purified isophthalic acid

How Ingredients Influence Unsaturated Polyester Properties

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Fiber reinforced polyester composites have achieved remarkable commercial acceptance in a variety of applications. Polyesters based on isophthalic acid (the 1,3-isomer of phthalic acid) have high strength, toughness, outstanding corrosion resistance, and are easy to fabricate. This makes isopolyesters the preferred choice in gel coats, pipes and tanks, structural molding, and automotive appearance parts.

The remarkable versatility of fiber reinforced isopolyesters is largely derived from the almost unlimited possibility for easy modification of the basic polymer structure. Major variables include selection of glycols, the choice of unsaturated coreactant, proportions of these ingredients used, and processing.

As manufacturer and marketer of three basic chemicals for isopolyesters — isophthalic acid, maleic anhydride, and styrene monomer — BP has actively monitored trends and developments in the unsaturated polyester industry.

This brochure outlines the information BP has collected on the effect of ingredients on unsaturated polyester properties and performance. Most of the data is from work conducted by BP laboratories. Some information comes from the laboratories of affiliated companies as well as from recognized industry and academic sources. This compilation is intended as a guide to available information. BP welcomes dialogue with manufacturers and users of polyesters about issues that this work may engender.

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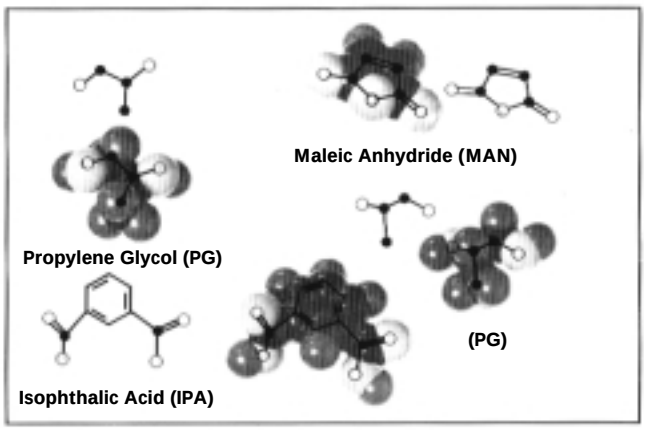


Illustration 1: Polyester reactants.

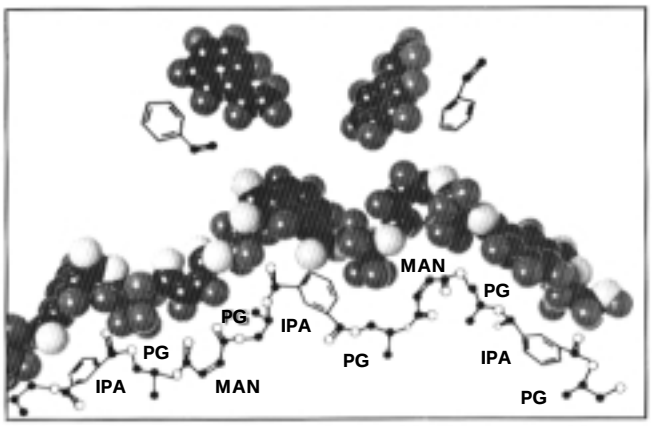


Illustration 2: Liquid polyester with styrene monomer.

The Chemistry of Unsaturated Polyesters

Unsaturated polyesters are the product of a condensation reaction between difunctional acids and alcohols, one of which (generally the acid) contributes olefinic unsaturation. This polymer is dissolved in styrene or other monomeric material containing vinyl unsaturation. With heat or chemically activated free radical initiation, the polyester and reactive diluent crosslink into a solid, non-melting network. Illustrations 1 through 3 show a simplified model of the basic materials required to form a thermoset polyester.

With this picture in mind, the methods of varying the polyester to tailor it to specific application requirements are readily apparent. The principal polyester variations effected by constituent changes are the frequency of crosslinking sites (crosslink density), the degree of steric protection afforded to vulnerable functional groups and the rotational freedom within the polymer chains.

Additional effects on properties are produced by polyester molecular size — a joint function of the ratio of ingredients and processing variables — and by coreactant selection and concentration.

Even this brief overview of polyesters indicates that several routes are usually available to achieve a particular property. A goal of this brochure is to suggest useful paths of investigation to resin formulators seeking cost effective resins to meet specific end use requirements. While the particular emphasis will be on the role of ingredients in polyesters based on isophthalic acid, many of the trends observed in our laboratory can be extrapolated to other types of unsaturated polyesters.

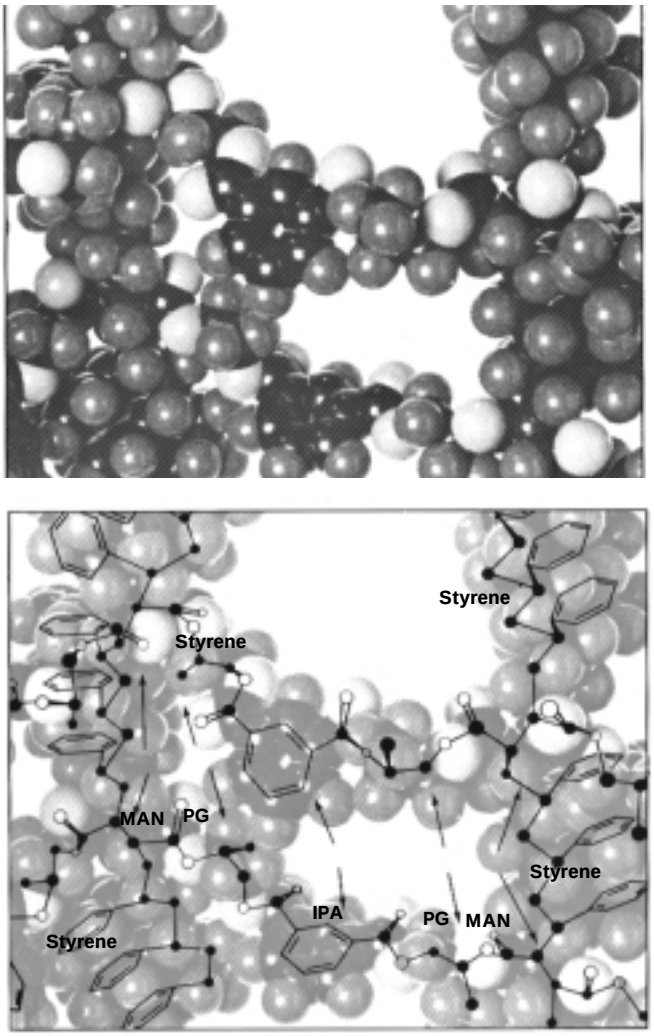


Illustration 3: Cured isopolyester.Oxygen is light gray, hydrogen is dark gray, and carbon is black. The ball and stick diagrams omit hydrogen; black circles represent carbon and open circles are oxygen.

Processing Affects Polyester Properties

The brief description of processing included here is intended only as a basis for the discussion of processing's influence on properties. A more complete review of BP's recommendations for unsaturated isopolyester processing is available in other publications.

Equipment for processing good quality unsaturated polyesters includes: a heated kettle with agitator, temperature measurement devices, reactant addition and sampling ports; an overhead system with efficient fractionating and total condensers; and an apparatus for safely diluting the polyester with monomer.

Good quality unsaturated polyesters are processed by a two stage reaction in which aromatic and saturated acids are reacted with all the glycol until at least one functional group of all the diacid has final properties as determined by test methods that reflect polymer size, such as acid number or viscosity.

Esterifying the slower reacting acids with a substantial glycol excess produces low molecular weight, hydroxyl terminated oligomers that react in the second stage to more evenly distribute unsaturated functionality throughout the polymer.

The esterification reaction is accelerated by efficiently removing the water of reaction (hence the need for an efficient partial condenser), higher than atmospheric pressure, and/or certain catalysts.

The polyester chain grows as acid and hydroxyl groups combine and release water. Unreacted acid and hydroxyl groups left in the reaction mixture can be monitored by conventional wet chemical techniques to indicate the course of the reaction.

Figure 1 illustrates the growth of polymer size and increase in viscosity as the available end groups are consumed. Because virtually all isopolyesters are formulated with a hydroxyl excess, acid number is commonly used to quickly indicate the remaining level of reactive material. Excessive residual carboxyl functionality contributes to viscosity drift and greater vulnerability to chemical attack in end use applications. Therefore, the preferred method for controlling polyester molecular weight is to adjust initial hydroxyl excess, rather than prematurely end the esterification reaction.

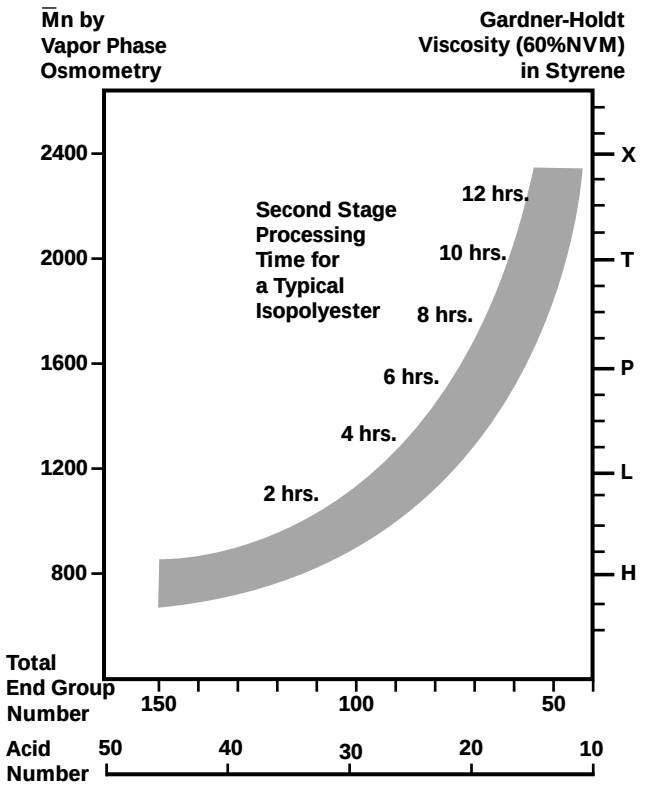
Evaluating the Unsaturated Polyester

A variety of tests are available for determining the identity and properties of polyester resins as solutions and as cured solids. Tests used in process quality control must give quick, accurate results, be convenient to perform, and be low in cost when performed frequently. Other tests are used to predict long term performance in actual use.

Tests of the wet or uncured resin and knowledge of the resin formulation and ingredients can tell the molecular weight, level of unsaturation, probable thickening rate and cure response. Conventional tests of uncured resin and their implication for the resin formulator and user are shown in Table 1.

The focus of this brochure is on unsaturated resins themselves, however, in most applications the resins are combined with fibrous reinforcement or fillers. The user of the final product is most concerned with the properties of the composite which are affected by both the resin and the reinforcement.

Figure 1: Molecular Weight Increases as End Groups Disappear During Esterification



Certain properties are dominated by reinforcement and the contribution of the cured resin is masked. Figure 2 illustrates the correlation of cured resin and composite tensile elongation for most of the resins studied by BP. Until the sample is elongated about 2.5 percent, the tensile elongation of the composite is influenced by the resin. Thereafter, it is determined by the stiffness of the reinforcement.

Other composite properties, such as flexural strength (stress perpendicular to the orientation of most of the reinforcement), are largely determined by the resin. Corrosion resistance is among the properties that relate to the interaction between reinforcement and resin and that is best determined by testing a laminate.

To most clearly focus on resin contribution to laminate performance and avoid the scatter of test results inevitable with composite testing, most properties discussed in this brochure are based on testing of clear or unreinforced castings of resins. Laminate testing is used only for corrosion resistance and flexural fatigue evaluations that are functions of resin/reinforcement interaction.

Figure 2: Reinforcement Masks Resin Tensile Elongation Properties

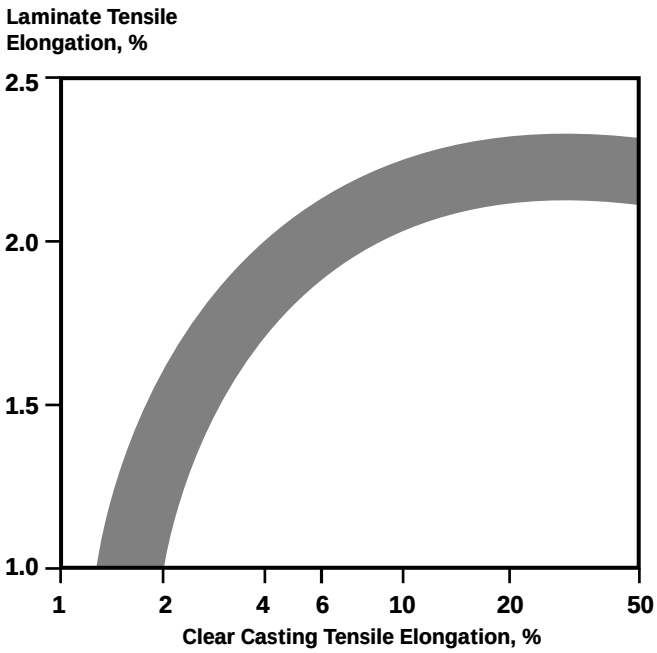


Table 1: Laboratory Test of Uncured Resin

Property	Test Method	Predictive Significance
Hydroxyl Number	ASTM E222	Corrosion resistance and thickening rate, indirectly indicates molecular weight.
Acid Number	ASTM D1639	Same as hydroxyl number.
Gel	SPI Test	Reactivity and demolding time.
Molecular Weight	Vapor Phase Osmometry	Number average MW, used to calibrate gel permeation chromatography.
Molecular Weight	Gel Permeation Chromatography	Number and weight average MW as well as distribution.
Composition	Infra-Red Spectroscopy	Can be run on styrenated resin and cured resin, qualitative test.
Composition	NMR Spectroscopy	Sample must be dry and monomer-free both qualitative and quantitative.
Non-Volatile material	SPI Test	Monomer content. With viscosity it indicates molecular weight.
Viscosity	ASTM D1824, D2196, SPI Test	Handling and thixotropic properties. Also indicates molecular weight.

