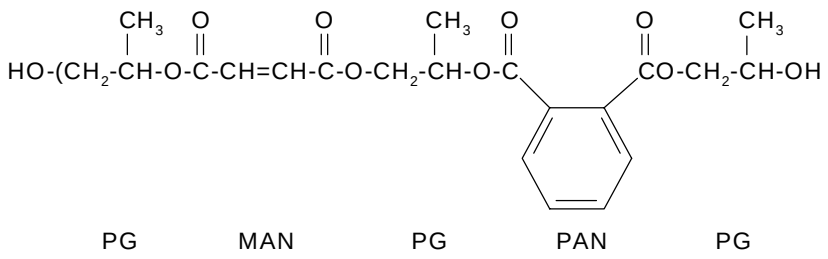
Unsaturated Polyesters (94/95S7)

The chemistry of unsaturated polyesters (UPRs) and vinyl esters (VEs) is highly flexible and adaptable and is intimately linked to their characteristics in product fabrication and to finished product properties. Depending on the application the physical properties and chemical resistance of the end product can often be designed by judicious selection of reaction feedstocks that form the resin backbone and the type and amount of vinyl monomer/diluent. The physical properties and chemical resistance of the cured resin is greatly related to the molecular structure of the three-dimensional thermoset polymer network and to the nature and amount of fillers and additives.

Conventional unsaturated polyester resins are viscous liquid mixtures of relatively low molecular weight polymers. The resins are formed stepwise by stoichiometric polycondensation reactions between various combinations of saturated and unsaturated dibasic (dicarboxylic) acids or anhydrides (e.g. phthalic anhydride, maleic anhydride, and isophthalic acid) with polyols, specifically dihydric alcohols (diols) (e.g. propylene, ethylene, and higher glycols and oxides). An idealized polymer resulting from a typical formulation might have the following structure:



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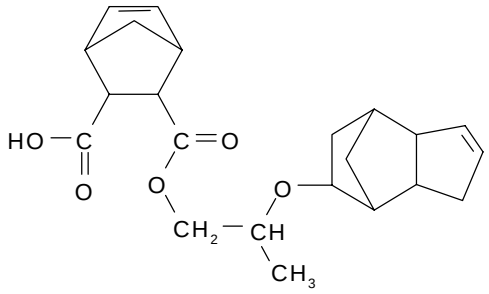
The unsaturated acid functionality is key in enabling crosslinking (curing) of the low molecular weight polymers in the mixture, during product fabrication. In most cases, this quality is derived from the use of 1,2-olefinic acids, primarily maleic anhydride or maleic acid. As a second step in production, the prepared resins are mixed with large proportions (25 to 50 percent) of a solvent that is also a copolymerizable vinyl monomer, usually styrene. The monomer serves as the diluent, which lowers the viscosity at ambient conditions for the mixture to be appropriately used in fabrication, and as the crosslinking agent in the thermosetting reaction. The stoichiometry is such that the styrene can be completely consumed in the crosslinking reaction during fabrication. The term “reactive diluent” is sometimes used to denote the role of styrene in these systems.

Dicyclopentadiene (DCPD) is a low cost byproduct of refineries and olefin units. It has been available for a number of years in the United States, but only recently has it been recovered and available in the European Union (EU). DCPD is increasingly used as an alternative to isophthalic acid (IPA) and PAN in producing lower cost resins with lower viscosity and somewhat lower strength. However, DCPD based resins also have good thermooxidative resistance at high temperatures. Thus, besides being used as low

performance, general purpose resins, they also are used in certain electronics applications. DCPD must be reacted first with maleic anhydride and maleate esters of glycols.

Idealized DCPD Propylene Glycol Maleate Adduct



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Considering that UPRs were developed in the mid-1940s, there has been a remarkable lack of integration of resin manufacturers with feedstock suppliers and/or with manufacturers of FRP and other resin products. One reason for this is that UPR/VE/FRP are specialty (performance) businesses, from production of many of the important feedstocks and additives through the fabricated products. Feedstock choices have been opportunistic and performance driven and the chemistry is somewhat more flexible than with many thermoplastics and other thermosets. Exceptions are the dominant basic feedstocks, maleic anhydride and styrene, and (less so) specific glycols and phthalates. Some of these feedstocks are commodities, but UPRs generally comprise only a partial, or even minor, aspect of the market (such as with styrene). Thus, backward integration would have limited attraction. Also, few of the fabricated end products are commodities (e.g. in the sense of plastic film or bottles). Nonetheless, there has existed an extraordinary partnership between UPR and FRP interests over the years since the industry's inception. The joint interests of this partnership have been in improving end product performance, increasing design options, developing new markets, and reducing resin costs and styrene emissions.