Current Status of Unsaturated Polyester Resins

MONA MALIK, VEENA CHOU DHARY & I. K. VARMA


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Current Status of Unsaturated Polyester Resins

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1. INTRODUCTION

Unsaturated polyester (UP) resins are linear polycondensation products based on unsaturated and saturated acids/anhydrides and diols or oxides. These resins are generally pale yellow oligomers with a low degree of polymerization. Depending on the chemical composition and molecular weight (1200–3000 g/mol), these oligomers may be viscous liquids or brittle solids. The unsaturation in the backbone provides sites for reaction with vinyl monomers using free-radical initiators, thereby leading to the formation of a three-dimensional network. The solutions of unsaturated polyesters and vinyl monomers (reactive diluents) are known as UP resins. The dilute UP resin solution thus obtained has a viscosity in the range 200–2000 cps.

Polyester resins, because of their versatility and low cost, are widely used throughout the world. The commercial applications of the resins started in 1941. Unsaturated polyester laminating resins were first introduced on the market in 1946. UP resins are the most widely used thermosets in polymeric composites. They can be processed over a wide temperature range. Glass-fiber-reinforced UP resins are extensively used in building and construction; in the transportation, electric, and electronic industries; and for sanitary and domestic applications. The biggest use of these resins is in the construction industry, followed by transportation. The possibility of curing at room temperature and atmospheric conditions (i.e., ambient conditions) makes these resins very versatile materials for fabrication of large structures such as boat hulls, automobile bodies, aircraft radomes, and the like. Approximately 2.1 million [1] tonnes of UP resins were used for structural applications alone in 1997.

One of the major problems with these resins is their high shrinkage during the curing reaction (>7%). The glass fiber reinforcement becomes raised from the surface of the molding because of the shrinkage, leading to a poor surface finish. By selection of different acids/anhydrides and glycols and changes in the ratio of saturated/unsaturated component and the reactive diluent, the nature of the final network can be varied significantly to meet different performance requirements. Addition of low-profile additives (LPAs) (thermoplastics) in the resin formulation compensates for the thermal and polymerization shrinkage of UP resin, thereby leading to low-shrink or zero-shrink resin systems. The advent of low-profile, low-shrink technology has allowed molding compounds to compete successfully with steel in exterior automotive applications.

Considerable work has been reported on the synthesis, characterization, curing behavior, and properties of UP resins in the past [2–7].
In this paper, an attempt is made to review the state of the art of this important class of thermoset resins. It deals with classification, synthesis, modification, characterization, curing, properties, and applications of UP resins. The main focus in this review article is on the latest developments in this area.

2. CLASSIFICATION OF UNSATURATED POLYESTER RESINS

Polyester resins may be classified on the basis of their structure into the following groups: (1) ortho resins, (2) isoresins, (3) bisphenol-A fumarates, (4) chlorendics, and (5) vinyl ester (VE) resins.

Ortho resins, also known as general-purpose resins, are based on phthalic anhydride (PA), maleic anhydride (MA), or fumaric acid and glycols. PA is relatively low in price and provides an inflexible link in the backbone. However, it reduces the thermal resistance of laminates. Limited chemical resistance and processability are other problems associated with these resins. Among the glycols, 1,2-propylene glycol is the most important. Due to the presence of the pendant methyl group, the resulting resins are less crystalline and more compatible with commonly used reactive diluent (styrene) than those obtained using ethylene glycol, diethylene glycol (DEG), and triethylene glycol and give products with inferior electrical properties. Resins with high heat and chemical resistance are produced using neopentyl glycol or hydrogenated bisphenol-A.

Isoresins are prepared using isophthalic acid, MA/fumaric acid, and glycol. These resins are higher in cost than ortho resins and also have considerably higher viscosities, hence, a higher proportion of reactive diluent (styrene) is needed. The presence of higher quantities of styrene imparts improved water and alkali resistance to the cured resins. Isophthalic resins are thus of higher quality since they have better thermal and chemical resistance and mechanical properties.

For bisphenol-A fumarates, the introduction of bisphenol-A in the backbone imparts a higher degree of hardness and rigidity and improvement in thermal performance. They are synthesized by reacting ethoxy-based bisphenol-A with fumaric acid.

For chlorendics, to enhance flame retardancy, chlorine/bromine-containing anhydrides or phenols are used in the preparation of UP resins. For example, reaction of chlorendic anhydride/chlorendic acid with MA/fumaric acid and glycol yields the following resin with better flame retardancy than general-purpose UP resin. Other monomers used include tetrachloro or tetrabromophthalic anhydride. The bromine content must be at least 12% to make a self-extinguishing polyester [8].
For VE resins, bisacryloxy or bismethacryloxy derivatives of epoxy resins contain unsaturated sites only in the terminal position and are prepared by reaction of acrylic acid or methacrylic acid with epoxy resin (e.g., diglycidyl ether of bisphenol-A, epoxy of the phenol-novolac type, or epoxy based on tetrabromobisphenol-A). These resins were first commercialized in 1965 by Shell Chemical Company under the trade name of Epocryl. In 1966, Dow Chemical Company introduced a similar series of resins for molding purposes under the trade name of Derakane resins. The viscosity of neat resins is high; hence, reactive diluent (e.g., styrene) is added to obtain a lower viscosity solution (100–500 poise). Notable advances in VE resin formulations are low-styrene-emission resins, automotive grades with high tensile strength and heat deflection temperature, hybrid grades that balance performance and economy, and materials for corrosion resistance [9]. The effect of marine environment on a VE resin and its highly filled quartz composites has recently been reported [10].

3. SYNTHESIS OF UNSATURATED POLYESTER RESINS

Unsaturated polyesters have been synthesized by the reaction of unsaturated and saturated dibasic acids or anhydrides with dihydric alcohols or oxides. These resins are manufactured in heated cylindrical steel reactors equipped with a condenser to collect the aqueous by-products. In the presence of oxygen, some discoloration may be produced, which can be prevented by purging fresh nitrogen or carbon dioxide into the
reactor. These gases must be free of oxygen. UP resins are synthesized by the fusion-melt process, which is used mainly for the condensation of liquid glycols (e.g., propylene glycol) (PG) with dibasic acids having low melting temperatures such as PA, aliphatic dibasic acids/anhydrides (e.g., MA), and various halogenated intermediates. The rates of polyesterification reactions are influenced by the structure and stoichiometry of the glycol and dibasic acid components [11]. Generally, a 5% excess of glycol is added in the initial stages to prevent any glycol losses during polymerization. After adding the raw materials, the temperature of the reactor is increased to 100°C to start the exothermic reaction. Two main reactions are involved in this synthesis: (1) monoester formation and (2) polycondensation.

