press molding and hot press molding, a preimpregnated fiber is placed in presses and cured there.

In sheet molding and bulk molding, the resin is mixed with the reinforcing material, either in bulk form or as mats or sheets. To the resin a thickener is added. The articles are formed in presses. The situation is similar in wet-mat molding.

In pultrusion, the reinforcement fiber is wheeled off a spool, dipped into a resin mixture, and pulled through a heated die to cure the compound.

1.6.4 Coatings

Unsaturated polyester resins are used for a wide variety of coatings. The formulations are usually thixotropic. Curing is mostly achieved by UV-sensitive initiators.

1.6.4.1 Powder Coatings

Thermosetting powder coatings have gained considerable popularity over liquid coatings for a number of reasons. Powder coatings are virtually free of harmful fugitive organic solvents normally present in liquid coatings. They give off little, if any, volatiles to the environment when cured. This eliminates solvent emission problems and exposure risk of workers employed in the coating operations.

Powder coatings also improve working hygiene, since they are in dry solid form with no messy liquids associated with them to adhere to the clothes of the workers and the coating equipment. Furthermore, they are easily swept up in the event of a spill without requiring special cleaning and spill containment supplies.

Another advantage is that they are 100% recyclable. Over-sprayed powders are normally recycled during the coating operation and recombined with the original powder feed. This leads to very high coating efficiencies and minimal waste generation.

However, in spite of the many advantages, powder coatings traditionally have not been suitable for heat-sensitive substrates, such as wood and plastic articles, due to the high temperatures demanded to fuse and cure the powders.

Unsaturated polyester powder coatings are available that undergo rapid polymerization at low temperatures, making them particularly attractive for coating of heat-sensitive substrates.

Low temperature curable unsaturated polyester powder coatings contain polyols with active hydrogens. Allylic, benzylic, cyclohexyl, and tertiary alkyl hydrogen atoms are readily abstracted during free-radical-induced curing to form the corresponding stable allylic, benzylic, cyclohexyl, and tertiary alkyl free radicals, all of which promote curing at the surface of

Table 1.16 Special Applications of Polyester Resins

Application	Reference
Polyester concrete	[224]
Bone cement	[225]
Coatings	
Road paints	[226]
Electronic and microwave industries	[159]
Electrically conductive resins	[227]
Toner material	[228]
Compatibilizers	[229]
Pour point depressants	[230]
Reactive melt modifier	[231]

the coating film in an open air atmosphere. A suitable polyol is 1,4-cyclohexanedimethanol [232].

1.7 Special Formulations

Unsaturated polyester resins have a broad field of application. Unsaturated polyester resins for special purposes are summarized in Table 1.16.

1.7.1 Electrically Conductive Resins

Electrically conductive resins can be formulated by the addition of carbon black particles. The particles have a strong tendency to agglomerate in a low-viscosity resin. The agglomeration process generates electrically conductive paths already in the uncured state.

The fully cured resins containing carbon black above percolation concentration have a constant, temperature-independent conductivity, over a wide temperature range [227].

1.7.2 Poly(ε-caprolactone)-perfluoropolyether Copolymers

Basically, fluorinated materials are attractive modifying agents because of their unique properties such as chemical inertness, solvent and high temperature resistance, barrier properties, low friction coefficient, and low surface tension. These properties can be imparted to other polymeric materials by blending or copolymerization.

This type of modification has been usually achieved by the use of fluorine-containing comonomers of low molecular weight which usually lead to homogeneous UP resin and therefore have to be added in significant amounts to achieve an appreciable performance improvement. Furthermore, the high cost of fluorinated monomers leads to very expensive polymeric materials.

Unsaturated polyester resins can be modified by hydroxy-terminated telechelic[1] perfluoropolyethers as comonomers during the synthesis of the polyester [233]. A disadvantage of this approach is the reactivity of these materials. A fraction of perfluoropolyether does not react.

Another method of introducing fluorine into the unsaturated polyester resins is simply blending fluorinated materials. A problem arises, however, because fluorinated polymers are usually immiscible with non-fluorinated polymers. They segregate in a separate phase with poor adhesion to the non-fluorinated matrix, leading to poor mechanical properties. However, separate block or graft copolymers containing fluorinated segments can be prepared that are compatible with the unsaturated polyester resin.