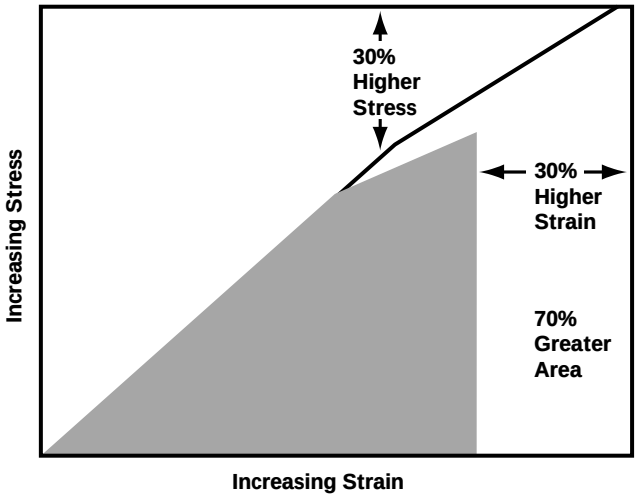
Resin Properties are Intertwined

Change in one property usually causes a change in some other property. The properties most desired by the end user are frequently inferred from several measurable variables.

For example, toughness, a most desirable property, is often defined as the area under the tensile stress/strain curve. Figure 3 depicts a hypothetical charting of destructive tensile stress of a clear resin casting. The area of the roughly triangular figure formed under the curve is proportional to the toughness of the tested resin. This property will be affected by changes in either ultimate tensile elongation or ultimate tensile strength. If each component of a multivariate property, such as toughness, changes slightly in the same direction, the cumulative change is much greater than each individual change. As illustrated in Figure 3, a 30 percent increase in both tensile elongation and tensile strength will result in a 70 percent increase in toughness.

Similarly, a difference in destructive stress testing of laminates can reflect a more substantial difference in non-destructive, cyclic stress. Table 2 shows that a clear cast isopolyester has 34 percent greater flexural

Figure 3: Tensile Stress/Strain Area Defines Toughness



Data obtained by ASTM D638 using Instron tester.

Figure 4: Strengths are Maximized at Intermediate Flexibility

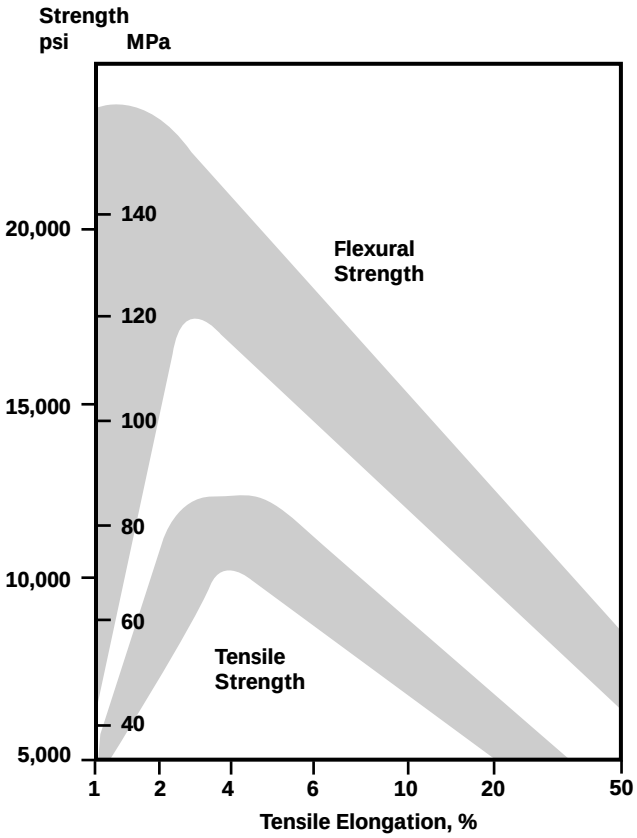


Table 2: Flexural Strength and Fatigue Testing

	Isopolyester Resin	Orthopolyester Resin	Iso Advantage Over Ortho
Clear Cast Flexural Strength (ASTM D790)	131 MPa 19,000 psi	98 MPa 14,200 psi	34%
Laminate Flexural Strength (ASTM D790)	221 MPa 32,000 psi	201 MPa 29,100 psi	10%
Flexural Load Sustainable for 1 Million Cycles by Laminate (ASTM D671)	80 MPa 11,600 psi	66 MPa 9,600 psi	21%

strength than an orthopolyester. When reinforced, the difference falls to 10 percent. However, when the laminate is subjected to flexural fatigue load testing, the difference is again apparent. (For details of the test and resin, see Figure 22 on page 16.)

Flexibility, which underlies many physical properties of resins is usually closely correlated with tensile elongation. Figures 4 through 6 show the relationship between tensile elongation and three other properties: flexural strength and tensile strength, stiffness (flexural and tensile modulus), and heat deflection temperature. The graphs indicate relatively invariable relationships between some properties: heat deflection resistance and high elongation are not compatible combinations of properties in the same class of resin. On the other hand, toughness can be increased in resins with low flexibility by increasing tensile elongation. In very flexible resins, toughness can be improved by reducing elongation.

Table 3 summarizes the physical tests and instrumental analyses that indicate resin characteristics and usefulness for various applications.

Figure 5: Clear Casting Stiffness Correlates with Tensile Elongation

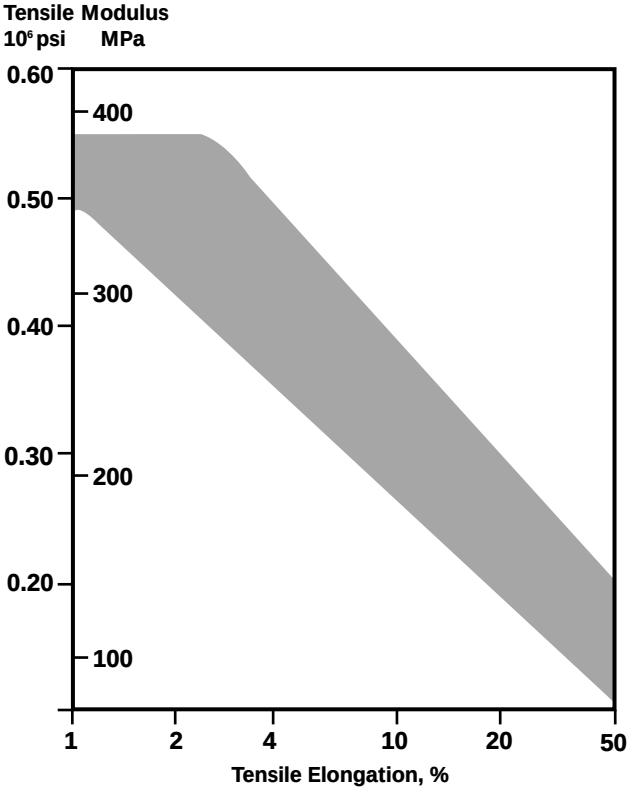


Figure 6: Heat Deflection Temperature versus Clear Casting Tensile Elongation

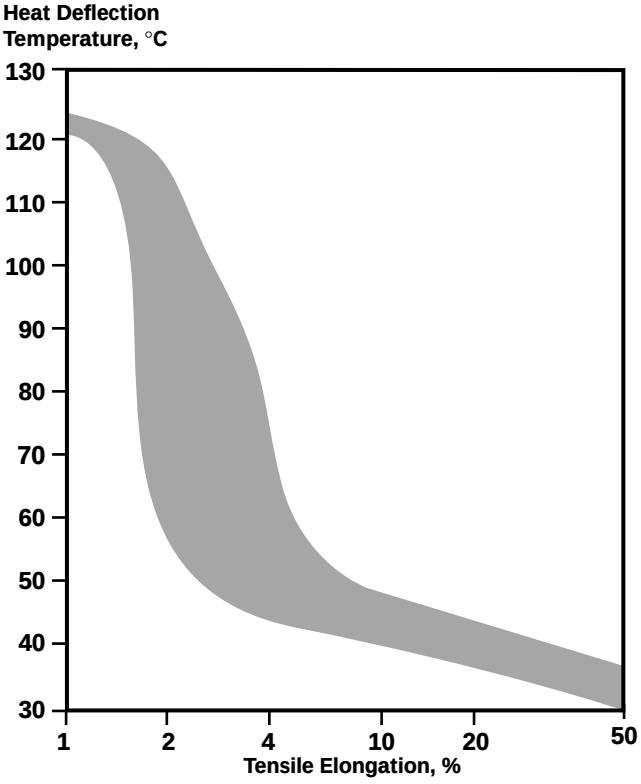


Table 3: Laboratory Tests of Cured Resins and Laminates

Property	Test Method	Significance
Tensile Strength	ASTM D638	Determine required part thickness
Tensile Elongation	ASTM D638	Flexibility
Flexural Modulus	ASTM D790	Stiffness, required part thickness
Heat Deflection temp.	ASTM D648	Service temperature, warp tendency
Permeability	ASTM D2684, D1653 (modified)	Dual laminate construction
Glass Transition temp.	Thermal gravimetric analysis	Electrical service temperature

Determination of Corrosion Resistance

Even in applications not normally referred to as corrosion resistant, the ability of reinforced isopolyesters to resist conditions that would cause deterioration in other materials is a valued attribute. In normal fabrication of corrosion resistant laminates, the surface is fiber free. Still, liquids may permeate the polyester to some extent, making the laminate vulnerable to attack of the resin, the glass fibers or the interface between them. Consequently, BP's preference is for corrosion testing of complete laminates with edges protected from exposure. Table 4 shows some common corrosion resistance tests which are conducted in BP laboratories.

Most of BP's testing has been conducted on laminates constructed and exposed in corrosive media by the procedures outlined in ASTM C581. Analysis of flexural properties and hardness at one, three, six and twelve months can be plotted on log-log graphs to project ten year performance. An example of such projections is shown in Figure 7. If the best straight line through the one year data indicates 50 percent or more retention of properties at ten years, the laminate is considered acceptable for commercial service in that medium. Advantages of this test method are that its acceleration is through two-sided exposure, not heat which can distort results. The test evaluates the resistance of the total laminate and is reliable. In BP's tests, property retentions have been reproducible to within 5 percent for flexural modulus and 10 percent for hardness and flexural strength.

Figure 7: Loss of Properties During One Year Predicts Long Term Resistance

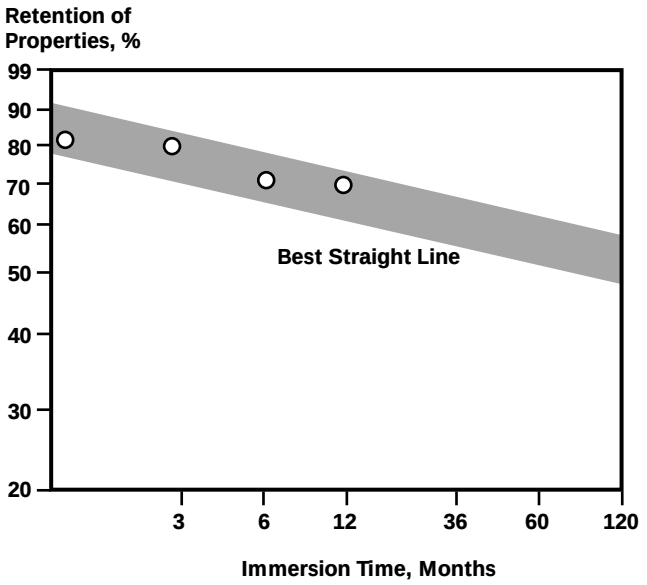


Table 4: Common Corrosion Resistance Tests

Property	Test Method	Significance
Strain Corrosion	ASTM D3681	Measures properties of FRP pipe.
Pipe Stiffness Retention	ASTM D2412	Conducted on stoppered pipe sections filled with chemical reagents.
Single-Sided Exposure	ASTM D4398	Measures time to blistering for marine gel coats and laminates.
Total Immersion	ASTM C581	Measures retention of flexural strength and hardness after one year. Compares resins on ability to protect glass fibers.

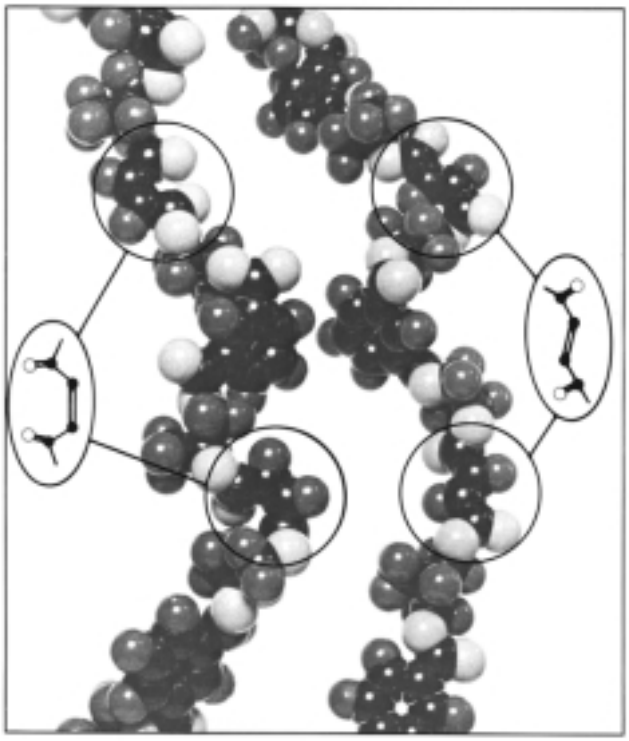


Illustration 4: Maleate versus Fumarate unsaturation.

Level of Unsaturation

The essential ingredient for an unsaturated polyester is the carbon-carbon double bond or olefinic unsaturation that will subsequently crosslink with the reactive diluent. In virtually all commercial resins, unsaturation is provided by maleic anhydride or fumaric acid. As shown by the molecular models, they are very similar in the esterified form, and their differences are minor compared with the effect of their use level in the polyester (Illustration 4).

The ratio of maleic or fumaric unsaturation to the total ingredients of the polyester is the primary determinant of reactive double bond frequency in the polymer. This frequency in turn determines the amount of crosslinking that can occur with a reactive diluent, such as styrene, and thus, strongly influences cured resin properties.

An unsaturated polyester could be made with only the unsaturated acid or anhydride and glycol or oxide. As saturated acid replaces unsaturated, the frequency of double bonds in the polymer will decrease causing an increase in flexibility as reflected by tensile elongation (Figure 8). The same trend is displaced, but still true, for resins made with quite different glycols. Figure 9 shows the increased tensile elongation associated with higher aromatic acid content in resins made with diethylene glycol.