The monoester formation takes place in the temperature range 60°C–130°C, while the polycondensation takes place above 160°C. Since it is a reversible reaction, therefore, water coming out of the reaction has to be removed continuously. In this process, phthalic resins require 15 h at 190°C to attain satisfactory molecular weight. At this temperature, some glycol is also lost, along with water of condensation, which can be prevented either by fractionating condenser systems or by adding acid catalysts [12] to promote the formation of volatile ethers that are lost as by-products. The molecular weight of UP resins is about 3000 g/mol or less at equilibrium state. Further increase in polycondensation leads to gel formation. Several new approaches have been used to increase $M_n$ to 5000 g/mol. On curing, such resins give networks with better toughness and mechanical strength [13].

The extent of reaction is controlled continuously by checking the acid number. This is done by withdrawing some prepolymer samples from the reactor and titrating them with 0.1 N alcoholic potassium hydroxide (KOH) solution. The acid number is recorded as milligrams of KOH per gram of resin and is related to the molecular weight by the equation

$$\text{MW} = \frac{56,100}{\text{Acid number}}$$

When the acid number drops to 200, xylene is added into the reactor at 3–6 wt% of the total material content, and refluxing is started. Xylene forms an azeotrope with water and accelerates its removal, which in turn increases the extent of reaction. The distillate is collected in a small receiver tank, in which xylene and water separate from each other. Xylene (upper phase) is continuously fed back to the reactor, and water (lower phase) is removed from the bottom of the tank.

When the acid number has reached 135, the reactor temperature is increased to 175°C–185°C. The reaction is carried out until the acid number has fallen to 50 ± 2. Then, cooling is started, and an inhibitor (hydroquinone) is added at 150°C. The activity of hydroquinones is enhanced by quaternary ammonium salts such as trimethylbenzyl ammonium chloride. Other inhibitors in use are 1,4-napthoquinones, chloranil, catechol derivatives, and the like. The inhibitor is usually added at 0.075 mol% of the total monomer content. When the temperature has fallen to 90°C–100°C, styrene is added and cooled as rapidly as possible to prevent polymerization of styrene. The resin thus produced has a pale straw color, mainly owing to inhibitor (hydroquinone).

Isophthalic acid and terephthalic acid are insoluble in the initial glycol/anhydride melt, which leads to agitation problems. Isophthalic acid reacts more slowly with glycols compared to PA. In this case, PG and MA react at lower temperatures, while isophthalic acid remains inert. MA preferably forms esters with primary hydroxyl group on PG,
leading to formation of PG maleate esters with a preponderance of terminal secondary hydroxyl groups. Maleate ester derivatives do not homopolymerize during processing in spite of having reactive double bonds in MA [14]. The isophthalic acid is esterified above 190°C. This condensation reaction proceeds much more slowly because of the nonavailability of primary hydroxyl groups. Subsequent reaction with isophthalic acid requires temperatures of 240°C for prolonged periods to dissolve it. Due to these prolonged heatings, maleate component gives rise to undesirable discoloration. Isophthalic resins attain higher molecular weights than phthalic resins due to the greater bond strength of the esters. These resins are stable at higher temperatures and give polymers with higher molecular weight. After polymerization is finished, the resin is cooled and blended with inhibited styrene. When cross-linked, their properties are superior to those of phthalic resins. A similar method has been used for preparation of halo and nonhalo polyesters from tetrachlorophthalic anhydride, tetrabromophthalic anhydride, and PA with DEG and MA. A wide range of rigid, semirigid, semiflexible, and flexible UP resins and chloropolyesters have been reported in the literature [15, 16].

VE resins are produced by the reaction of epoxy resins such as diglycidyl ether of bisphenol-A or \( N,N-O\)-triglycidyl amino-phenols [17] or epoxy novolacs with acrylic acid/methacrylic acid at 100°C–120°C in the presence of catalyst (imidazole). To inhibit the polymerization, hydroquinone is added, and the reaction is carried out in the presence of air. The progress of the reaction is monitored by determining the acid number at regular intervals. The reaction is allowed to continue until the acid number reaches a value below 10. The amber color resin is cooled to room temperature and diluted with a vinyl monomer for further applications.

4. SIDE REACTIONS DURING POLYCONDENSATION

4.1. Addition of Glycol Across the Double Bond (Ordelt Saturation)

The maleate double bond in UP is highly electron deficient due to the presence of electron-withdrawing carbonyl groups. Addition of glycol across the double bond (Michael addition) leads to reduction of unsaturation and branching, which leads to an uncertainty of chain end functionality. This reaction was first studied by Ordelt et al. [18–20]. The Ordelt reaction leads to the formation of a branched structure and a change in the functionality of UP resins.

\[
\text{HO} \quad \text{C} = \text{CH} \quad \text{CH} \quad \text{C} - \text{O} - \text{R} - \text{OH} + \quad \text{HO} \quad \text{R} - \text{OH} \rightarrow \quad \text{HO} \quad \text{C} = \text{CH}_2 \quad \text{CH} \quad \text{C} - \text{O} - \text{R} - \text{OH}
\]

Formulations containing a higher concentration of MA result in the reduction of 15% unsaturation in the final product, while fumaric acid retains a higher degree of unsaturation when substituted in the same formulations. This leads to products of higher reactivities and superior properties. Modeling of unsaturated polyester prepolymer structure has been done from a knowledge of fundamental molecular parameters, including
4.2. Isomerization

The strain energy across the double bond increases when MA, from its planar configuration of low conformational energy, changes into maleate diesters and oligomer. This increase is caused mainly because of steric hindrance. As the reaction temperature increases from 160°C to 180°C, maleate esters relieve the strain by transforming into more planar trans-fumarate isomer. This isomerization, which may be partial, occurs mainly in the presence of branched secondary glycols such as PG [23] or bulky aromatic dibasic acids, which subjects the maleate double bond to increased strain.

Glycol structure plays an important role in this isomerization, which is enhanced when bulky groups are close to the hydroxyls. It has been shown that linear glycols with even-numbered carbon atoms cause higher isomerization than odd-numbered linear glycol [24, 25]. Isomerization diminishes in going from ethylene glycol to 1,3-propylene glycol, from around 65–70% to 15%. The fact that there is one more methylene group in the 1,3-propylene glycol may be indicative of less spatial interaction between condensed groups. The isomerization is reported to be 95% with 1,2-propylene glycol, 39% with 1,4-butylene glycol, 55% with DEG, and 35% with 1,6-hexamethylene glycol at 180°C [26]. In 1,4-butylene glycol, there is one more methylene group, and a higher degree of isomerization (in comparison with the polyester from 1,3-propylene glycol) was observed. It has been attributed to spatial interactions between ester groups in close proximity. The spatial configuration of polyester chains is even more important than methylene groups within the glycol chain for cis-trans isomerization to occur. The condensation reaction proceeds more rapidly and gives polymer in less time if it is between linear ethylene and DEGs with MA. Maleate esters are slightly distorted from the planar configuration, which suppresses their ability to copolymerize with styrene monomers. The corresponding fumarate polymers show reactivities [27] almost 20 times those of maleate esters because they attain a planar configuration in the trans form. The mechanism and kinetics of this isomerization have been studied using 1H-NMR (nuclear magnetic resonance) [28], infrared analysis, and polarographic techniques. The signals at 6.27 and 6.85 ppm in NMR indicate the isomerization of maleate to fumarate. The rate of the isomerization reaction can be increased at lower temperatures by a cycloaliphatic amine catalyst (e.g., morpholine [29]).