Poly(ε-caprolactone)-perfluoropolyether block copolymers are prepared by ring opening polymerization of ε-caprolactone with fluorinated hydroxy ethers of the Formula (1.9). Titanium tetrabutoxide is used as catalyst [234].

$$\begin{gathered}\mathrm{H{-}(OC_2H_4)_n{-}OCH_2CF_2O{-}(C_2F_4O)_p{-}} \\ \mathrm{(CF_2O)_q{-}CF_2CH_2O{-}(C_2H_4O)_n{-}H}\end{gathered} \tag{1.9}$$

This polymer can be added to an ordinary unsaturated polyester resin and cured with conventional initiator systems.

Applications of fluorine-modified unsaturated polyester resins include thermosetting resins for gel coating with excellent resistance to corrosion, water and atmospheric agents, formulations for resins and foams, etc.

1.7.3 Toner Compositions

Toner resins, and consequently toners, are propoxylated bisphenol A fumarate resins that are crosslinked in a reactive extrusion process in the presence of the liquid 1,1-bis(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane as initiator [228].

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[1] From *τέλος*: end and *χηλή*: claw of a crab, an oligomer or polymer with well-defined end groups, often star branched, whereas *τῆλη* means far, therefore better telochelic.

1,1-Di(*tert*-butylperoxy)-3,3,5-trimethylcyclohexane has advantages in comparison to the conventionally used dibenzoyl peroxide. Dibenzoyl peroxide generates benzoic acid as a by-product, which is undesirable. Benzoic acid is difficult to remove from the crosslinked resin in that it condenses in a vacuum system, rapidly clogging the system and requiring frequent apparatus shutdowns for cleaning. As a result of the difficulty in the removal of the benzoic acid by-product, the crosslinked toner resin contains a significant amount of acids. Such acidity has been found to negatively affect the charging, the humidity sensitivity of the charging, and the background density properties of the toners.

Crosslinked resins are used in making toner. The resins can be subsequently melt blended or otherwise mixed with a colorant, charge carrier additives, surfactants, emulsifiers, pigment dispersants, flow additives, etc. The resultant product can then be pulverized to form toner particles.

UV curable resins for incorporation in toner particles are powders based on unsaturated polyesters and poly(urethaneacrylate)s with bis-ethoxylated 2,2-bis-(4-hydroxyphenyl) propane or bis-propoxylated 2,2-bis(4-hydroxyphenyl)propane [235].

The toner particles can be prepared by melt kneading the toner ingredients, i.e., toner resin composition, charge control agent, pigment, etc. After the melt kneading the mixture is cooled and the solidified mass is pulverized.

1.7.4 Pour Point Depressants

Copolymers of dialkyl fumarates and dialkyl maleates with vinyl acetate and vinylpyrrolidone are effective as flow improvers and pour point depressants, respectively. Among a series of similar polymers, copolymers based on didodecyl fumarate vinyl acetate are the most effective pour point depressants [230]. These polymers are suitable additives for improving the flow properties and viscosity index of lubricating oils.

1.7.5 Biodegradable Polyesters

Aliphatic polyesters are almost the only promising structural materials for biodegradable plastics. In fact, aliphatic unsaturated polyesters, succinic fumaric units, and 1,4-butanediol are biodegradable as such.

However, the condensation of aliphatic polyesters derived from diacids and diols failed to obtain high-molecular-weight polyesters. Effective transesterification catalysts, high vacuum technique, and chain extenders enable the synthesis of high-molecular-weight polyesters with improved mechanical properties [236].

1.7.6 Neutron Shielding

The deterioration of UP materials by neutron irradiation has been investigated [237].

Comparative characterizations between virgin samples and damaged samples have been done by SEM, ultrasonic scanning, and shore hardness tests. The received dose flow was 0.4 kGy.

The studies revealed that the damage proceeds continuously with the exposure. It is suspected that competing reactions occur during exposure: Reticulation, chain break, and oxidation. The presence of aromatic structure cores improves the behavior during irradiation [237].

A neutron shielding material based on a UP resin and inorganic boron compounds and alumina hydrate has been described [238].

The boron concentration should be $4-25 \times 10^{21}$ atoms per cm^3 and the hydrogen concentration $3-5.5 \times 10^{22}$ atoms per cm^3. Furthermore, it is important that these materials are self-extinguishable.

The boron compounds that can be preferably used as a mixture with boron carbide are zinc borate compounds $Zn_2O_{14.5}H_7B_6$, $Zn_4O_8B_2H_2$, or $Zn_2O_{11}B_6$ [238]. The former compounds contain hydrogen atoms.

As hydrogenated mineral compounds alumina hydrates and magnesium hydroxide may be used, but alumina hydrate $Al(OH)_3$ is preferably used.