Figure 8: Unsaturation Level Affects Tensile Elongation

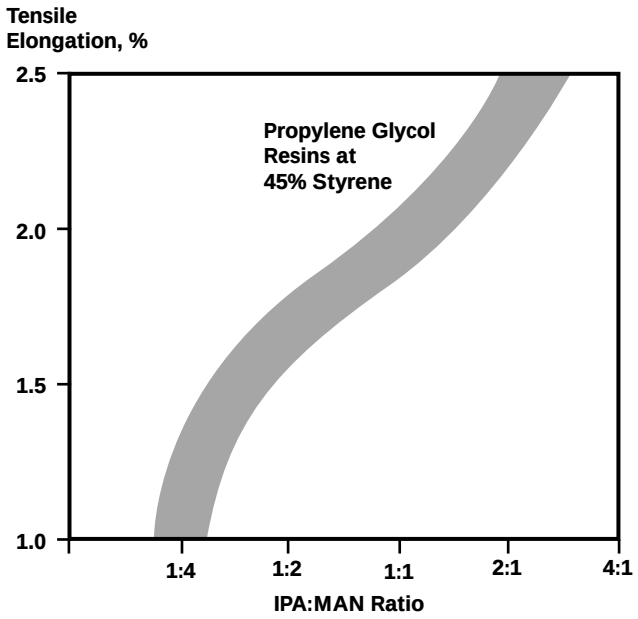
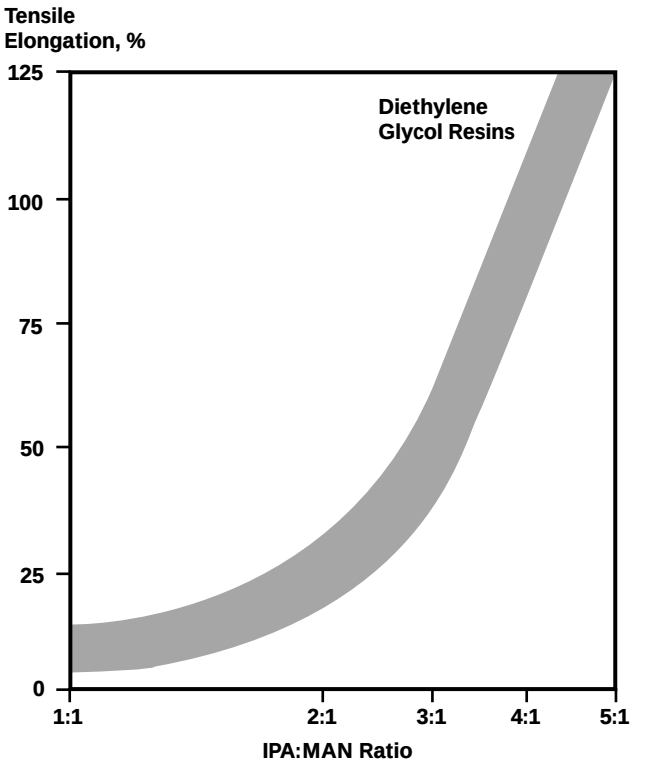


Figure 9: Tensile Elongation Increases as Reactivity Drops



Heat deflection temperature, as expected, decreases as crosslink density is reduced (Figure 10). However, as noted in the previous section, the effect of crosslink density of flexural and tensile strengths depends on resin flexibility. A rigid propylene glycol polyester becomes stronger and more flexible by increasing the aromatic acid content (Figure 11), while a very flexible diethylene glycol polyester exhibits lower strength as it is made more flexible by increasing aromatic acid content (Figure 12).

If the formulation of a polyester is known, the degree of unsaturation can be readily calculated in moles per unit mass (mol/kg). Table 5 shows a sample calculation for a polyester with two moles of unsaturation in 968 grams of polyester or a degree of unsaturation of 2.07 mol/kg.

Table 5: Example of Polyester Material Balance

Reactant	Mol	Kg
Isophthalic Acid	3.0	0.498
Maleic Anhydride	2.0	0.196
Propylene Glycol	5.5	0.418
Less Water	–8.0	–0.144
Yield	2.5	0.968

Unsaturation = 2.0/0.968 = 2.07 mol/kg

Figure 10: Heat Reflection Falls at Lower Unsaturation

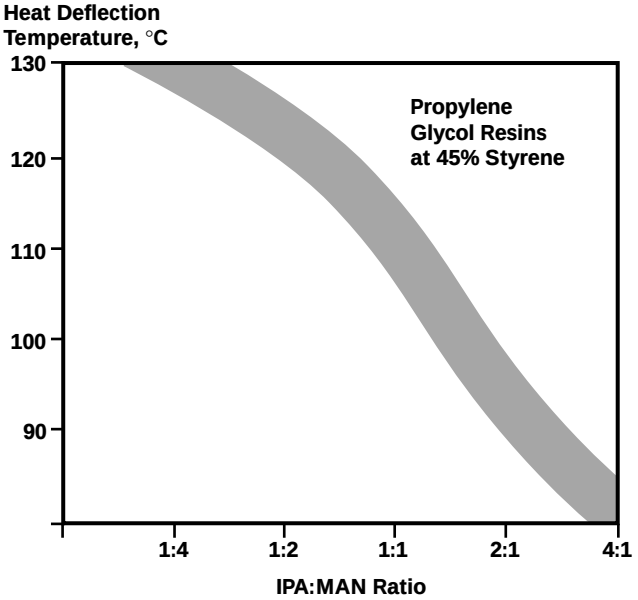


Figure 11: Strength of Rigid Resins Rises at Lower Unsaturation

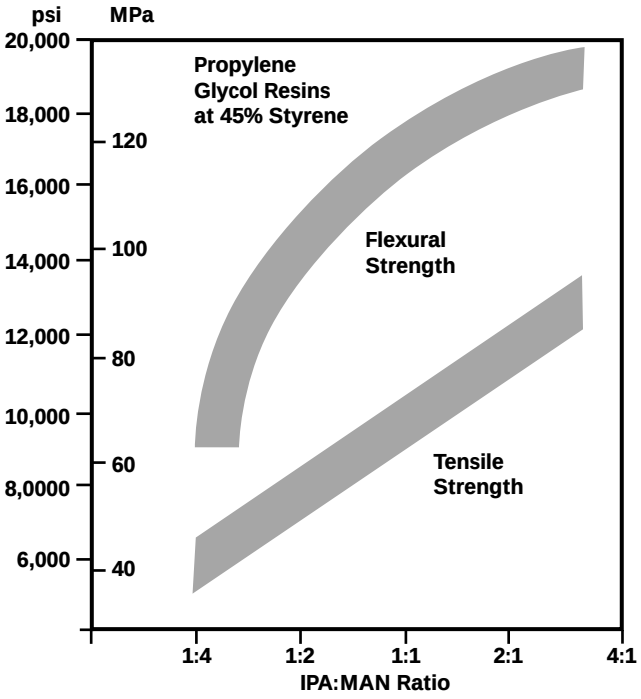
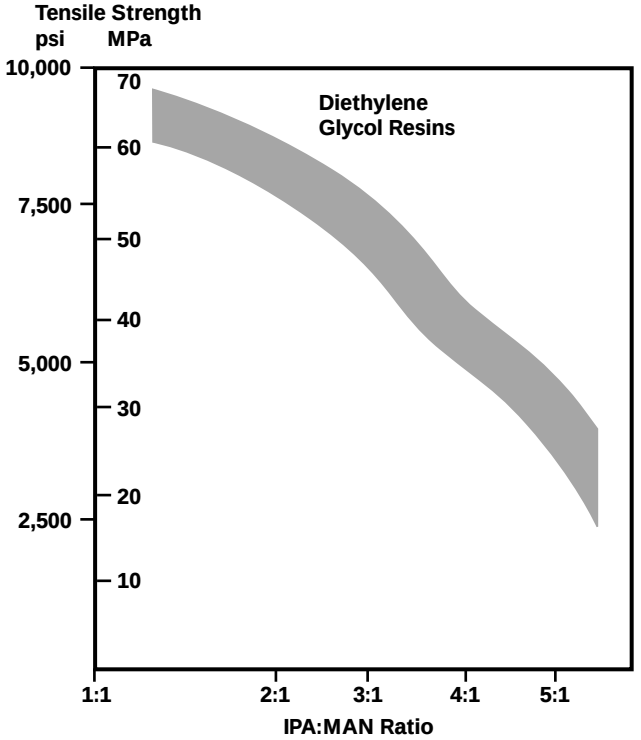


Figure 12: Strength of Flexible Resins Falls at Lower Unsaturation



These polyester double bonds react with the double bonds in styrene or other coreactant through a free-radical mechanism. This exothermic reaction is usually initiated by a peroxide or other free-radical source. Propagation time (a measure of the in-mold cure time) and peak exotherm as determined by the SPI gel test correlate well with the amount of unsaturation in the polyester if all other factors are constant. Figures 13 and 14 illustrate these trends for a series of resins made with propylene glycol and crosslinked with 45 percent styrene. Generally, higher polyester unsaturation levels will result in faster cure and higher temperatures.

Other Effects of Crosslink Density

Impact resistance is positively associated with flexibility. Thus, decreasing unsaturation will increase impact resistance, reducing molded part damage during fabrication and shipping.

Resins with higher unsaturation levels can tolerate more inert filler because the crosslink density remains sufficiently high to provide good strength as the resin portion of compound volume is reduced.

The higher heat deflection temperatures of more highly unsaturated resins allows service at higher temperatures.

Sources of Unsaturation

While theoretically a great variety of unsaturated difunctional acids and anhydrides could be used to provide the required double bonds in the polyester, virtually all commercial unsaturated polyesters incorporate maleic anhydride (cis configuration) or fumaric acid (trans configuration).

Maleic anhydride is usually less expensive than fumaric acid. It can be readily melted and handled as a liquid. The anhydride form reacts faster than the acid and one less mole of esterification water is released during processing.

Maleic acid readily isomerizes to form furmaric acid. During esterification, the maleate structure can rearrange into the fumarate configuration. The extent of isomerization is reported to be dependent on the type of glycol used. Table 6 shows the amount of isomerization observed.

The advantage of total trans configuration (fumaric acid) was reported to be typical of a more linear and crystalline polymer: greater hardness, high moduli or stiffness, lower elongation, higher heat distortion temperature, reduced gel and propagation times, and higher exotherms. The trend of these differences is to make the polymer more rigid.

Figure 13: Unsaturation Level Affects Propagation Time

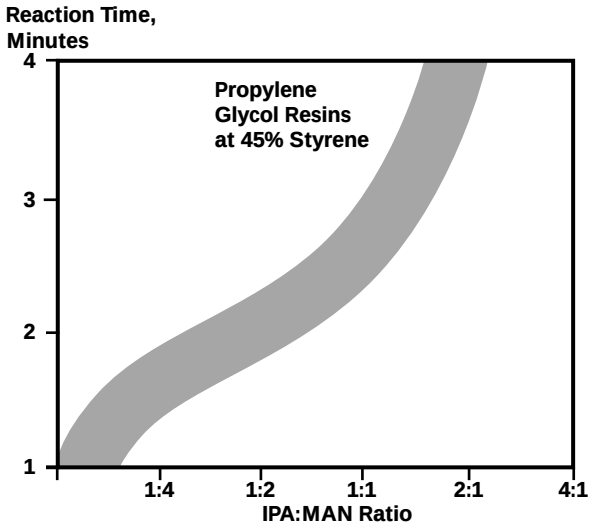


Figure 14: Unsaturation Level Affects Peak Exotherm

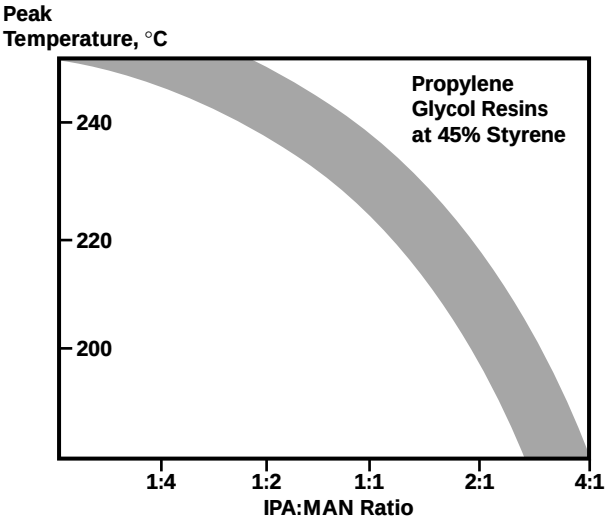


Table 6: Isomerization of Maleic to Fumaric During Polyesterification

Glycol	Amount Isomerized (%)
Propylene Glycol	95
Neopentyl Glycol	72
Ethylene Glycol	70
Diethylene Glycol	65

From Curtis et al., 19th Annual SPI RP/C conference

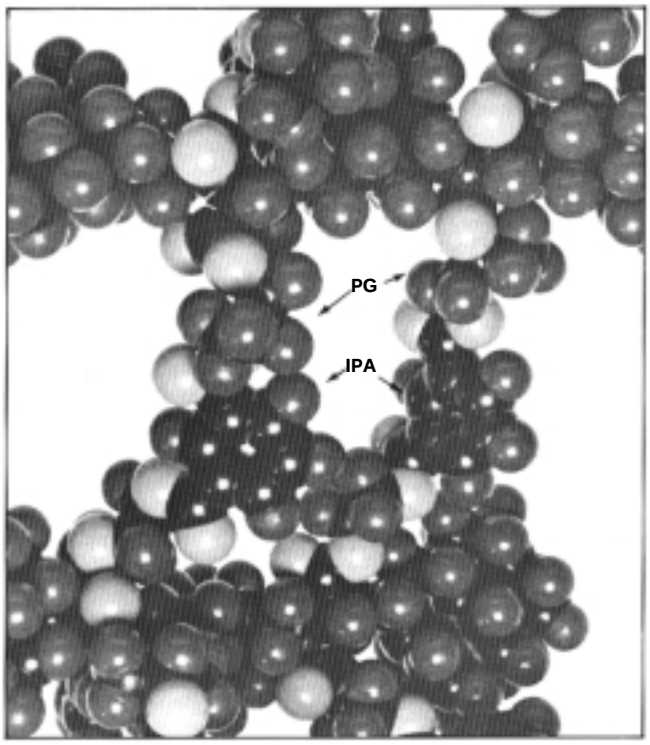


Illustration 5: Cured isopolyester.