4.3. Transesterification

At high temperature, the polyesterification reaction is often accompanied by transesterification, which is in fact an alcoholysis or an acidolysis of the polyester chains by hydroxyl or carboxyl groups of monomers and/or macromolecules.

The transesterification would redistribute molecular mass and functional end groups of UP molecules. It results in a statistical distribution of macromolecular units and chain ends. Some amount of transesterification reaction also takes place in the final stages of manufacture, which modifies the final molecular distribution by limiting development of higher molecular weight polymers.
4.4. Dehydration of α-Diols

Under the conditions of polyesterification reaction, dehydration of α-diol also takes place, thereby leading to the formation of (1) DEG or dipropylene glycol from 1,2-ethanediol or 1,2-propanediol, respectively, and these dihydroxy compounds react with the carboxylic species and modify the mechanical properties of the final product; and (2) compounds with a low boiling point, such as tetrahydrofuran (THF) in the case of 1,4-butandiol or cyclic ethers and propanal in the case of 1,2-propanediol in the presence of strong acids.

Intramolecular ring closure between polymer end groups has been suggested in the polyesterification reaction between MA and 1,5-pentanediol [30].

5. MODIFICATION OF POLYESTERS

Modification of polyesters has been done to improve fracture toughness, impact resistance, and solubility in water and to reduce $T_g$ and viscosity of polymers. Toughness of the polymers increases due to the presence of flexible units in the backbone, such as long-chain diols (e.g., DEG, dipropylene glycol, triethylene glycol) or long-chain saturated acids (e.g., adipic acid). Newer UP resin technology capable of providing 50% lower styrene emission levels compared to standard resins has been developed [31]. Partial replacement of MA with maleopimaric acid yielded UP resin with higher Vicat distortion temperatures than usual commercial samples prepared from PA, MA, and PG, while mechanical properties such as modulus and strength were similar [32]. An acyclic diene metathesis polymerization technique has also been used to prepare UP resins [33].

“All-trans” unsaturated polyesters from diesters of fumaric acid and a variety of aliphatic and aromatic diols in organic solvents such as THF or acetonitrile have been prepared using enzyme lipase at ambient temperatures [34–36]. These enzymes were previously used to catalyze the preparation of optically active polyesters [37–39]. In
THF, low molecular weight oligomers were obtained, while in acetonitrile, the average molecular weights of the unsaturated all-trans polyesters were comparable with the values obtained for industrially prepared products [40]. The presence of the trans double bond facilitates cross-linking and has an important influence on the rheological and mechanical properties of the UP and the cured end product. All-trans [41] enzymatically and chemically synthesized UPs are crystalline compared to the commercial amorphous UP. Thermal analysis of the samples of all-trans enzymatically and chemically prepared UP gave the same endotherms. The tensile strengths of enzymatically prepared polyesters were similar to those for the industrial product.

UV-curable, waterborne unsaturated polyesters prepared using 60/40 (mol%) trimellitic anhydride, tetrahydrophthalic anhydride, and the equimolar mixture of ethylene glycol, DEG, and PG showed balanced coating properties such as good tensile strength and weatherability, as well as proper viscosity [42]. Unsaturated polyesters have also been prepared using 1,4-bis(2-carboxyvinyl)benzene acid chloride and bisphenols or 4-hydroxycinnamic acid [43].

Preparation of fluorine-containing UP resin has been achieved using telechelic macromers based on hydroxy-terminated perfluoro polyethers with different molecular weights [44].

Poly(ethylene glycol) (PEG) or liquid hydroxyl- or carboxyl-terminated rubbers have also been copolymerized with UP resin. PEGs with the number-average molecular weight $M_n$ ranging from 600 to 1000 g/mol have been used [45–52]. Reaction of carboxyl-terminated UP with various PEG monomethyl ethers of molecular weights from 350 to 2000 g/mol was carried out at a high temperature (230°C) for several hours according to the following reaction sequence [53]:

The block copolymer thus prepared had predominantly one PEG end group per polyester segment.

Introduction of PEG end groups leads to phase-separated and partly crystalline block copolymer. The $T_g$ of the resins decreased with increasing length of the PEG end group. The solubility of styrene increased at room temperature. Processable resins with about 20 wt% styrene content could be prepared.

Rheological changes during thickening and molding have been achieved [54] using a modified UP resin and introducing a thermally breakable diketo group onto the UP resin by salt formation according to the following scheme:
These groups are stable at room temperature, but can be broken at elevated temperatures. These modified resins showed a fast viscosity increase during thickening and a stable viscosity during room temperature storage.

Synthesis of a variety of novel para-linked aromatic liquid crystalline polyesters containing unsaturated fumaroyl units has been reported recently [55–58]. These polyesters were prepared by reaction of fumaroyl chloride with t-butyl, phenyl, and phenyl ethyl hydroquinones using both interfacial and melt polycondensation techniques [57].
The melt polycondensation of hydroquinone derivative and fumaroyl chloride was carried out at 145°C–175°C for several hours. The \( t \)-butyl–and phenyl ethyl–substituted polyesters were thermotropic nematic liquid crystals above their \( T_g \), while the phenyl-substituted polyester showed a nematic texture above the melting point. The \( t \)-butyl–substituted polyester formed a lyotropic phase in styrene above 50wt% polyester, which could be processed into a film and cross-linked with benzoyl peroxide. Investigation on thermotropic block copolyesters containing aliphatic unsaturated units have also been carried out. Polymers with a rigid block content of 75% or above exhibited nematic phases after melting [59].

Specific properties of UP resins can be tailored using special additives. Low flammability of UP resins or systems have been developed by adding aluminum hydroxide [60, 61] and organic compounds containing halogen or phosphorus [62, 63]. In UP systems containing styrene, the evaporation of styrene can be reduced by addition of pyrogenic silicic acid with hydrophilic and hydrophobic end groups [64] or substituted succinic acid [65].