1.7.7 Bone Cement

An unsaturated polyester, made from propylene glycol and fumaric acid, is suitable as resorbable bone cement. Depending on the molecular weight, poly(propylene) fumarate is a viscous liquid. A filler of calcium gluconate/hydroxyapatite is used. An injectable form of a resorbable bone cement can be crosslinked in situ. The material cures to a hard cement degradable by hydrolysis [239]. Bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide has been found useful as photoinitiator for poly(propylene) fumarate, for the treatment of large bone defects [240].

Citric acid and sodium bicarbonate as the foaming agent develop porosity in the material by generating carbon dioxide during the effervescence reaction [225].

1.7.8 Compatibilizers

An unsaturated polyester is a suitable compatibilizer for styrene butadiene and nitrile butadiene rubber (NBR) rubber blends. By the addition of 10 parts unsaturated polyester per 100 parts of rubber, the degree of compatibility was greatly enhanced. The rheological and mechanical properties of the blends were also improved [229].

1.7.9 Reactive Melt Modification of Poly(propylene)

Melt blending of poly(propylene) with a low-molecular-weight unsaturated polyester in the presence of peroxide in a batch mixer and a twin-screw extruder improves the morphology. Under these conditions competitive degradation and crosslinking reactions take place. These reactions result in a significant change in the viscosity ratio.

Rheological studies show that depending on the process conditions some reacted PP/UP blends have a pronounced suspension behavior due to the presence of the dispersed polyester gel particles in a low-molecular-weight poly(propylene) matrix.

Infrared studies of the blends suggest the presence of block or graft structures that promote the compatibility in the treated blends. Such blends are suitable as compatibilizers for blends of poly(propylene) with high-molecular-weight thermoplastic polyester blends [231].

1.7.10 Toner Resins

Examples of linear unsaturated polyesters are low-molecular-weight condensation polymers formed by saturated and unsaturated diacids and diols. The resulting unsaturated polyesters are crosslinkable in two ways:

1. Due to double bonds along the polyester chain, and
2. Due to the functional groups, such as carboxyl, hydroxy, and others, amenable to acid-base reactions.

Suitable diacids and dianhydrides include succinic acid, isophthalic acid, terephthalic acid, phthalic anhydride, and tetrahydrophthalic anhydride. Unsaturated diacids or anhydrides are fumaric acid, itaconic acid, and maleic anhydride. Suitable diols include propylene glycol, ethylene glycol, diethylene glycol, and propoxylated bisphenol A.

A particularly preferred polyester is poly(propoxylated bisphenol A fumarate). A propoxylated bisphenol A fumarate unsaturated polymer undergoes a crosslinking reaction with a chemical crosslinking initiator, such as 1,1-di-(*tert*-butylperoxy)cyclohexane. The crosslinking between chains will produce a large, high-molecular-weight molecule, ultimately forming a gel.

The toners and toner resins may be prepared by a reactive melt mixing process wherein reactive resins are partially crosslinked. For example, low melt toner resins and toners may be fabricated by a reactive melt mixing process comprising the following steps [241]:

1. Melting reactive base resin, thereby forming a polymer melt, in a melt mixing device.
2. Initiating crosslinking of the polymer melt with certain liquid chemical crosslinking initiator and increased reaction temperature.
3. Retaining the polymer melt in the melt mixing device for a sufficient residence time that partial crosslinking of the base resin may be achieved.
4. Providing sufficiently high shear during the crosslinking reaction to keep the gel particles formed during crosslinking small in size and well distributed in the polymer melt.
5. Optionally devolatilizing the polymer melt to remove any effluent volatiles.

The high-temperature reactive melt mixing process allows for very fast crosslinking which enables the production of substantially only microgel particles, and the high shear of the process prevents undue growth of the microgels and enables the microgel particles to be uniformly distributed in the resin.

Toner compositions have been described that are based on a binder resin, a colorant, and a fatty acid metal salt. The binder resin is an unsaturated crystalline polyester resin [242]. The crystallinity imparts good low-temperature fixability to the toner.

To get a crystalline polyester with an appropriate crystalline structure having the necessary glass transition temperature and melting point, 1,4-butanediol and 1,6-hexanediol are preferably used as diol components. The acid component is fumaric acid. The crystallinity and melting point can be further controlled by glycerin and trimellitic anhydride which results in branched molecules.