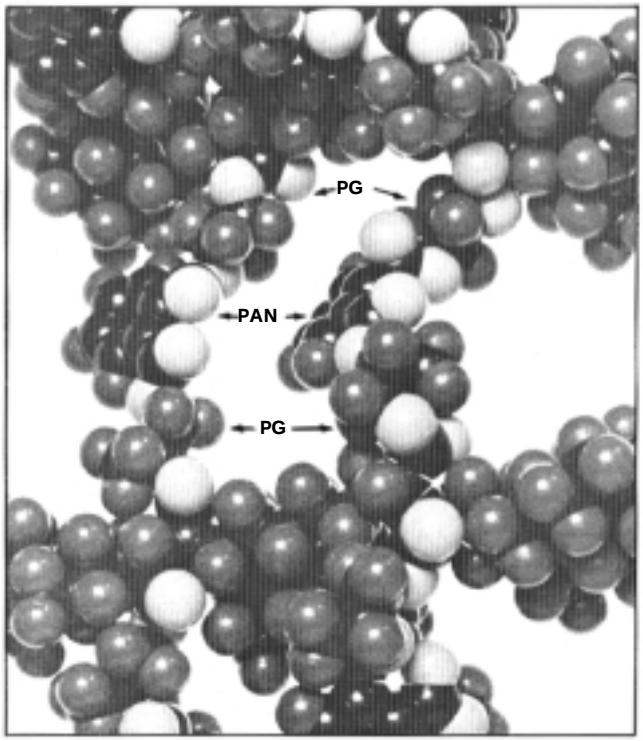


Illustration 6: Cured orthopolyester.

Three Isomers of Phthalic Acid

There are three isomers of phthalic acid: orthophthalic acid (1,2-benzenedicarboxylic acid), isophthalic acid (1,3-), and terephthalic acid (1,4-). Orthophthalic acid, the only one of the three that can form an anhydride, is normally used in that form.

Each phthalic isomer has particular advantages and liabilities when used in polyester production. Research by BP indicates that polyesters made from isophthalic acid (IPA) offer substantially better properties than equivalent formulations made with phthalic anhydride (PAN).

The properties of terepolyesters are generally better than orthopolyesters and are often quite similar to those of isopolyesters. Terepolyesters generally have a higher heat deflection temperature but offer less aromatic solvent resistance and less UV stability.

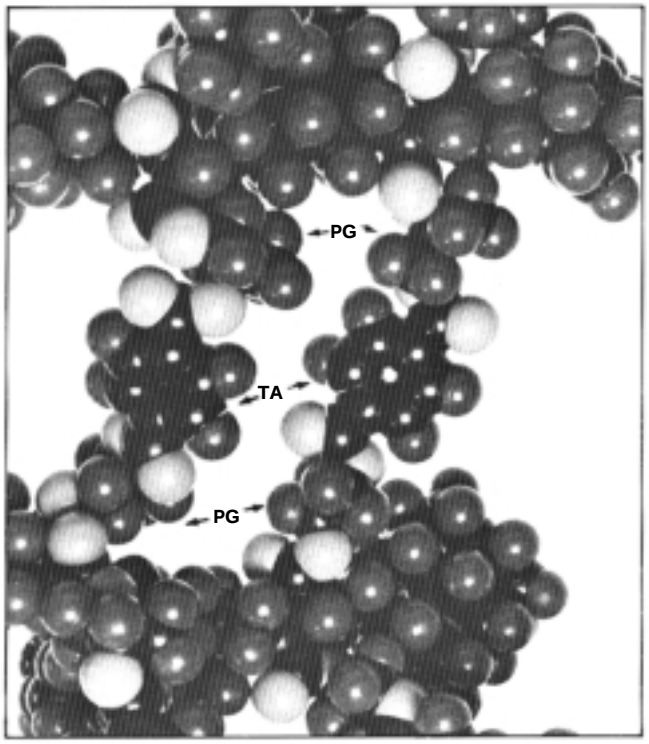


Illustration 7: Cured terepolyester.

Cost Differences

A resin manufacturer's cost analysis includes raw material costs, processing costs and ancillary costs associated with special handling of any product. Such an analysis is an overly simple view of the real cost and value of the user. Customer oriented cost analysis must include not only resin purchase price and fabrication costs, but life-cycle cost factors such as maintenance, useful life before replacement and performance in multiple environments. The manufacturer producing high-quality resins can offer the savings of longer service life in more varied conditions.

The combination of better physical properties and superior corrosion resistance reported for isophthalic polyesters in this section can be exploited in several ways:

- Thinner laminates can match performance of lower quality resins at lower cost and less weight;
- The safety margin for catastrophic stress can be increased;
- Useful product life can be extended;
- Maintenance costs can be reduced;
- Product defect incidence caused by manufacturing stresses can be reduced.

Differences in Material Handling and Processing

The ortho isomer is normally used as the anhydride which reacts faster initially and releases one, rather than two, moles of esterification water. Phthalic anhydride can be melted, providing some convenience for plants equipped to pump hot liquids to storage and process units.

Terephthalic acid is the slowest reacting of the three phthalic acids. Catalysts or pressure are required to esterify TA within a reasonable time period.

Isophthalic acid reacts more readily than TA, but its initial rate is slower than phthalic anhydride. The esterification of isophthalic acid can be catalyzed to provide reaction times approximating those of anhydride esterification. A summary of typical processing times with and without catalysts and pressure is shown in Table 7.

The K_1 reported in Table 8 for orthophthalic acid is not indicative of the initial reaction rate of the anhydride. Note the significantly lower K_2 of ortho versus iso. The practical implication of the low K_2 is a much slower reaction rate for the second acid group of orthophthalic acid based polyesters. Consequently, it is much more difficult to obtain high polyester molecular weight with phthalic anhydride than with the iso or tere conformations. Efforts to push orthopolyesters to high molecular weight increase the risk of gelation and aggravate the sublimation

Table 7: Properties of Phthalic Acids and Anhydride*

Reagent	M.P. °C	Solubility in H_2O @ 20°C	Ionization Constants* in Water K_1	K_2
Orthophthalic Acid	231	0.7	110×10^{-5}	0.6×10^{-5}
Isophthalic Acid	348.5	0.01	33×10^{-5}	3.2×10^{-5}
Terephthalic Acid	300 (subl.)	0.002	31×10^{-5}	1.5×10^{-5}
Phthalic Anhydride	131	—	—	—

*Kirk-Othmer, Encyclopedia of Chemical Technology, 2nd ed.

rate of phthalic anhydride. These efforts also negate the ortho resin's inherent advantages of fast reaction times and light color.

The sublimation tendency of phthalic anhydride requires caution during processing and can indirectly influence cured properties. Sublimed phthalic anhydride fumes are flammable and can cause fractionator and condenser plugging. Condensed phthalic anhydride and low molecular weight phthalic esters can drip back into the resin kettle during final stages of processing and after the reaction is complete. These low molecular weight materials have relatively high water solubility, act as plasticizers of the cured resin and reduce corrosion resistance.

Because terephthalic acid requires catalysis for efficient processing, the consequences of residual catalyst in cured resin must be evaluated in end use applications. BP's experience indicates that certain catalysts may be detrimental to corrosion resistance properties. TA resins cooked with catalysts generally have dark color and poor shelf life. Gel characteristics can also be affected.

Liquid Resin Properties

Equivalent formulations made with the different phthalic isomers will have somewhat different liquid properties resulting from the different target end properties. Resins based on isophthalic or terephthalic acid will normally be processed to higher molecular weights and will show higher viscosities and lower end group counts (acid numbers and hydroxyl numbers) than equivalent phthalic anhydride formulations. To obtain proper solution viscosity for particular end uses, such as spray application, somewhat more styrene dilution or relatively more glycol may be required with IPA than with phthalic anhydride. Stopping the isopolyesterification reaction at a lower molecular weight (higher acid number) is generally not recommended as many of the cured resin advantages will be lost.

Terephthalic polyesters made with primary glycols such as neopentyl have poor solubility in styrene compared with ortho and isopolyesters. Blends of glycols and highly branched or cyclic glycols have been suggested to improve TA resin solubility.

Table 8: Processing Time Variation of Phthalic Acid Isomers

Aromatic Acid	PAN	PAN	IPA	IPA	IPA	TA	TA	TA
Max. Temp., °C	200	232	232	232	232	232	232	232
Catalyst*	No	No	No	No	Yes	No	No	Yes
Pressure	No	No	No	Yes	No	No	Yes	No
First Stage Time, hrs.	24.0	5.5	9.0	4.5	4.3	48.7	14.0	8.5
Second Stage Time, hrs.	—	9.5	10.0	10.0	11.0	9.5	10.0	7.5
Total Time, hrs.	24.0	15.0	19.0	14.5	15.3	58.2	24.0	16.0
Final Visc. @ 60 NVM	T	T-U	V	V-W	U-V	V	V	V

Data are averages from many cooks of equimolar amounts of maleic anhydride and aromatic acid condensed with propylene glycol. Times will vary depending on equipment.

*Fascat 4100, hydrated monobutyltin oxide, a product of M&T Chemical, Inc. Meets U.S. FDA specifications for crosslinking polyesters used in food contact applications, Title 21 CFR 177.2420.

Cured Resin Differences

The magnitude of the differences caused by the various phthalic isomers depends on the selection and proportion of other ingredients in the polyester. High reactivity resins designed for SMC application contain only 10 to 15 percent aromatic acid in the cured polymer, whereas the aromatic acid can be well over 30 percent of some flexible resins.

Comparing equivalent formulations based on different aromatic acids is complicated by the differences caused by processing parameters. As indicated above, orthophthalic resins are rarely processed to the same molecular weight as iso- and tere-based resins. Orthophthalic resins that are specially processed to the molecular weight range easily attained with isophthalic acid are susceptible to premature gelation and may contain low molecular weight species.

To demonstrate the differences attributable solely to the isomeric structure, most of the comparisons reported here are with very high-quality, laboratory-prepared orthophthalic resins that are unmatched by commercial phthalic resins. The greater advantage of commercial iso resins over commercial orthophthalic polyesters is evident in comparing the differences shown in Figure 15 to Figures 16 and 17. An isophthalic high reactivity resin prepared in BP's laboratory showed about 5 to 10 percent higher physical properties than a comparable orthophthalic polyester made to the same standards. Tensile toughness, a multivariate property, is more than 20 percent better with the isopolyester. In contrast, high reactivity commercial isopolyesters are at least twice as tough as equivalent commercial orthopolyesters.

Formulations with a high ratio of aromatic to unsaturated acids amplify the difference IPA can make. Figure 18 shows tensile stress/strain data from a series of flexible resins made with diethylene glycol. For these formulations, at equivalent ultimate tensile elongation, the iso resins have 65 to 75 percent higher tensile strength.

Figure 15: Toughness of Rigid Laboratory High Reactivity Resins

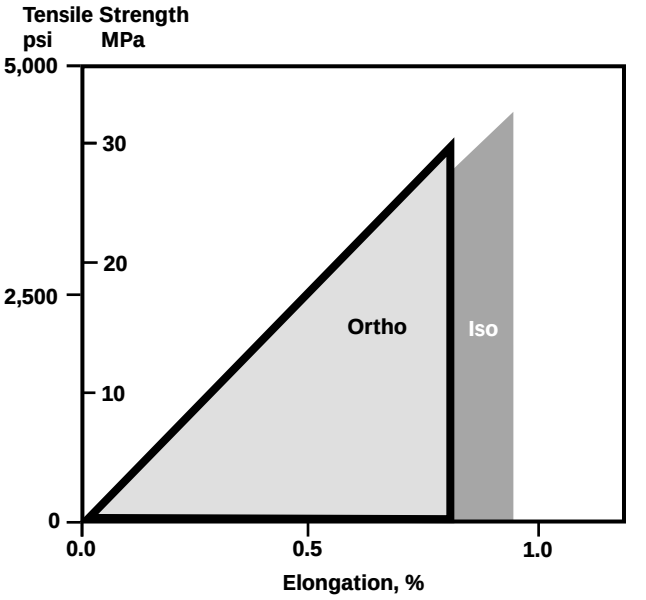
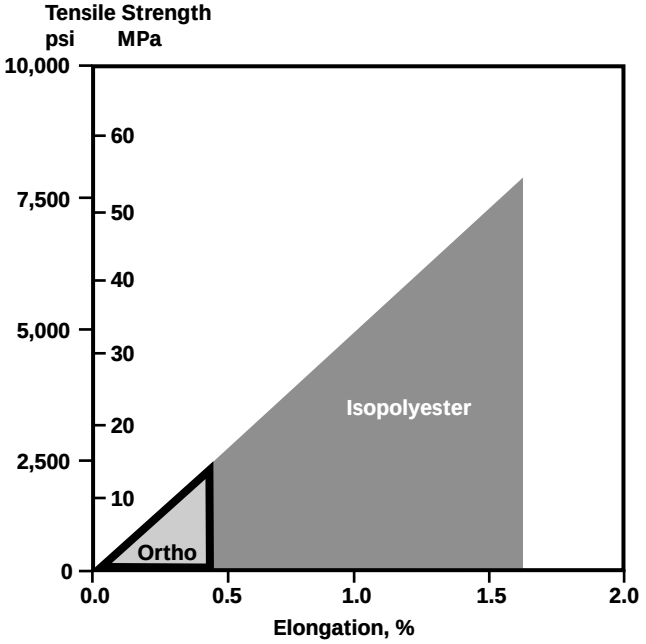


Figure 16: Toughness of Rigid Commercial High Reactivity Resins



At a 1:1 ratio of aromatic to unsaturated acids, isopolyesters offer 15 to 20 percent better strength, ultimate elongation (Figure 19), and heat deflection temperature (Figure 20) than orthopolyesters. The isopolyesters are more than 40 percent tougher than the ortho resins.

Isopolyesters can endure substantially higher load than orthopolyesters in laminate flexural fatigue tests of medium reactivity resins (1:1 and 3:2 ratios of aromatic to unsaturated acids). This series of tests (Figure 22) follow ASTM method D 671; non-destructive loads were applied cyclically until stress relaxed to half of original. The orthopolyesters included a commercial resin whose fatigue resistance was significantly lower than that of the laboratory prepared resins.