To eliminate the inhibiting effect of atmospheric oxygen on curing of UP resin coatings and to obtain a tack-free surface, paraffin wax is generally added. A relatively small amount of paraffin wax (0.1% in hard paraffin wax and approximately 1% in the case of stearin) is sufficient for this purpose. The wax or stearin is initially soluble in UP resin coating, but as the curing advances, its solubility is reduced. It thus forms an impermeable surface layer that is a barrier to atmospheric oxygen and for evaporation of styrene from the resin formulation. LPAs (for reducing thermal shrinkage) and thickening agents are described separately below.

6. CHARACTERIZATION OF UNSATURATED POLYESTER RESINS

The UPE resins are comprised of molecules of different molecular weights, chemical compositions, and degrees of branching. A thorough characterization of resin is essential for the quality control of resin manufacture and structure-property correlation in polyester. Molecular characterization of resin has often been carried out by hydroxyl and acid number determination. However, these techniques are not capable of distinguishing differences between samples.

The unsaturated polyester resins have been characterized by gel permeation chromatography (GPC) [66–68] and high-performance liquid chromatography (HPLC) [69, 70]. Number-average molecular weights, determined by GPC with polystyrene (PS) calibration, were found to be in good agreement with values obtained by vapor phase osmometry (VPO) and end-group analysis. GPC with UV detection at a pair of suitable wavelengths can determine the mole ratio of unsaturated acid and saturated acid as a function of molecular weight. Conventional GPC with PS calibration provides good molecular characterization of UP resins with a slight tendency to overestimate \( M_n \) and, in the case of samples containing high molecular weight fractions, to underestimate \( M_w \) values. Studies on compositional sequence distribution in UP resins have been carried out by \( ^{13} \)C-NMR spectroscopy [71].

7. LOW-PROFILE ADDITIVES

There are several processing problems associated with neat UP resins. Some of these are surface-quality flaws such as sink-mark formation, part-surface waviness, dimensional control problems such as warpage, and inability to reproduce the mold accurately.
These problems are due to UP resin/styrene polymerization and thermal shrinkage. Polymerization shrinkage during cure has been measured by dilatometer [72, 73]. The amount of shrinkage is reduced by addition of fillers or fibrous reinforcements, but is not eliminated. Inclusion of 2–5% (by weight of the molding compound) low-profile thermoplastic additive (LPA) in the resin formulation [74] helps compensate for the polymerization shrinkage. The weight percentage of LPA on the basis of organic resin alone is 7–20%. The function of LPA is to compensate for the thermal and polymerization shrinkage of the UP resin at minimum cost. The LPA does not participate in the free-radical polymerization; however, it is known to have an effect on compound viscosity and thickening. Low-shrink and low-profile unsaturated polyester resins are commonly used in several reactive processing manufacturing techniques, such as compression molding of sheet molding compound (SMC) and bulk molding compound (BMC), thick molding compound (TMC), resin transfer molding (RTM), pultrusion, hand lay-up, and resin casting processes [75]. The performance of LPA is affected by the processing conditions, which in turn depend on the process used. For example, RTM is generally a low-pressure (<100 psi), low-temperature (<100°C) process, whereas SMC is a high-temperature (150°C mold temperature), high-pressure (500–1000 psi) process.

Several thermoplastics, such as polyethylene (PE) [76, 77], PS [76–78], poly(vinyl acetate) (PVAc) [73], poly(methyl methacrylate) (PMMA) [76, 78–80], thermoplastic polyurethanes (PUs) [81], styrene-butadiene block copolymer, and polycaprolactone diol, have been used as LPAs.

Among these, PVAc-, PMMA-, and PU-based LPAs are most widely used. For cured samples, the fractional volume shrinkage generally decreases linearly with increasing LPA concentration. The volume shrinkage control is reported to be best with PVAc, followed by PMMA and PS [74].

There are several controversial views regarding the effects of concentration of LPAs on polymerization shrinkage. For example, polymerization shrinkage has been reported to decrease [82], increase [83], or be independent of increase in PVAc concentration [84]. It is reported to increase with PU molecular weight or decrease with PVAc molecular weight. At an LPA content less than 10 wt%, the effectiveness of volume shrinkage control was observed as PU > PVAc > PMMA > PS. However, when the LPA content exceeded 10 wt%, PU was less effective in volume shrinkage control than PVAc or PMMA. For a neat UPE resin having a 2:1 molar ratio of styrene to polyester –C=O– bonds, the fractional volume shrinkage is around 7.2–7.4%. Adding 10 wt% of PVAc or PMMA reduced it to 2.8–4.0%. The extrapolated LPA concentration to give zero volume shrinkage is estimated to be around 15 wt%.

### 7.1. Mechanism of Action

The curing of thermosetting polyester leads to volume shrinkage, which is compensated by expansion of the thermoplastic phase and development of a void structure within this phase.

The action [72, 85, 86, 87] of LPAs is believed to involve the formation of a two-phase structure between LPA and UP resins. Polyester/styrene resin solutions containing PU or PVAc as the LPA are initially miscible. During curing, these thermoplastics become incompatible with the polyester/styrene copolymer due to a significant change in its polarity and phase separation. Phase separation occurs at the very beginning of the reaction [88–91].
At low concentrations of PVAc, the final morphology is composed of discrete particles of LPA dispersed in the cured UP matrix; at a concentration higher than a critical value, a co-continuous structure is obtained. An easy way to determine this critical concentration is by the transition from translucent to cured opaque products. When the reaction starts, the initiator decomposes to form free radicals, initiating polymerization, which links adjacent UP chains through connecting styrene monomers by both inter- and intramolecular reactions. Unreacted styrene and UP resin also collect in the thermoplastic phase. As the polymerization continues, the temperature and degree of polymerization increases, causing a shrinkage of the UP phase. Polymerization shrinkage in the UP phase causes a large stress in the LPA phase, leading to formation of microvoids in the LPA phase. The polymer coils become tightened to form the so-called microgel structure [92–95]. As the polymerization proceeds, the concentration of the microgel increases continuously, leading to macrogelation. Due to the increase in temperature, the volumes of LPA and unreacted monomer inside it increase, thereby compensating for polymerization shrinkage. During the cooling process, the bulk coefficient of thermal expansion of LPA and the UP phase are similar above $T_g$, but below $T_g$, UP shrinks much less than LPA, creating more voids in the LPA phase. The subsequent microvoid formation at the interphase between the LPA and the cross-linked UP phases, as well as inside the LPA phase due to the microstress cracking, leads to the volume shrinkage compensation [96]. The polyester microgel structure formation and curing behavior are strongly affected by the compatibility of LPA and UP resin. PVAc has better compatibility with the UP resins than PMMA does. For UP resins mixed with LPAs, the thermoplastic LPAs may be considered as diluents. Increase of the diluent concentration favors the intramolecular cross-linking reaction of UP with styrene monomer and microgel formation. Methyl methacrylate (MMA), contrary to PVAc, is not miscible with UP/styrene resin, but forms a relatively stable dispersion after thorough mixing. PMMA, along with styrene and some UP, is dispersed as a 50–100 µm liquid globule in the continuous styrene/UP phase. During the curing process, the continuous phase cross-links to form a network. Curing also takes place in the liquid globules, resulting in the precipitation of fine particles coated with PMMA. Further heating and subsequent cooling lead to formation of voids.