The fatty acid metal salt is added to the toner to accelerate the oxidation reaction of the double bonds of the unsaturated polyester resin when the toner is heated in a fixing process [242]. The fatty acid metal salt is preferably microencapsulated to avoid accelerating the oxidation reaction of double bonds of the unsaturated polyester resin before use. Examples of the fatty acid metal salts include metal salts of octyl acid, naphthenic acid, tall oil, and soybean oil-based fatty acids. The fatty acid metal salt is added in amounts of 0.1–10%. When the added amount is too small, the promoting effect of the oxidation reaction is hardly produced. However, when the added amount is too large, the electric properties of the toner deteriorate. As for the core material of the encapsulation, natural resins or synthetic resins can be used. Specific examples of natural resins include dextrin, glue, casein, soybean protein, albumin, rosin, shellac, asphalt, gilsonite, tar, nitrocellulose, etc. Specific examples of the synthetic resins include poly(vinyl acetate), EVA, acrylate polymers, and poly(urethane) resins. Some colorants for the toner resin composition are listed in Table 1.17.

Table 1.17 Colorants for Toners [242]

Compound	Color index
Naphthol Yellow S	10316
Hansa Yellow 10G	11710
Hansa Yellow 5G	11660
Hansa Yellow G	11680
Hansa Yellow GR	11730
Hansa Yellow A	11735
Hansa Yellow RN	11740
Hansa Yellow R	12710
Pigment Yellow L	12720
Benzidine Yellow G	21095
Benzidine Yellow GR	21100
Permanent Yellow NCG	20040
Vulcan Fast Yellow 5G	21220
Vulcan Fast Yellow R	21135
Anthrazane Yellow BGL	60520
Permanent Red F2R	12310
Permanent Red F4R	12335
Permanent Red FRL	12440
Permanent Red FRLL	12460
Permanent Red F4RH	12420
Vulcan Fast Rubine B	12320
Lithol Rubine GX	12825
Permanent Bordeaux F2K	12170
Helio Bordeaux BL	14830
Bon Maroon Light	15825
Bon Maroon Medium	15880
Indanthrene Blue RS	69800
Indanthrene Blue BC	69825

The content of the colorant in the toner is some 3–10%. The colorants are subjected to a surface treatment. Surface treatment agents for colorants are collected in Table 1.18.

Table 1.18 Surface Treatment Agents for Colorants [242]

Compound
Gum rosin
Wood rosin
Tall rosin
Abietic acid
Levopimaric acid
Dextropimaric acid and salts
Rosin-modified maleic acid resins
Rosin-modified phenolic acid resins

Master batches, which are complexes of a colorant with a resin, can be used as the colorant [242]. The master batches can be prepared by mixing the resins with the colorants and kneading the mixture under a high shearing force. An organic solvent can be added to increase the interaction between the colorant and the resin. Dispersing devices capable of applying a high shearing force such as three-roll mills are used. As dispersant aids modified poly(urethane) dispersants, polyester dispersants, and acrylic dispersants can be added.

The average particle diameter of the colorant in the dispersion should not be greater than 1 μm. When the average particle diameter of a colorant in the dispersion is too large, the image qualities of the resultant toner images will deteriorate.

This will particularly occur when images are formed on a transparent film for use in overhead projection, because the particle diameter of the colorant in the resultant toner is large and the toner images have low transparency. The average particle diameter and particle diameter distribution of a colorant can be determined by laser diffraction.

Further, charge controlling agents can be added to the compositions. Charge controlling agents are shown in Table 1.19.

The toner is manufactured by the following steps [242]:

1. Dispersing or dissolving a colorant in the binder resin,

Table 1.19 Charge Controlling Agents for Toners [242]

Basic Compounds
Nigrosine dyes
Triphenyl methane dyes
Chromium-containing metal complex dyes
Molybdic acid chelate pigments
Rhodamine dyes
Alkoxyamines
Quaternary ammonium salts
Fluorine-modified quaternary ammonium salts
Alkylamides
Phosphorus compounds
Tungsten compounds
Metal salts of salicylic acid
Commercially Available Products
BONTRON® 03 (Nigrosine dye)
BONTRON® P-51 (quaternary ammonium salt)
BONTRON® S-34 (metal-containing azo dye)
BONTRON® E-82 (metal complex of oxynaphthoic acid)
BONTRON® E-84 (metal complex of salicylic acid)
BONTRON® E-89 (phenolic condensation product)
TP-302 (molybdenum complex of quaternary ammonium salt)
TP-415 (molybdenum complex of quaternary ammonium salt)
COPY CHARGE® PSY VP2038 (quaternary ammonium salt)
COPY BLUE® (triphenyl methane derivative)
COPY CHARGE® NEG VP2036 (quaternary ammonium salt)
COPY CHARGE® NX VP434 (quaternary ammonium salt)
LRA-901 (boron complex)
LR-147 (boron complex)

2. Dispersing the toner composition liquid in aqueous medium, and
3. Polymerizing the polyester resin to prepare the particles.

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