Figure 17: Toughness of Resilient Commercial High Reactivity Resins

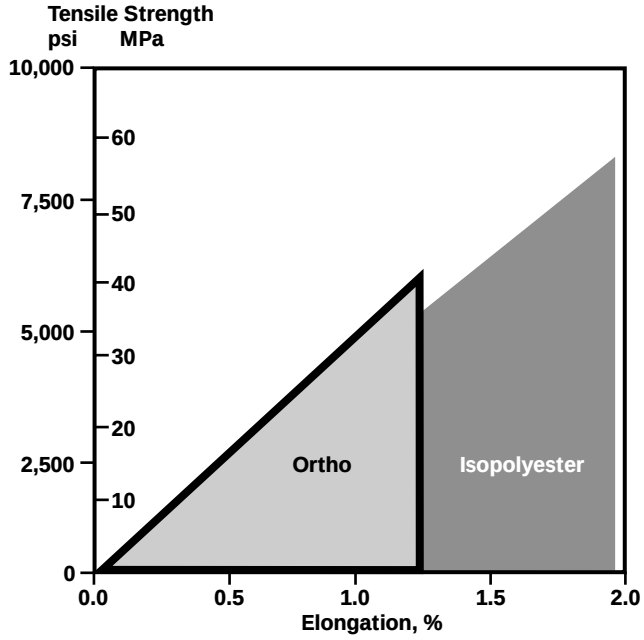


Figure 18: Tensile Stress of Flexibilized Unsaturated Polyesters

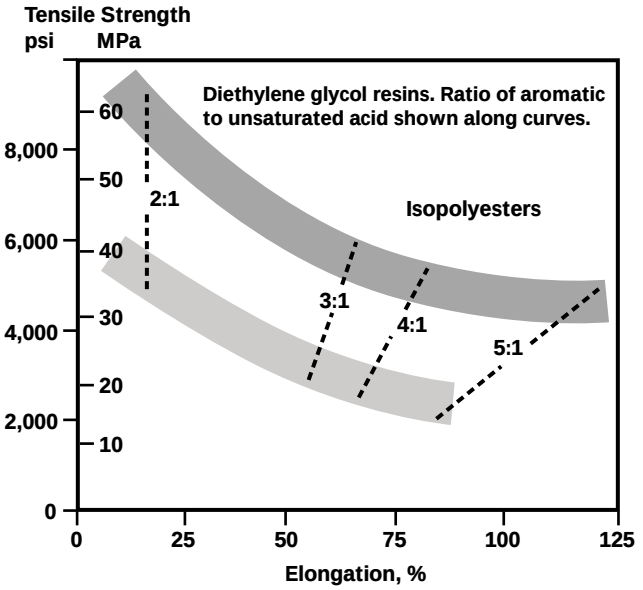
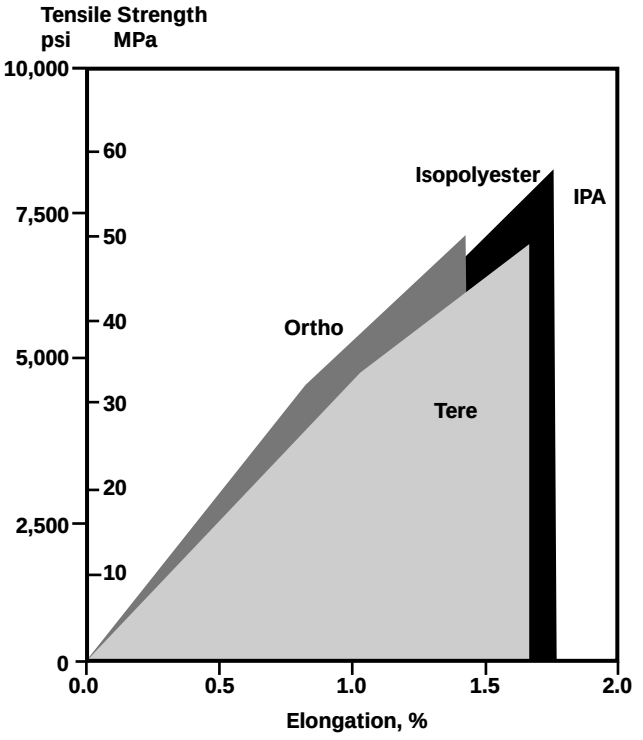


Figure 19: Toughness of 1:1 Polyesters in Tensile Stress/Strain



Most physical properties of 1:1 terephthalate polyesters are not substantially different than 1:1 isopolyesters. The most dramatic differences are the higher heat deflection temperature (Figure 20) and lower hardness (Figure 21) of the terephthalate polyesters. Isopolyesters are about 15 percent tougher than equivalent terepolyesters (Figure 19).

Figure 20: Heat Deflection Temperature of 1:1 Polyesters

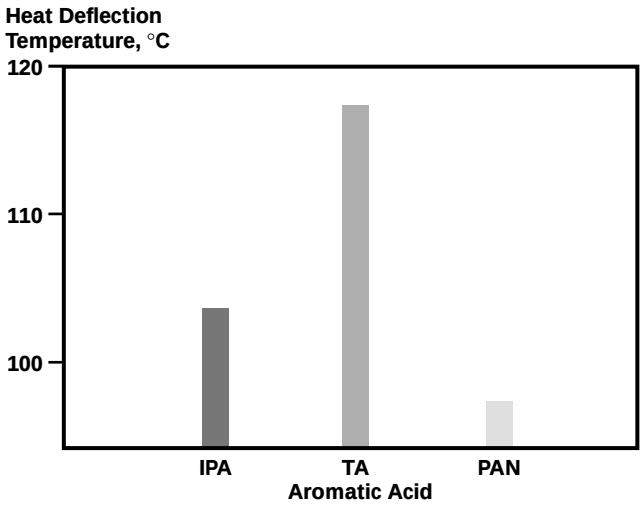


Figure 21: Hardness of 1:1 Polyesters 45% Styrene

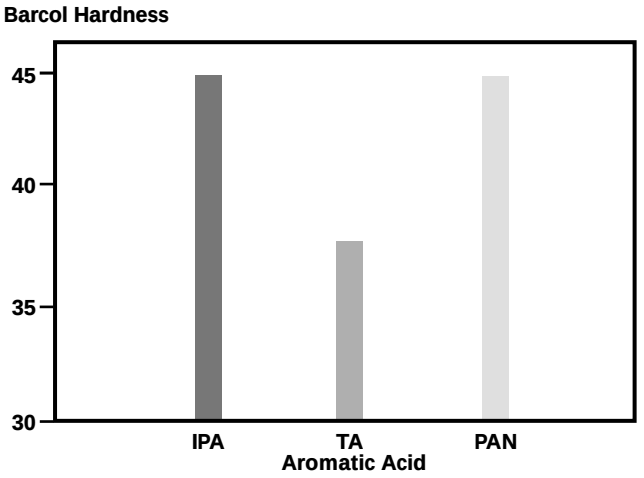
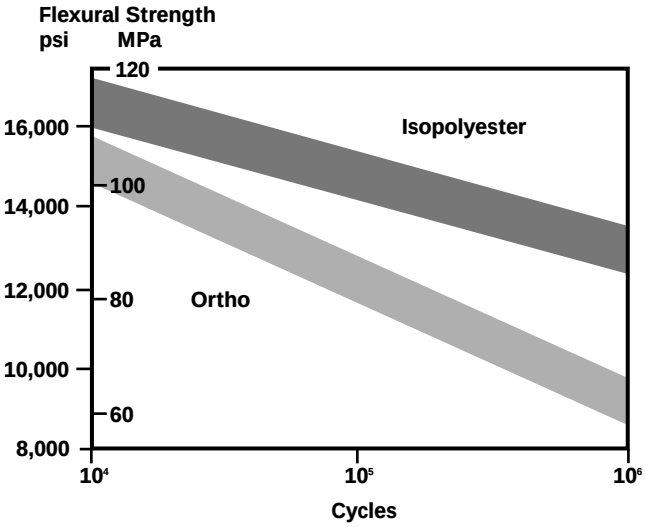


Figure 22: Flexural Fatigue of Laminates



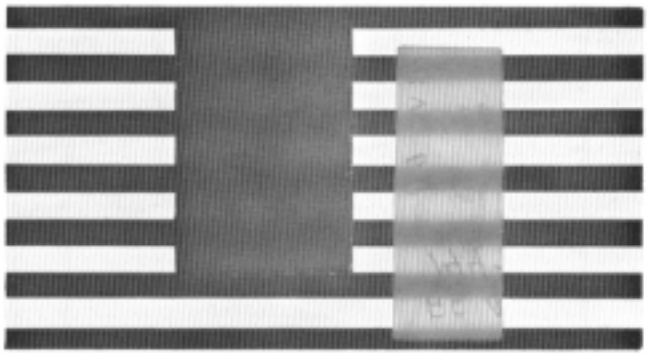


Illustration 8: After six days in boiling water, orthopolyester (on left) has become cloudy and opaque while isopolyester is still clear.

Isopolyesters Offer Balance of Properties

Many applications for unsaturated polyesters depend to some extent on the resistance of these resins to attack by environments that corrode metals. Resins with equimolar ratios of unsaturated to aromatic acids generally exhibit the best balance of corrosion resistant properties.

The traditional preference for isopolyesters over orthophthalates for corrosion resistance is dramatically illustrated by the results of laminate immersion in representative media (Figures 23, 24 and 25). Even when a phthalic anhydride resin is processed in two stages to a very low acid number and high molecular weight (HMW), its ten year projected properties drop to unacceptable levels. A lower molecular weight (LMW) orthopolyester processed to more typical commercial properties deteriorated to unacceptable levels within the year of immersion.

Several factors may cause the lower resistance of orthopolyesters to attack by aqueous solutions. As evident in the molecular models (Illustration 6), orthophthalate ester linkages are more visible, hence are more susceptible to attack than the ester linkages of isopolyesters. The hydrolytic stability of orthopolyesters is far inferior to that of isopolyesters as shown by clear castings after six days boiling water immersion (Illustration 8). A further vulnerability is the possibility of free phthalic anhydride or low molecular weight phthalate esters that may drop into the orthopolyester resin near the end of processing.

Figure 23: 35% HCl at 49°C

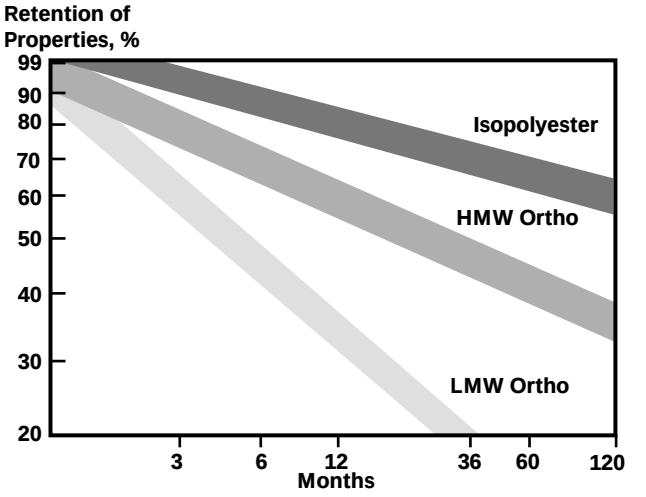


Figure 24: 25% Ethanol at 71°C

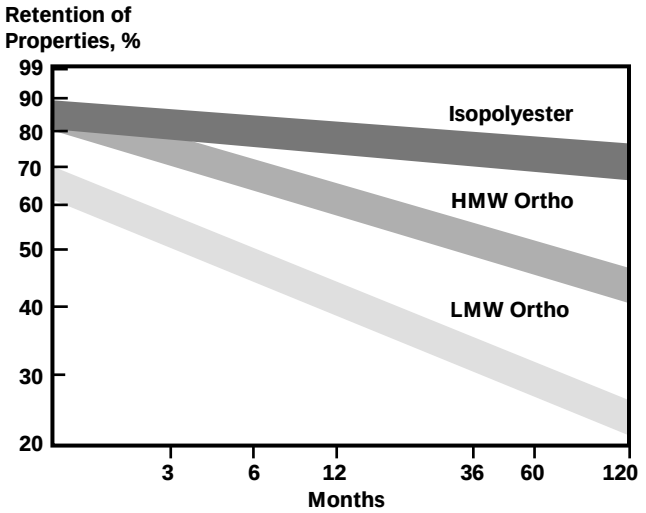
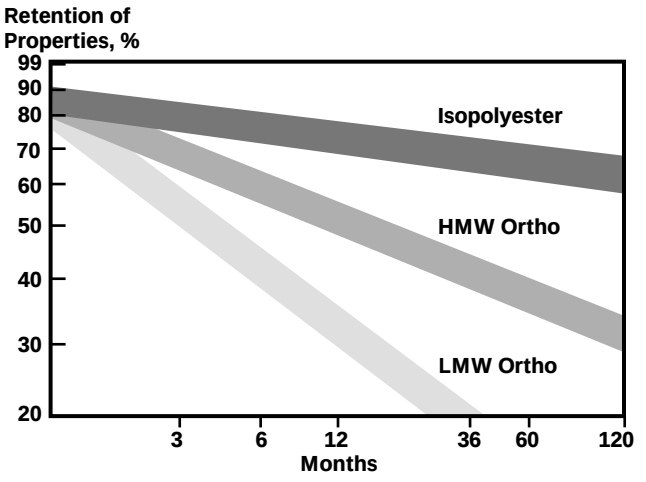


Figure 25: 1 N NH_4OH at 38°C



Terepthalate Corrosion Resistance

BP's immersion studies showed no advantage for terephthalate polyesters at temperatures up to 93°C (Figures 26, 27 and 28). Isopolyesters demonstrated better resistance to dilute acids and bases than terepolyesters. The TA resins failed in benzene while the iso resin softened, but maintained strength and modulus.