### 7.2. Selection Criteria

The factors considered in selecting an LPA are (1) molecular weight [97], (2) dipole moment, and (3) glass transition temperature $T_g$. The molecular weight of LPA is important. The shrinkage decreases significantly with increase in molecular weight of LPA until an optimum value is reached. Further increase in molecular weight does not affect the shrinkage. In the case of PVAc, the useful range is 10,000–250,000, preferably between 25,000 and 175,000. Introduction of a few carboxylic groups in LPA helps in the maturation of SMC. Copolymerization of vinyl acetate or MMA with acrylic acid, methacrylic acid, or maleic acid yields copolymers with a controlled concentration of acid groups.

The polarities of uncured and cured UP resin are significantly different. The dipole moment of uncured UP resin is estimated to be 2.0–2.5, while for cured resin, a 0.2–0.8. LPA with a large dipole moment would be very compatible with the highly polar unreacted resin; however, on cure, the LPA becomes increasingly incompatible with the resin due to the large difference in polarity. Hence, the difference in dipole moment would act
as a driving force for phase separation. The glass transition temperature of LPA, if lower than the curing temperature, will be advantageous because the expansion would be increased in the rubbery state.

8. THICKENING AGENTS

The carboxylic acid end groups in unsaturated polyester resins are able to react with oxides and/or hydroxides of group II-A metals, such as MgO and Mg(OH)₂, which quite often will result in at least a 1000-fold increase in viscosity (up to >106 cp or 103 Pas) in 2–3 days. Such a maturation or thickening process of UP resins is an essential step that precedes curing in the processing of SMC, for which the rate of thickening and the resulting viscosity determine the moldability of the compound [77, 98].

The mechanism of the maturation process using MgO has been the subject of extensive investigation [80, 99–101]. Several theories have been proposed to account for this phenomenon. Some of these are as follows:

The dicarboxylic acid end groups of UP chain react with MgO, generating very high molecular weight species, thereby resulting in a large increase in viscosity and chain entanglement.

Reaction of MgO and one polyester carboxylic end groups. The basic magnesium salt then complexes with carbonyl or the −OH group of UP resin.

The reaction of basic salt of magnesium with the extra carboxylic acid end group, followed by aggregation of magnesium ions.
9. CURING OF UNSATURATED POLYESTER RESINS

The curing reaction [93] of UP is a free-radical chain growth cross-linking polymerization between the reactive diluent (e.g., styrene monomer) and UP resin. Polyester molecules are the cross-linkers, while styrene serves as an agent to link the adjacent polyester molecules. Depending on the temperature and other processing conditions, some of the species remain unreacted after curing in the form of residual monomer and soluble polymer that do not contribute to the network structure.

A wide range of peroxides and azo and azine compounds can be used as initiators, depending on the curing temperature. For room temperature curing, as in the case of large hand lay-up structures, methyl ethyl ketone peroxide (MEKP) is used; for moderate temperature (~60°C–90°C) curing, benzoyl peroxide is used. For hot press or oven curing (~130°C–150°C) di-i-butyl peroxide or i-butyl perbenzoate is used. A mixture of initiators is used when a large temperature increase is expected.

To accelerate the decomposition of peroxides, some metal compounds, tertiary amines, and mercaptans can be used. Cobalt naphthenate (CoNp) and cobalt octanoate (CoOc) are the most widely used accelerators.

\[
ROOH + Co^{2+} \rightarrow RO^+ + OH^- + Co^{3+}
\]
\[
ROOH + Co^{3+} \rightarrow ROO^- + H^+ + Co^{2+}
\]

CoNp is used at about 0.01%. The excess of it causes too much acceleration, resulting in darkening color and bubble formation in the cured products. Cure characteristics of UP resins are affected by the use of cobalt promoter [102]. A three-dimensional network is formed as a result of copolymerization between the unsaturated monomer present in the resin (e.g., styrene) and the maleate and fumarate double bonds of the polyester. Microgels are formed as a result of this copolymerization even at very low percentage conversion (~3–4%). The initial studies on copolymerization of UP resin with styrene revealed an early onset of gelation and a decrease of final conversion, which was attributed to segmental immobility in a cross-linked network [103]. Differences between theoretical and experimental reactions of UP resin with different styrene/polyester ratios have been reported [104].

The occurrence of cyclization and the formation of compact microgel-like particles at the very beginning of polymerization have been suggested [102, 105]. The network structure depended on the concentration and type of polyester resin. It was observed that gel conversions of UP resins were much higher than those predicted by the classical Flory-Stockmeyer theory [106]. This delay in cross-linking has been explained on the basis of competition between intermolecular (network formation) and intramolecular (cyclization) cross-linking reactions. Hild and Okasha [107], on the other hand, explained the delay in gelation as due to reduction of reactivity of polyester vinyl groups with the progress of the reaction, while Minnema and Staverman [108] attributed it to the shielding of pendant vinyl groups.

The curing process of UP resins can be divided into four stages: induction, microgel formation, transition, and macrogelation [109]. In the induction period, the free radicals are consumed by the inhibitor, and very little polymerization takes place. In the second stage, spherical structures (microgel particles) with high cyclization and cross-
link density are formed. In the transition stage, the (C=\text{C}) double bonds buried inside the microgel undergo intramolecular cross-linking, while those on the surface react with monomers or microgels. This results in growth of microgel. Finally, macrogelation takes place by intermolecular microgels and microgel clusters. This stage is accompanied by a sharp increase in viscosity.

Thus, the curing reaction of the UP-styrene system can be described in four steps:

1. Intermolecular cross-linking with or without linking through styrene monomers.
2. Intramolecular cross-linking with or without linking through styrene monomer.
3. Chain branching on the polyester molecule by styrene.

Although all reactions affect the curing kinetics, only the first two contribute to the network formation. The intramolecular cross-linking reaction resulted in the retardation of gelation by reducing the polyester coil sizes. The shrinkage of polyester coils due to the intramolecular cross-linking reaction was observed by GPC [110].

The cross-linking reaction proceeds as inter- or intramicrogel reaction [111–115]. The formation of microgels affects not only the cure behavior, but also the rheological changes. Mazumdar and Lee studied the chemorheological changes using rheometry, electron spin resonance (ESR) spectroscopy, and dynamic light scattering goniometry and suggested a mathematical model to explain the shear effect on resin viscosity changes [116].