Figure 26: 25% H_2SO_4 at 93°C

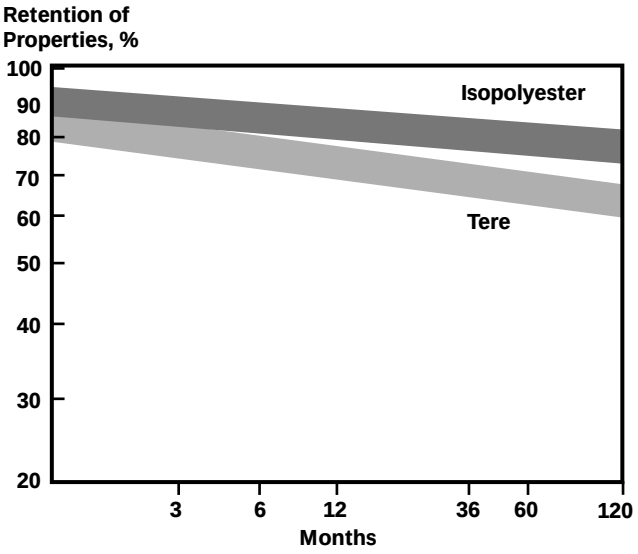


Figure 27: Benzene at 23°C

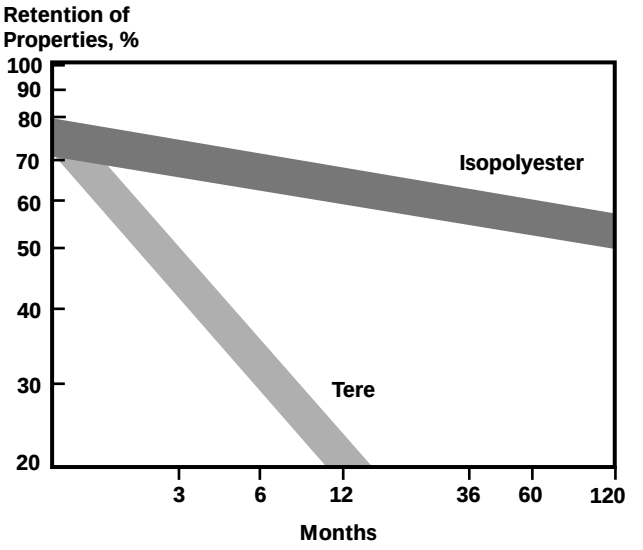
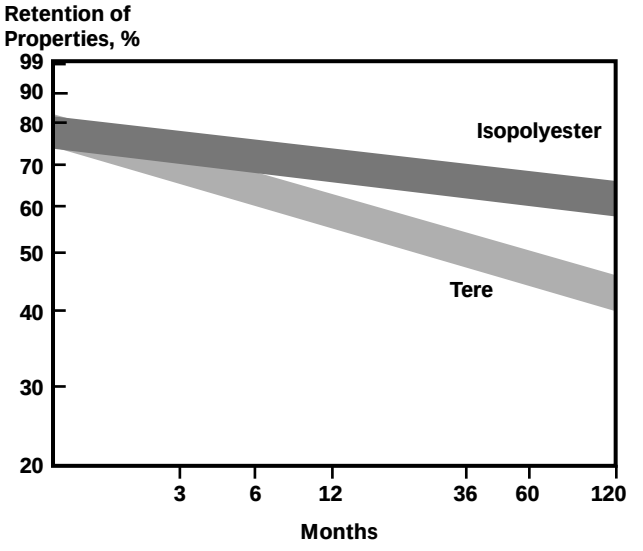


Figure 28: 5% NaOH at 23°C



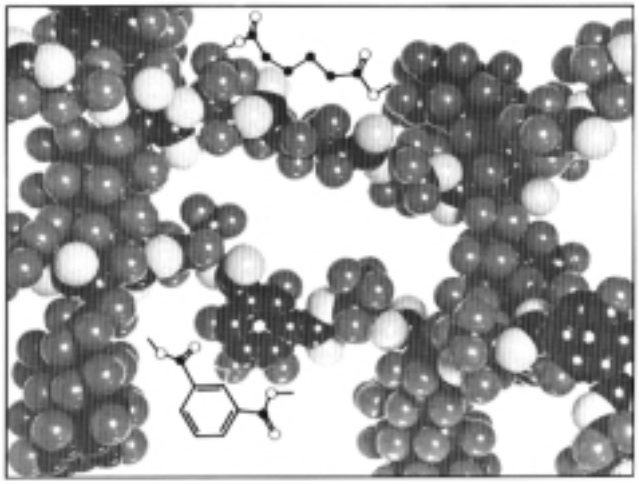


Illustration 9: Adipate (upper section) versus isophthalate structure.

Modification with Aliphatic Acids

Aliphatic acids, particularly adipic acid, can replace part of the aromatic portion of an unsaturated polyester to offer higher tensile elongation without drastically reducing heat distortion temperature.

The aliphatic chain is more flexible than the aromatic ring; thus the effects shown in Figures 29 and 30 are not surprising. Adipic acid in the polyester backbone acts as a flexibilizer, lowering stiffness and increasing elongation. Because crosslink density is essentially constant, the reduction in heat distortion temperature is modest up to the 50 percent replacement level. Above this level, heat distortion temperature drops rapidly.

The steric hindrance protecting the ester linkage is much lower with aliphatic acids than with isophthalic acid. Therefore, polyesters containing a substantial fraction of adipic acid suffer severe loss of corrosion resistance and hydrolytic stability.

The degree of property degradation is partially dependent on glycol. Polyesters with about 20 percent molar substitution of adipic acid for isophthalic acid that are condensed with a highly branched glycol such as neopentyl glycol, offer a good balance of flexibility and toughness with acceptable corrosion resistance for many applications. Adipic-modified polyesters made with ether glycols are readily susceptible to corrosion by many common media.

Figure 29: Adipic Acid Reduces Stiffness

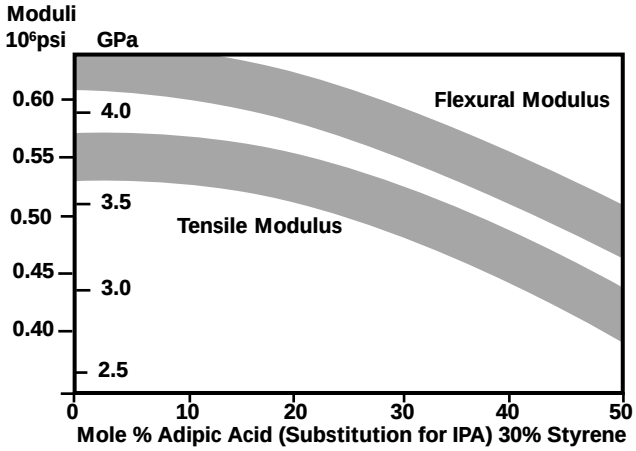


Figure 30: Adipic Acid Substitution Increases Tensile Elongation

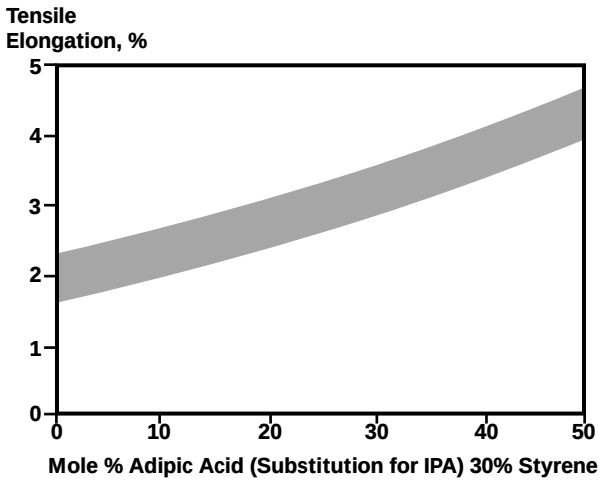
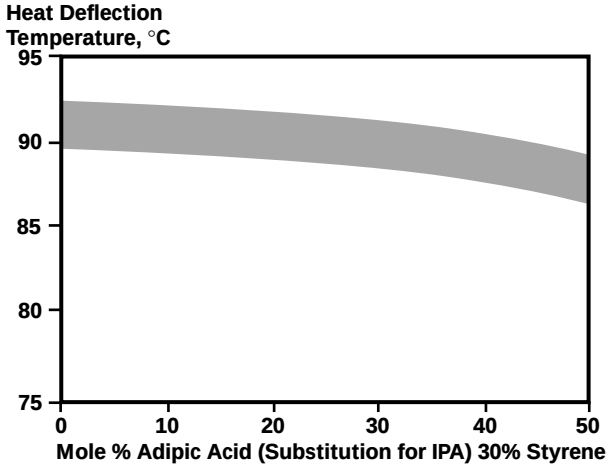


Figure 31: Adipic Acid Substitution Slightly Decreases Heat Deflection Temperature



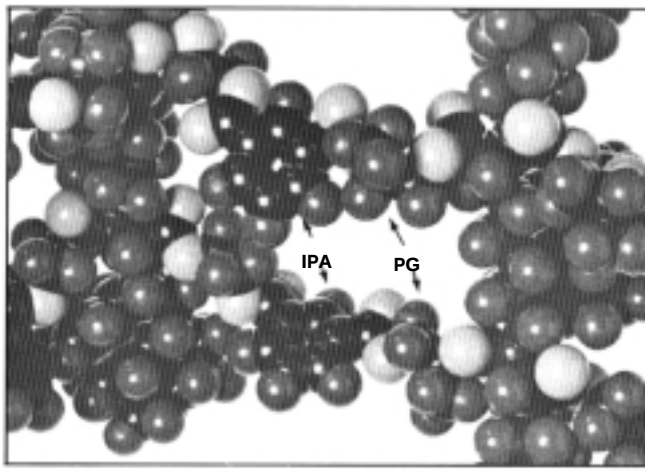


Illustration 10: Isopolyester made with propylene glycol.

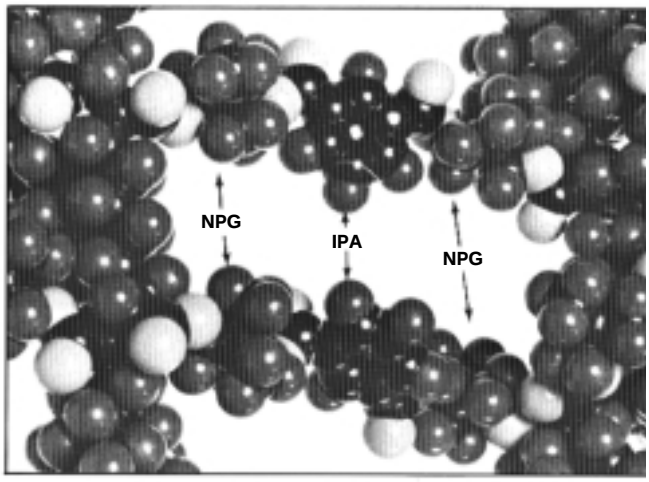


Illustration 11: Isopolyester made with neopentyl glycol.

Glycols

As partner in every ester linkage, glycols are important determinants of polyester properties. BP is not a manufacturer of glycols, therefore, we have looked primarily at glycols as coreactants with isophthalic acid and maleic anhydride without attempting to exhaustively investigate the full range of available materials. The trends described are both what we have observed and what have been reported by generally available trade and academic sources.

The effects of glycols are analogous to those of acids: bulkier, more branched or cyclic glycols offer more ester protection and less rotational freedom; longer chains offer more flexibility; larger glycols reduce unsaturation level modestly with associated changes of properties.

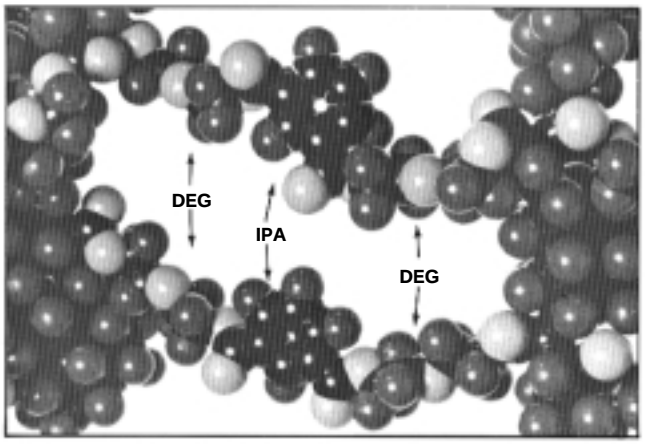


Illustration 12: Isopolyester made with diethylene glycol.

Types of Glycols

The common glycols used in unsaturated polyester synthesis can be classified as aliphatic, branched, and etheric. Typical examples of each type are ethylene glycol, propylene glycol and diethylene glycol. Each class of glycol has advantages and liabilities for unsaturated polyester application. Within each class, increasing molecular weight causes reduced polymer unsaturation level which generally correlates with changes in resin properties.

Manufacturers considering any specific glycol should obtain full handling and safety information from their glycol supplier. Many glycols require special storage, handling and processing to avoid degradation or excessive sublimation.

Characteristics of Aliphatic Glycols

Straight-chain glycols, such as ethylene glycol and 1,4-butane diol, are not as commonly used as branched or ether glycols. Ethylene glycol esters have poor styrene solubility; 1,6-hexane diol is a solid at room temperature and its initial reaction product with IPA is quite waxy. Higher molecular weight aliphatic glycols should impart flexibility comparable to that of adipic and other aliphatic acids.

Branched Glycols

Propylene glycol, the lowest molecular weight member of the class, is the base point for most of the comparisons in this brochure. The branched glycols tend to be low boiling (propylene glycol), easily sublimed (neopentyl glycol) or heat sensitive (1,3- butane diol and trimethylpentanediol). Branched glycols offer excellent protection to ester linkages and thus have outstanding corrosion resistance. The pendant methyl groups restrict rotation; therefore, cured resins based on branched glycols are more rigid than resins using aliphatic or ether glycols of equivalent molecular size.

Ether Glycols

The common ether glycols combine the good flexibility offered by longer aliphatics with styrene solubility and useful resin viscosity. The most obvious drawback to ether glycols is the lack of steric protection given the ester linkages. Ether glycols are generally unacceptable for corrosion resistant applications.

Other Hydroxyl Sources

A partial list of alternatives to glycols includes alcohols, oxides and polyhydric materials.

Alcohols are polyester chain terminators and act to limit polymer growth. They cannot be the sole source of hydroxyl functionality in polyesters. If introduced to the reaction mixture before all dibasic acids are partially reacted, alcohols can esterify with free acid to form non-reactive, plasticizing species.

Ethylene and propylene oxides can be substituted for the equivalent glycols. When used with anhydrides, oxides esterify without producing water; the reaction can be explosively exothermic and is often done under pressure in continuous reactors.

Polyols, such as trimethylolethane and pentaerythritol, introduce branching to the basic polyester chain. Caution must be exercised to avoid gelation during processing with polyols and viscosity in styrene is generally higher than with comparable linear polyesters.

The Effects of Increasing Glycol Molecular Size

Within a given class of glycol, the effects on curing and cured resin properties relate well to the change in unsaturation level caused by varying glycol molecular size. If all else is constant, as glycol size increases, the unsaturation level of the polymer is reduced; exotherm during cure drops (Figure 32) and propagation time is extended (Figure 33). Cured resins based on larger glycols are less stiff (Figure 34), have higher ultimate tensile elongations (Figure 35) and lower heat deflection temperatures (Figure 36).