Studies on the morphology of UP and VE resins revealed a two-phase structure consisting of microgels in the PS phase. The two-phase structure of VE matrices, unlike that of UP resins, was organized rather than random structured. This may be the contributing factor to the excellent hydrolytic stability of VE resins [117].

Various methods employed to study the curing behavior of UP resins are differential scanning calorimetry (DSC) [118], infrared spectroscopy (IR) [119], gel time studies, dynamic mechanical thermal analysis (DMTA) [120], and electron spin resonance spectroscopy [121]. The effects of temperature and the concentration of initiator, promoter, reactive diluent, additives, and thickening agents on the curing kinetics of UP resins were studied by the above techniques over the whole conversion range. The cure characteristics of thermosetting resins such as VE resin are also affected by the presence of reinforcements due to surface-resin interaction [122].

### 9.1. Differential Scanning Calorimetry

The curing of thermoset is a complex process in that several steps and different reaction processes are involved. As a result of the overall process, heat accompanying the curing is liberated. Assuming that the cure reaction is the only thermal event, the reaction advancement is directly proportional to the rate of heat generation, and the ultimate extent of conversion is proportional to the total heat that the system is capable of liberating, which can be measured by the DSC technique.

To determine the heat evolved in the total conversion of all reactive groups, one has to associate an exothermic heat per mole of both the polyester >C=\text{C}< double bonds reacted and the reactive diluent (vinyl monomer) >C=\text{C}< double bonds reacted, providing that these two reactive groups are the only ones that contribute to the overall exothermic effect.
The peroxide-initiated copolymerization of UP resin with solid monomers such as zinc acrylate was followed by gelation curves and DSC [123]. The effect of various parameters, such as curing temperature, initiator concentration, promoter concentration, additives [124], and thickening agents [125, 126] has been studied by DSC techniques.

The curing of UP resin and VE resin depends on concentration, as well as the nature of reactive diluents. Styrene is still the main reactive diluent in these formulations. Apart from styrene, other unsaturated compounds, such as vinyl toluene, α-methyl styrene, diallyl phthalate, methacrylates, acrylonitrile (AN), and triallyl cyanurates, have also been used. Partial replacement of styrene by AN reduces the resin cure [127]. The DSC scans of VE resins having 4% benzoyl peroxide and containing 50% MMA (sample a) are shown in Fig. 1. A sharp exotherm was observed in the temperature range 100°C–155°C. The exotherm peak position was at 125°C. Partial replacement of MMA by vary-

**FIG. 1.** Differential scanning calorimetry scans of vinyl ester (VE) resins (recorded in static air at 10°C/min) having 4% benzoyl peroxide and 50% methyl methacrylate (MMA)/glycidyl methacrylate (GMA) as the reactive diluent: (a) VE + 50% MMA; (b) VE + 50% GMA; (c) VE + 20% GMA + 30% MMA; (d) VE + 40% GMA + 10% MMA.
ing amounts of glycidyl methacrylate (30% wt/wt) decreased the characteristic curing temperatures of VE resin.

Isothermal DSC scans recorded for a particular composition at various temperatures showed that the reaction occurs at a fast rate as the temperature increases. The induction time and the time of maximum rate are shorter with increasing temperature. The ultimate overall conversion increases with temperature. In the beginning of the curing process, a nearly azotropoic copolymerization mechanism dominates. At these initial stages, the cross-link density of the reaction system is not sufficiently high to influence appreciably the propagation mechanism of the styrene and polyester vinylene groups. As the reaction proceeds, the cross-link density increases to some extent so that the mobility of vinylene units in the large polyester molecules declines remarkably, while that of small styrene monomers is less affected. Consequently, the relative probability of the styrene propagation reaction is elevated, causing a higher conversion of styrene than of polyester vinylene.

Macrogel formation is the main feature in the curing of UP resins. At low temperatures, at which the cross-linking reactions are quite moderate, prior to the peak of the DSC rate profile, the intermicrogel cross-linking reaction is dominant over the intramicrogel cross-linking reaction. In the later stage of the reaction following the peak of the DSC rate profile, intramicrogel reactions are more favorable than intermicrogel ones [128]. The intermicrogel reaction enhances polyester vinylene conversion more than styrene conversion since styrene tends to copolymerize with polyester vinylene with a smaller cross-link length of styrene. In contrast, the intramicrogel reaction is more favorable with styrene conversion due to the extensive branching growth of styrene on polyester >C=C< bonds inside the microgels with a larger cross-link length of styrene.

The kinetics of the cure of UP and VE resins obeys the autocatalytic rate equation

\[
d\alpha/dt = (k_1 + k_2\alpha)^m(1 - \alpha)^n
\]

where \(\alpha\) is extent of conversion, \(k_1\) and \(k_2\) are kinetic rate constants, and the overall reaction order \(m + n\) is generally considered equal to 2. Two model elementary rate equations for radical and monomer have been proposed to describe the free-radical polymerization of UP resin [129]. The activation energy of the curing reaction has been determined using this expression and was found to be around 46 kJ/mol [130] for UP resins and 80 kJ/mol for VE resins [131]. The heat of polymerization of the double bonds in the polyester heavily depends on the type of prepolymer and have been reported in the range 54–104 kJ/mol [132, 133].

The mechanism and the kinetics of the cross-linking of UP resin are strongly affected by the presence of bismaleimide resins as coreactive monomers. Martuscelli and others studied the structure of such an intercross-linked network; during the curing of VE resins with styrene as a diluent, it was observed that polymerization was random initially, but as the resin advancement took place, styrene homopolymerization tended to dominate [134, 135]. Styrene monomer was found to react at a slower rate, yet it reached a greater extent of conversion than VE resin [136]. The properties of cured resin depend on the initiator system [137].

9.2. Effect of Additives on Curing Exotherm

9.2.1. Low-Profile Additives

The three major reactions (styrene–polyester vinylene, styrene-styrene, and polyester vinylene–polyester vinylene) in low-shrinkage resins are the same as those in pure styrene-UP copolymerization. The structure formation, however, can be different.
Addition of the LPAs such as polycaprolactone diol (isocyanate terminated) on curing kinetics revealed a decrease in exotherm [138]. The final degree of conversion was also lower for resins containing LPAs. The curing reaction rate decreased with an increase in LPA concentration [139]. The compatibility of LPA with UP resin had a strong influence on the polyester microgel formation and the curing behavior. The curing reaction of UP resins with the addition of LPAs is an inhomogeneous free-radical chain growth cross-linking copolymerization. When the ratio of styrene to UP unsaturation was kept constant, PVAc did not have any effect on cure kinetics, maximum conversion, or \( T_g \). In the cure of UP resin, the overall reaction rate is a summation of the intramicrogel cross-linking reaction rate and intermicrogel cross-linking reaction rate. The diffusion barrier effect of LPA may reduce the later reaction (intermicrogel cross-linking). Increase of the LPA concentration facilitates the UP resins to form coils in the styrene monomer and to undergo an intramolecular reaction, which may cause a delay of gelation. Microgel formation is enhanced by such intramolecular reactions, which become more compact. Many pendant polyester vinyl groups may be trapped in the compact microgels thus formed. The radical concentration profiles obtained from isothermal and scanning ESR experiments for uncured UP resin with and without PVAc were very different, indicating a difference in reaction mechanism.