Figure 32: Glycol Effects on Peak Exotherm

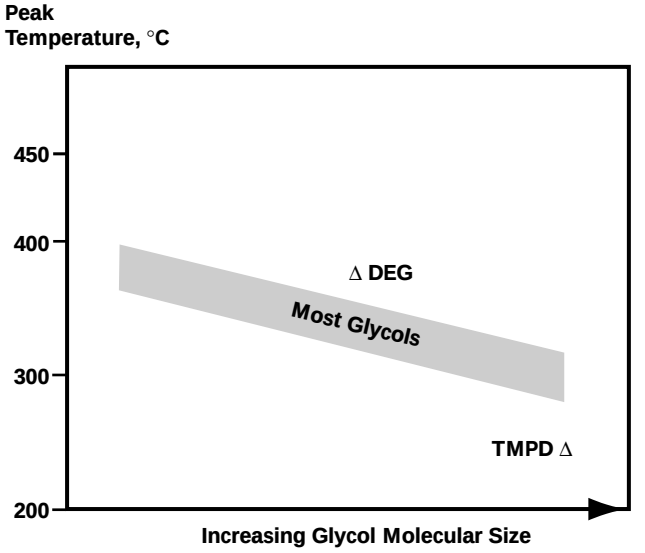


Figure 33: Glycol Effects on Propagation Time

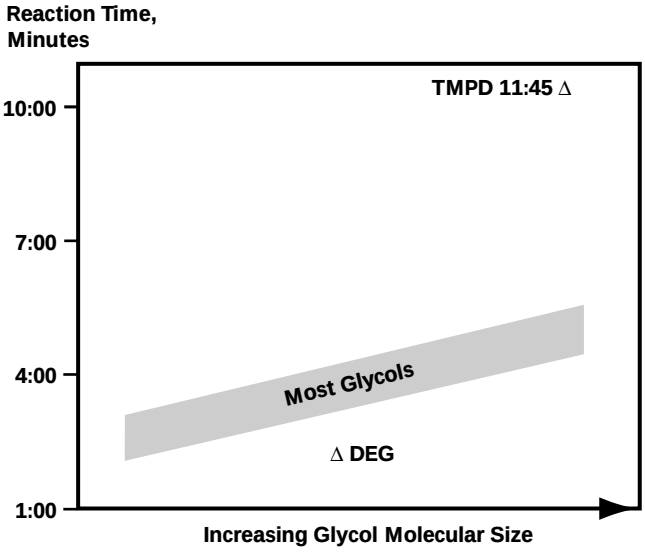


Figure 34: Glycol Effects on Flexural Modulus

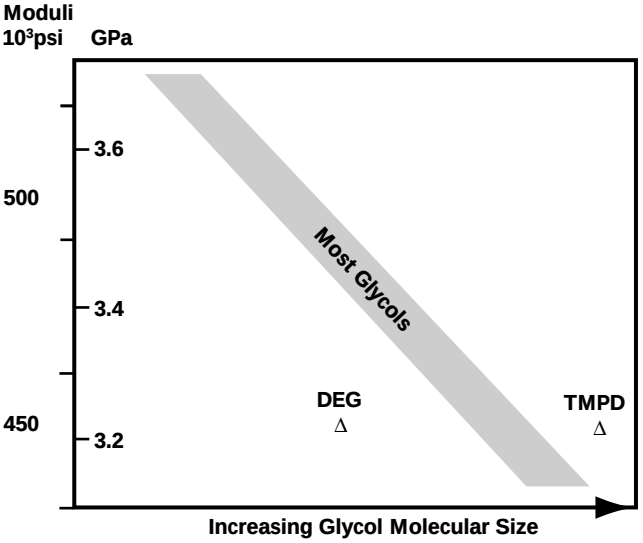


Figure 35: Glycol Effects on Tensile Elongation

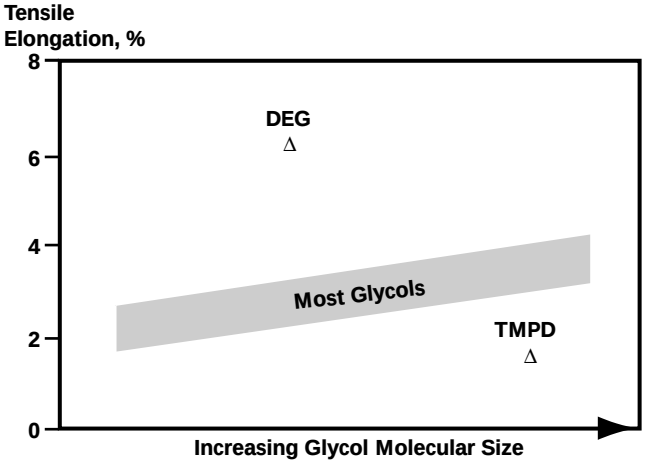
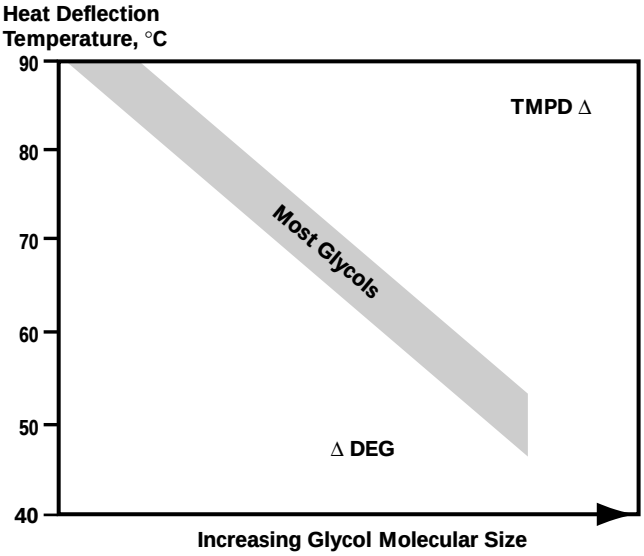


Figure 36: Glycol Effects on Heat Deflection Temperature



Glycol Excesses During Processing

Some glycol is volatilized and carried through the fractionation column with water evolved during polyesterification. The rate of loss depends on factors including the efficiency of the fractionator, heat input rates and the nature of the glycol. The sixth column of Table 9a reports the glycol excess typically used in pilot plant synthesis of unsaturated polyesters. These excesses should be modified to match experience with particular reactors or to meet the requirements of specific formulations.

Table 9a: A Synopsis of Glycol Considerations

Glycol	Classifications	Number of Pendant Methyls	Molecular Weight	Boiling Point, °C	Typical Equivalent Excess, %
Ethylene	Aliphatic	0	62	197.5	5
Propylene	Branched	1	76	187.3	10
1,3 Butylene	Branched	1	90	204.0	10
Neopentyl	Branched	2	104	Sublimes 213	2
Diethylene	Aliphathic Ether	0	106	245.5	5
Dipropylene	Branched Ether	2	134	231.9	5
Trimethyl-pentanediol (TMPD)	Branched	3	146	215	7
Triethylene	Alipatic Ether	0	150	228	5

Table 9b: A Synopsis of Glycol Considerations

Glycol	Processing and Liquid Resin Effects	Effects on Cured Resin Properties
Ethylene	Causes incompatibility with styrene	Magnifies influences of acids.
Propylene		Good corrosion resistance and structural properties.
1,3 Butylene	Heat sensitive	
Neopentyl		Improves corrosion and weather resistance.
Diethylene		Excellent flexibility, poor corrosion resistance.
Dipropylene		Compromise of flexibility with corrosion resistance.
Trimethyl-pentanediol (TMPD)	Heat sensitive	Good corrosion resistance, embrittles resin. Slow to fully cure.
Triethylene		Excessive flexibility, poor corrosion resistance.

Unsaturated Coreactants

The most widely used reactive diluent for unsaturated polyesters is styrene. Styrene has low viscosity and high solvency, is widely available, and is low cost. Its drawbacks are flammability and potential health hazards at high emissions. Some alternatives to styrene are listed in Table 10a and 10b. Material safety data sheets (MSDS) should be obtained from suppliers before evaluating any reactive monomer.

The dual function of coreactants is to dissolve the polymer for ease of handling and application and to crosslink the polyester chains to form a thermoset, solid plastic.

Most effects of increasing resin dilution on liquid resin properties are self-evident: easier handling and application, faster wetting of reinforcement and fillers, but increased emission of vapors from the solution.

The effects of styrene to polyester ratio on cured resin properties are more complex. Sufficient coreactant is needed to bridge the gap between unsaturation sites of adjacent polyester chains during crosslinking. To obtain good aging properties, all polyester unsaturation should react with monomer. Additional monomer will react with itself to form longer side chains or bridges between the polyester chains. Excessive monomer self-polymerization will tend to force cured resin properties more toward polystyrene than polyester properties.

BP's investigations indicate that cured resin properties are optimized within a fairly narrow range of polyester dilution with monomer. This range is specific to the resin formulation, but with most common formulations a strikingly consistent ratio of monomer to polyester unsaturation optimizes most properties.

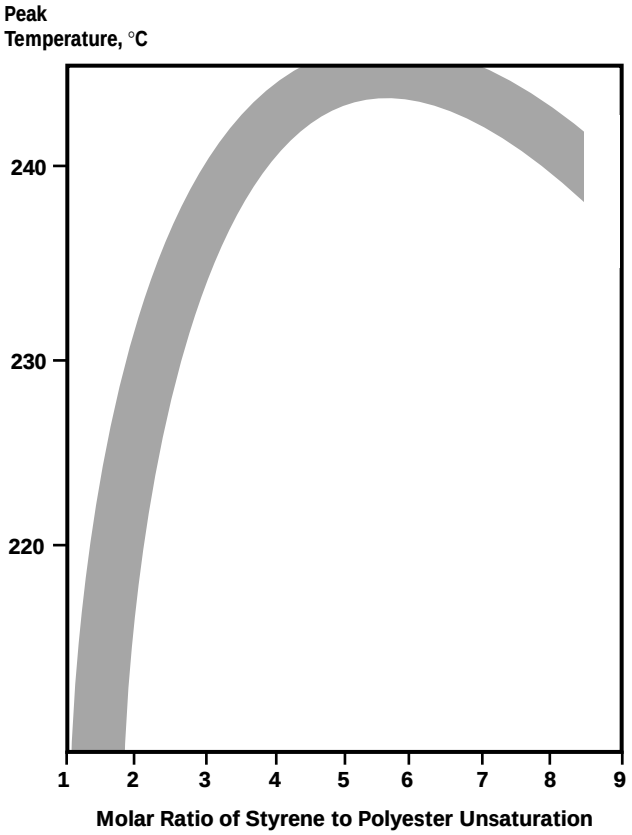
The ratio of monomer to polyester unsaturation can be determined by dividing the moles of monomer unsaturation per 1000 g (9.6 for styrene) by the moles of maleic anhydride (and/or other unsaturation contributor) per 1000 g of polyester and multiplying by the ratio of monomer to polyester in the final resin solution.

$$\frac{\text{moles monomer unsaturation/1000 g}}{\text{moles polyester unsaturation/1000 g}} \times \frac{\text{\% monomer}}{\text{\% polyester}}$$

An example of calculating polyester unsaturation level is shown on page 9.

Because styrene has more unsaturation per unit weight than polyesters, more styrene in the resin solution increases the total amount of unsaturation. Consequently, the total exotherm is higher (Figure 37). Propagation time is longer (Figure 38) with more styrene. The peak exotherm temperature drops at very high styrene levels because heat is dissipated during the long propagation time.

Figure 37: Styrene Content Affects Peak Exotherm



A wide range of vinyl compounds can be used alone or in combination to dissolve and crosslink polyester resins. Typical effects that can be obtained from coreactant modifications include viscosity control, lower exotherm, improved UV stability, lower emissions, higher elongation, different cure temperatures, and better optical clarity. The best balance of cost and performance is frequently reported with blends of styrene with one or two other vinyl compounds. Resin formulators investigating any coreactant should obtain and follow the manufacturer's precautionary information.

Table 10a: Crosslinking Solvents for Unsaturated Polyesters

	Molecular Weight	Boiling Point, °C	Density at 20°C	Unsaturated Mol/kg
Styrene	104	145	0.906	9.61
Vinyl Toluene	118	168	0.897	8.47
t-Butylstyrene*	160	219	0.884	6.25
Chlorostyrene*	138.5	177-185	1.984	7.22
Divinyl Benzene*	131	200	0.929	7.63
Alpha-Methylstyrene*	118	165	0.911	8.47
Diacetone Acrylamide*	169	M.P. = 57	0.998 at 60°C	5.91
Hydroxyethyl Acrylate*	116	82 at 5mm Hg	1.104	8.62
Hydroxypropyl Acrylate*	130	77	1.056	7.69
Methyl Methacrylate*	100	100	0.944	10.00

Table 10b: Crosslinking Solvents for Unsaturated Polyesters, Styrene is the Basis for Comparison

	Liquid Properties	Cured Properties
Styrene	Low Viscosity High Solvency Good Reactivity	High Strength High Modulus
Vinyl Toluene	Higher Viscosity Slightly Shorter Cure	Lower Elongation Slightly Higher Heat Deflection Temperature Less Shrinkage
t-Butylstyrene*	Higher Viscosity	Better Weathering
Chlorostyrene*	Higher Viscosity Shorter Cure	Good Weathering, Higher Heat Deflection Temperature Some Flame Retardancy
Divinyl Benzene*	Higher Viscosity Faster Cure	Harder Higher HDT
Alpha-Methylstyrene*	Lower Emissions Lower Exotherm Longer Cure	Lower Physical Properties
Diacetone Acrylamide*	Much Higher Viscosity Much Longer Cure	Higher Heat Deflection Temperature
Hydroxyethyl Acrylate*	Higher Viscosity Slightly Longer Cooler Cure	Better Weathering Softer, Less Stiff, Lower Shrinkage
Hydroxypropyl Acrylate*	Similar to Hydroxyethyl Acrylate	
Methyl Methacrylate*	Lower Viscosity	Better Weathering, Less Odor, More Clarity More Shrinkage

*Generally used in combination with other coreactants.

Fully cured resin properties indicate a pattern of difference as styrene level is changed. With the same polyester, higher styrene levels will tend to increase the space between sites of crosslinking, thus the stiffness of the cured resin is reduced. Figure 39 shows lower flexural and tensile moduli as more styrene is introduced into the polyester. The curves for strengths and heat distortion temperature indicate that these properties are maximized at an intermediate level of styrene.

This information indicates that polyesters should be reacted with sufficient styrene to obtain somewhat over three moles of monomer unsaturation for each mole of polyester unsaturation. Styrene dilution beyond this point tends to cause polystyrene-like properties to dominate the cured polyester.

With very strong resins, such as the example used for Figures 37 to 41, the introduction of styrene above the 3.6 unsaturation ratio will tend to degrade strengths. However, with a very flexible resin such as those reported in Figure 18, more styrene will strengthen the resin because the flexible resin is not as strong as polystyrene. Tensile elongation of this resin would, of course, be lower with more styrene.

The optimum level of styrene indicated by unsaturation ratio may differ from the level required for easy handling of the liquid resin and thorough wetting of reinforcement and fillers. Resin manufacturers may be able to resolve such discrepancies by careful polyester processing to different endpoints (see page 3), by reformulating to different polyester molecular weights or by using blends of lower viscosity coreactants with styrene.

Figure 38: Styrene Content Affects Propagation Time

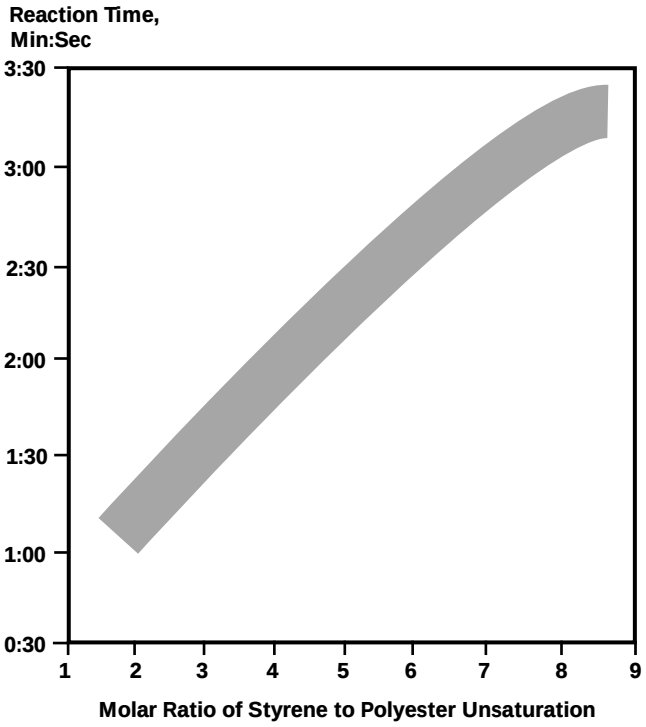


Figure 39: Styrene Content Affects Stiffness

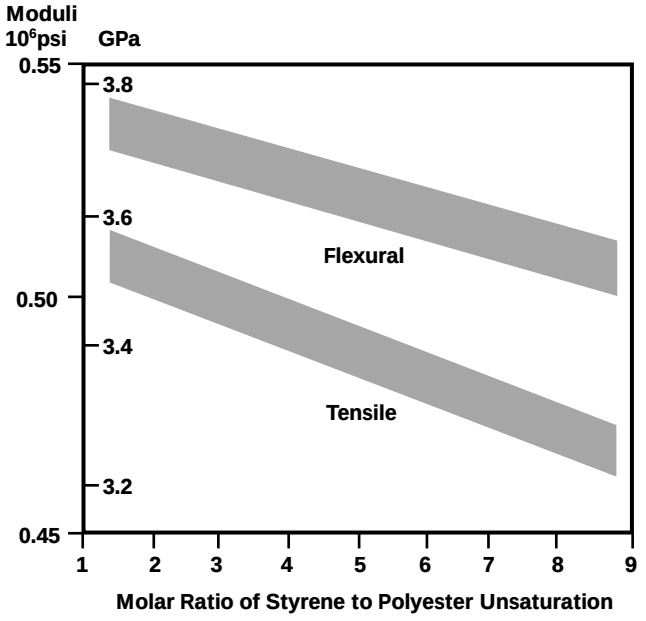


Figure 40: Styrene Content Affects Strength

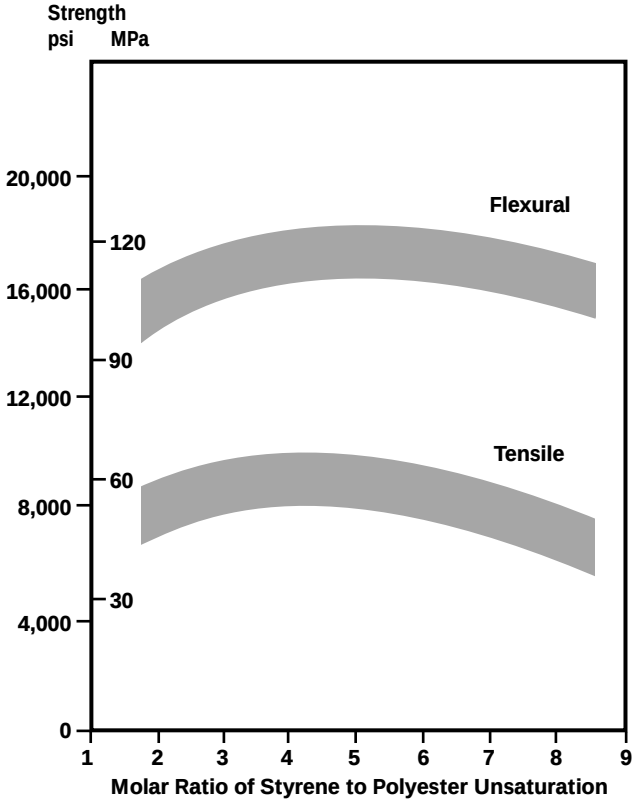
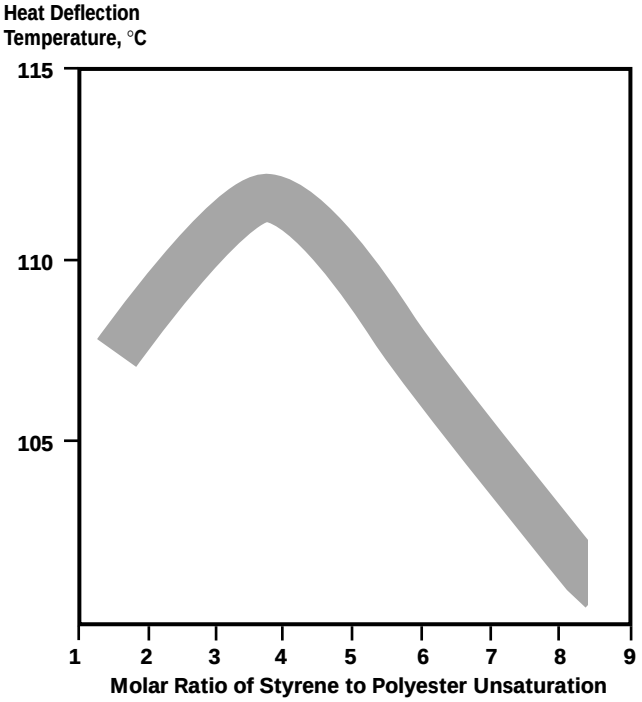


Figure 41: Styrene Content Affects Heat Deflection Temperature



Glossary

Aromatic Acid
Generally carboxyl functional groups on benzene ring. In this bulletin benzene dicarboxylic acids are frequently termed aromatic acids.

BMC
Bulk Molding Compound. A resinous mixture of short reinforcement fibers, fillers, thermoplastic additive and high reactivity resin designed for compression molding.

cis-Configuration
Functional groups attached to olefinic unsaturation located on the same side of the bond axis. Also see trans configuration.

Composite
An aggregation of dissimilar materials, especially combinations of glass fiber and resin.

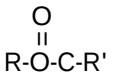
Corrosion Resistance
The ability of a material to resist degradation by environmental factors, especially the ability to resist softening or solvation by liquids.

Crosslink Density
A measure of the frequency of crosslinking sites on the polyester chains.

Cure Time
The time required in the SPI gel test to reach peak exotherm from 65°C (150°F).

Elongation
The maximum extensibility of a material without failure.

Ester
Any compound containing the ester functional group:



Esterification
The chemical reaction of acid or anhydride with alcohol, glycol or oxide that forms an ester.

Exotherm
The heat released during chemical reaction, such as during olefinic and vinyl crosslinking.

Flexural Fatigue
The loss of resistance to flexural stress that occurs with repeated, nondestructive stress.

Flexural Modulus
The ratio of flexural stress to deflection a measure of stiffness.

Flexural Strength
The flexural stress sustainable without fracture.

Flexural Stress
Stress applied perpendicular to the plane of the test sample.

Gel Coat
A surface or appearance layer of unreinforced resin, often containing pigmentation and thixotropic additives.

Gel-Coated Laminate
A laminate fabricated with a gel coat on one or both sides.

Gel Time
The time required for a resin to solidify in the SPI gel test.

Gelation
The phenomenon of resin solidification through molecular growth.

Glycol
Any compound containing two hydroxyl functional groups.

Hardness
The resistance to penetration by the metal stylus of a Barcol or similar hardness tester. Hardness is used to follow the development of resin cure.

HDT
Heat distortion temperature.

Heat Distortion Temperature
The temperature at which a sample coupon is deflected 10 mils by 1820 kPa (264 psi).

IPA
Abbreviation for isophthalic acid.

Iso-
Prefix designating an isomeric structure especially the 1.3 substitution on a benzene ring or simple branching at the end of a straight chain.

Isomer
Compounds with different geometry but identical chemical formulas.

Isomerization
Conversion of a compound from one isomeric form to another.

Isophthalate
Monomeric or polymeric esters of isophthalic acid.

Isopolyester
Polyesters based on isophthalic acid.

Laminate
Composite materials especially sheet and tubes fabricated of thermoset plastic generally reinforced with fibers.

MAN
Abbreviation for maleic anhydride.

Olefinic Unsaturation
Reactive carbon-to-carbon double bond.

Ortho-
A prefix designating 1.2 substitution on an aromatic ring.

Orthophthalate
Monomeric or polymeric esters of phthalic anhydride.

Orthopolyester
Polyesters based on phthalic anhydride.

PAN
Abbreviation for phthalic anhydride.

Peak Exotherm
The highest temperature reached during cure in the SPI gel test.

Polyesterification
Esterification of difunctional carboxyl and hydroxyl-containing materials producing a polyester.

Polyol
Molecules with more than two hydroxyl functional groups.

Polyterephthalate
Polyesters based on terephthalic acid; the term includes both saturated polyesters, such as fibers, and unsaturated polyesters.

Propagation Time
The difference between gel and cure time in the SPI gel test; a measure of in-mold set time.

Reactivity
A measure of the amount of reactive functional groups in a material; especially the amount of maleic unsaturation in a liquid polyester.

SMC
Sheet Molding Compound. Partially thickened, compression molding compound containing medium-length reinforcement, filler, and other additives.

Strain
The physical deformation of a material by applied force.

Stress
The force applied to a material.

TA
Abbreviation for terephthalic acid.

Tensile Modulus
Ratio of stress to strain during tensile elongation, a measure of stiffness.

Tensile Strength
The greatest longitudinal stress that can be survived without fracture.

Tensile Stress
Force applied parallel to the plane or length of a sample coupon.

Tere-
Prefix denoting benzene ring substitution in the 1,4 positions.

Terephthalic polyester
Polyesters based on terephthalic acid.

Thermoplastic
Polymers that melt with heat and become solid when cooled.

Thermoset Resin
Polymers that irreversibly solidify through crosslinking when heated.

Toughness
Strength without brittleness; defined by classical mechanics as the area under tensile stress-strain curve.

trans-Configuration
Functional groups attached to a olefinic group and located diagonally across the bond axis. Also see **cis**.

Unsaturated Polyester
Polyester containing reactive olefinic unsaturation usually derived from maleic anhydride.

Vinyl Compound
Compound containing carbon-to-carbon double bond as a terminal functional group, especially styrene or other reactive diluents.

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A Summary of Trends

Tables 11a, 11b and 11c summarize the information given in this brochure on how formulation variables affect properties of unsaturated polyesters. The statements in this table are necessarily general and assume only one variation at a time.

Table 11a: How Formulation Variables Affect Properties of Unsaturated Polyesters

Formulation Variables	Strength	Moduli (Stiffness)	"Flexibility" or Tensile Elongation
Source of Unsaturation			
Maleic versus Fumaric	No Effect	Fumaric Higher	Maleic Higher
Level of Unsaturation	Depends on Resin Flexibility	Positive Correlation	Negative Correlation
Types of Nonolefinic Acids Isophthalic Acid versus			
Phthalic Anhydride	Iso Higher	Ortho Higher	Iso Higher
Terephthalic Acid	Iso Somewhat Higher	Iso Usually Higher	No Trend of Difference
Adipic Acid	Iso Higher	Iso Higher	Adipic Higher
Type of Glycol			
Straight Chain Aliphatic Glycols	Effect Varies	—	Increased
Branched Glycols	Effect Varies	Generally Higher	Effect Varies
Ether Glycols	Effect Varies	—	Increased
Molecular Weight	Effect Varies	Negatively Correlated	Positively Correlated
Level of Coreactant	Lower on Both Sides of Peak	Varies	Can be Optimized

Table 11b: How Formulation Variables Affect Properties of Unsaturated Polyesters

Formulation Variables	Toughness	Hardness	Heat Distortion Temperature
Source of Unsaturation			
Maleic versus Fumaric	Maleic Higher	Fumaric Higher	Fumaric Higher
Level of Unsaturation	Depends on Flexibility	Positive Correlation	Positive Correlation
Types of Nonolefinic Acids Isophthalic Acid versus			
Phthalic Anhydride	Iso Better	No Trend of Difference	Iso Higher
Terephthalic Acid	Iso Somewhat Higher	Iso Higher	Tere Higher
Adipic Acid	Adipic Higher	Iso Higher	Iso Higher
Type of Glycol			
Straight Chain Aliphatic Glycols	Generally Better	–	Lower
Branched Glycols	—	Higher	Higher
Ether Glycols	Generally Better	–	Lower
Molecular Weight	Positively Correlated	Generally No Effect	Negatively Correlated
Level of Coreactant	Can be Optimized	Generally No Effect	Lower on Both Sides of Peak

Table 11c: How Formulation Variables Affect Properties of Unsaturated Polyesters

Formulation Variables	Corrosion Resistance	Shrinkage	Peak Exotherm of Curing
Source of Unsaturation			
Maleic versus Fumaric	No Effect	No Effect	Fumaric Higher
Level of Unsaturation	Optimized at 1:1	Positive Correlation	Positive Correlation
Types of Nonolefinic Acids			
Isophthalic Acid versus			
Phthalic Anhydride	Iso Better	No Effect	No Effect
Terephthalic Acid	Iso Better	No Effect	No Effect
Adipic Acid	Iso Better	Adipic Greater	Usually Higher
Type of Glycol			
Straight Chain Aliphatic Glycols	Lower	No Effect	–
Branched Glycols	Better	No Effect	Can Lower
Ether Glycols	Lower	No Effect	–
Molecular Weight	Effect Varies	Negatively Correlated	Negatively Correlated
Level of Coreactant	Positively Correlated For Many Media	Positively Correlated	Positively Correlated Over Normal Range

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BP
Sales Administration and Customer Service
150 West Warrenville Road
Naperville, Illinois 60563-8460
Toll-free: 877/701-2726
Fax: 630/961-7700

BP
Building A, Chertsey Road
Sunbury-on-Thames
Middlesex TW16 7LL
United Kingdom
Telephone: 44 (0) 1932 767627
Fax: 44 (0) 1932 767914

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