9.2.2. Thickening Agents

Curing of UP resin during thickening has been investigated using DSC and viscometry [125]. Thickening of UP resin with group II-A elements leads to formation of microdomains of aggregates for polyester chain segments through linking and coordination of MgO. In these microdomains, the molar ratios of styrene to PE would be lower than in the original resin. This would lead to a reduction in reactivity of styrene and polyester C=C bonds. It is generally observed that [140] in the cure of thickened UP resins, the heat of reaction decreases when compared with nonthickened ones. During the initial period of thickening, induction time and the time to reach the maximum rate increased as the degree of thickening increased, while the trend was reversed in the later period of thickening. The final C=C conversion was reduced when compared with those for the neat UP resin. Conversion with styrene was higher than that of polyester C=C bonds. The curing reaction of UP resin thickened with isocyanate-terminated polyester has been explained on the basis of microgel formation [141].

9.3. Infrared Studies

Reaction conversion can be determined by an IR technique from the consumption of styrene >C=C< bonds at 912 and 992 cm\(^{-1}\) (C–H out-of-plane bending in \( \text{CH}_2=\text{CHR} \)) and the consumption of polyester >C=C< bonds at 982 cm\(^{-1}\) (C–H out-of-plane bending in trans \( \text{CHR}=\text{CHR} \)) characteristics of styrene and polyester, respectively. During the reaction, the styrene consumption can be determined easily from the peak area change at 912 cm\(^{-1}\), but the consumption of polyester >C=C< bonds cannot be followed directly from the peaks at 982 and 992 cm\(^{-1}\) because they overlap each other. A subtraction method has been used to separate the overlapping peaks [142, 143]. Final conversion of methacrylate end groups of VE resin diluted with styrene has been evaluated by Fourier transform infrared (FTIR) spectroscopy [144]. The polyester/styrene cross-linking reactions at 26°C were studied by Urban et al. [145]. Their study indicated that, during the cross-linking reaction, styrene polymerized, forming atactic polystyrene segments that
were an integral part of the polyester/styrene network. Dell Erba et al. [146] investigated the conversion profiles of both the styrene and polyester unsaturations in the temperature range 336–363 K using FTIR spectroscopy. The effects of comonomer compositions on the curing kinetics of UP resins using DSC and IR have been reported by Huang and Chen [112, 113].

9.4. Dynamic Mechanical Thermal Analysis

Small curing changes can be monitored easily by dynamic measurements [147]. For the sample cured at room temperature [148], two apparent glass transition regions (at 65°C and 115°C) were exhibited in the DMTA trace, but only one transition was observed for the “fully” cured sample. This anomalous behavior was explained in terms of the influence of the additional cure that occurred during the DMTA experiment. As the sample is heated, it enters the glass transition region. As the temperature is increased further, the thermal energy provides sufficient molecular mobility to recommence the curing process, causing a shift in the transition region and an increase in the modulus. Similar behavior has been reported in polyesters based on bisphenol-A and has been attributed to additional cure during the DMTA experiment.

The dynamic mechanical behavior of UP resins showed three relaxations: α, β, and γ in order of appearance with decreasing temperatures. According to Tanaka [149] and Cook and Delatycki [150–152], the α-transition occurs due to the activation of relatively long-range motions involved in glass transition phenomenon. The β-transition is mainly due to activation of motions in the polyester main chain or may be due to the relaxation of styrene-based bridging units, while the γ-transition may be related to some motion of the phenyl groups in the styrene sequences [153–155]. Dynamic mechanical spectroscopy combined with solid-state $^{13}$C-NMR has been used to characterize the molecular motion responsible for the gamma and beta secondary relaxations in UPE networks. In DEG networks, the gamma transition is assigned to restricted phenyl group rotation in the styrene cross-links, whereas the motion of molecular groups in the vicinity of the residual maleic double bonds account for the β-transition [156].

10. MECHANICAL PROPERTIES

The rigidity of the prepolymer, the type and concentration of reactive diluent (vinyl monomer), and the cross-link density are the major contributing factors to the mechanical strength of the cured UP and VE resins [157–161]. An increase in cross-link density results in an increase in modulus, glass transition temperature, and decrease in strain to failure and impact energy. Cross-linking in UP resin is due to unsaturation provided by maleate/fumarate linkage in the backbone. The higher the concentration of these units, the higher is the cross-link density. The microstructure of the cured UP resin is heterogeneous, consisting of highly cross-linked domains surrounded by less cross-linked areas [162–166]. The heterogeneity of the microstructure is influenced by the concentration of the catalyst (MEKP [167]), accelerator (cobalt octoate), and temperature of curing and postcuring [168], which in turn affect the $T_c$ of resins. The effect of chemical composition and structure of UP resins on the miscibility, cured sample morphology, and mechanical properties of styrene/UP/LPA ternary systems has been reported recently [169].
The amount and type of reactive diluent also influence processing characteristics of UP resins and the properties of the cured resin. Styrene is the most commonly used vinyl monomer in polyester resins. This is due to its low cost, high compatibility, and reactivity with the 1,2-disubstituted double bond of polyesters. The reactivity ratio of styrene and maleic/fumaric acid esters is about 0, indicating that this system has a tendency to form copolymers in which the sequence of the monomer unit alternates. Styrene imparts good mechanical properties and heat distortion resistance to cured resins. The styrene content in these resin formulations ranges from 30% to 60%. An increase in styrene content reduces the cross-link density, which leads to a reduction in tensile and flexural strength and modulus. Most general-purpose resins contain between 30% and 35% styrene. An excessive amount of styrene increases the curing time and imparts styrenelike properties to the cured UP resins. Isophthalate resins ($M_n$ ranging from 484 to 1712 g/mol) based on equimolar quantities of MA, isophthalic acid, PG, and DEG exhibited $T_g$ from 251 to 267 K. By using styrene as the diluent (molar ratio of $C=C$ double bond in styrene and UP resin of 2–5) resins with different $T_g$ could be prepared. A relatively high fraction of styrene gave a cured product with reasonably high $T_g$ values (approaching pure PS) and low moisture absorption [170]. Small quantities of $\alpha$-methyl styrene added to UP and VE resin acts as an exotherm peak depressant and increases curing time [171–173]. Addition of vinyl toluene increases the cross-linking. It is also of high reactivity and is less volatile than styrene. Partial substitution of styrene by acrylates such as MMA or methyl acrylate improves weather resistance and adhesion to glass fibers.

The mechanical properties of UP resins can be improved by the addition of styrene and AN. AN copolymerizes readily with styrene and gives products with better mechanical properties. The hardness of the samples increases as small amounts of AN are added and reaches a maximum point. Maximum increase in hardness is achieved at 40% styrene and 12% AN for PG-based products. Maximum increase in impact strength (IS) occurs at 40% styrene and 20% AN for PG-based products. DEG-based products have a very soft texture without AN. Their hardness increases at 40% AN composition. AN increases the solubility of the resin in styrene and hence prevents phase separation, which leads to improved mechanical properties [174]. Resins with better heat resistance are produced using trialkyl cyanurate, which is less volatile. However, it is less reactive than styrene. Diallyl isophthalate compositions, although more expensive, have better heat resistance and can withstand temperatures up to 220°C.

The rigidity of the polyester backbone also affects the mechanical properties. Substitution of tetrabromo or tetrachloro phthalate units in UP resins increases the molecular rigidity, which leads to an improvement of tensile strength and modulus [175, 176]. Young’s modulus and compressive strength are influenced by the molecular weight of the glycol [177]. The isophthalic resin showed higher tensile and flexural properties than the ortho resins. Terephthalic acid provides a higher heat deflection temperature than isophthalic acid. Cured BPA fumarate and chlorendics show brittle behavior with low elongation at break.

VE resins combine the excellent thermal and mechanical properties of epoxy resins with the ease of processing and rapid curing of polyester resins. Epoxide backbones of different molecular weights produce greater toughness and resiliency, solvent resistance, and heat resistance. The mechanical properties of various UP resins are given in Table 1.

UP resins are limited by their brittleness, especially when good impact behavior is required. This problem can be overcome by blending it with liquid rubber [178–180],

---

**UNSATURATED POLYESTER RESINS**

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TABLE 1
Mechanical Properties of Cured Unsaturated Polyester Resins

<table>
<thead>
<tr>
<th>Property</th>
<th>Ortho resin</th>
<th>Iso resin</th>
<th>BPA fumarate</th>
<th>Chlorendic</th>
<th>VE resin bisphenol-A–based resin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength, MPa</td>
<td>55</td>
<td>75</td>
<td>40</td>
<td>20</td>
<td>80</td>
</tr>
<tr>
<td>Tensile modulus, GPa</td>
<td>3.45</td>
<td>3.38</td>
<td>2.83</td>
<td>3.38</td>
<td>3.5–3.9</td>
</tr>
<tr>
<td>Elongation, %</td>
<td>2.1</td>
<td>3.3</td>
<td>1.4</td>
<td>—</td>
<td>4.0</td>
</tr>
<tr>
<td>Flexural strength, MPa</td>
<td>80</td>
<td>130</td>
<td>110</td>
<td>120</td>
<td>140</td>
</tr>
<tr>
<td>Flexural modulus, GPa</td>
<td>3.45</td>
<td>3.59</td>
<td>3.38</td>
<td>3.93</td>
<td>3.7</td>
</tr>
<tr>
<td>Heat distortion temperature, °C</td>
<td>80</td>
<td>90</td>
<td>130</td>
<td>140</td>
<td>100</td>
</tr>
</tbody>
</table>

which leads to the toughening of UP resins. This method has only limited success because of poor solubility of the rubbery component in the unreacted resin, as well as the poor chemical reactivity of rubber toward the polyester functionalities. The NH₂ [181] end groups of a butadiene-AN copolymer show enhanced reactivity toward an unsaturated polyester matrix. Chemical modifications of rubbers [182] have been done to increase their reactivity with UP end groups. For example, hydroxy-terminated polybutadiene was converted to isocyanate-terminated rubber, which could react with hydroxy groups of UP resin or an amino-terminated butadiene-acrylonitrile (ATBN) rubber was converted to maleimido end-capped rubber (ITBN) capable of reacting with ester double bonds of UP resins. The reaction between ATBN and MA proceeds via two steps: (1) the formation of a maleamic acid intermediate and (2) cyclization via dehydrating agents.

Both the modulus and the yield stress decreased on addition of ATBN or ITBN, but this effect was less pronounced for the UP/ITBN blend. A substantial increase of toughness was obtained in the UP/ITBN blend. This may be due to the chemical interaction among the components during the curing process, which leads to improved adhesion among the phases.

Another example of toughening agent for UP resins is a polyisobutene rubber modified by grafting succinic anhydride onto its end groups. Toughness increased to a large extent when polyisobutylene–succinic anhydride was used as a modifier. The best results were achieved with the highest grafting degree of the rubber. Liquid polybutadiene and its copolymers with AN are immiscible with commonly used VE resins. Modification of low molecular weight hydroxy-terminated polybutadiene through reaction with diisocyanate and alcohols rendered the polymer more compatible and yielded a tougher cured product [183]. Nylon 6,6 oligomers, obtained from industrial wastes, have been used to modify UP resins to prepare semi-interpenetrating polymer networks [184].

The increasing use of UP matrix composites exposes them to a variety of hygrothermal conditions that can affect the (1) thermomechanical properties of a composite and the matrix and (2) the deformation and residual stresses that result from thermal and swelling strain in the laminate.
The absorption of moisture into a resin generally results in a reduction of the glass transition temperature $T_g$ and a reduction of the modulus and strength, coupled with an increase in strain to failure, a small increase in thermal expansion coefficient below $T_g$, and dilation (swelling). The effects of solvent exposure on the viscoelastic properties of resins (UP and VE resins) have been investigated by dynamic mechanical analysis. The chemical structure of the resin was found to be a determinant in the changes produced after solvent exposure.

11. APPLICATIONS

Unsaturated polyester resins either in the form of pure resin or in the compounded form with fillers find a wide range of applications. Their main applications are in the construction industry (nonreinforced or glass-fiber-reinforced products), automotive industry, and industrial wood and furniture finishing.

Some of the important products based on UP resins are cast items such as pearl buttons, knife and umbrella handles, and encapsulated electronic assemblies. Polyester compounds have been formulated for the manufacture of bathroom fixtures. Floor tiles have been manufactured by mixing UP resin with fillers such as limestone, silica, china clay, and more.

The applications of UP resins in a variety of areas such as transportation, electrical appliances, and building and construction are largely due to development of bulk and sheet molding compounds using glass fibers.

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