

Chemical/Physical Reactions of Renfil™  
With  
Unsaturated Poly Ester Resins  
During Polymerization

Much has been made of the lignin content of Renfil™ and the interaction of Renfil™ with the unsaturated polyester resins during the polymerization and curing of fiberglass composites. The following narrative will attempt to describe some of the interactive chemistry that involves Renfil™ and polyester resins. Much of the chemistry that will be discussed evolved from studies that were performed at Texas Tech University.

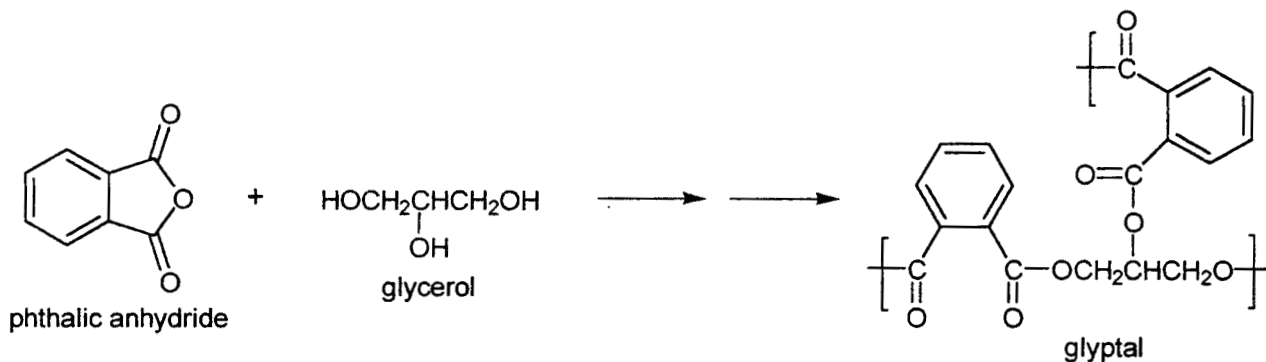
Lignin is understood to consist of natural polymeric products arising from enzyme initiated dehydrogenative polymerization of three alcohol monomers: (1) trans-coniferyl, (2) trans-sinapyl, and (3) trans-p-coumaryl alcohol. Diagrams of these three monomers of lignin are attached. The monomers have methyl esters attached to the main, p-hydroxyphenylpropylene group. Hardwoods contain all three of these precursors, while soft woods only two, and grasses contain predominantly the less stereo-hendered coumaryl group. It is believed that Renfil™ contains from 5% to 15% by mass of these compounds as low molecular weight oligomers, i.e. dimmers and trimers. These lignin precursors are readily extracted from the Renfil™ and function as reactive moieties during the cross linking chemistry of the unsaturated polyester resins. Even the higher molecular weight lignin fraction of the Renfil™ is reported to have one unsaturated double bond per every 40-60 C<sub>9</sub> subgroup, and, therefore, Renfil™ would too provide a reaction site for the free radical initiated styrene polymerization.

Also attached is a brief description of the general chemistry associated with unsaturated polyester resins. The chemical units that make up unsaturated polyester resins are very similar to the structures just described as lignin monomers. The ring structures of the phthalic and maleic anhydrides mimic the phenyl groups of the lignin, while the double bonds in the structures of the polyglycols provide the free radical bonding sites for the styrene cross links. The styrene monomer used to dissolve the polyester resins and ultimately provide the cross linked structure of the cured resin is itself very similar in structure to the lignin monomers.

So, if it assumed that good miscibility exists between the lignin monomers extracted from the Renfil™ and the bulk unsaturated polyester resin, how does this effect the polymerization chemistry. We believe that when the Renfil™ is added to the polyester resin the following events occur. Styrene monomer is drawn into the Renfil™ structure, which has a high oil adsorption number, while the lignin monomers are being extracted by the polyester resin. Then when the catalyst initiates the free radical reactions that lead to the final cross-linked structure, the lignin is also available to participate. Because the lignin fractions have longer chains than the ethylene groups of the styrene cross links, a more flexible (tougher) cross-linked structure is formed. This tougher structure, together with the chemical bonding produced with the Renfil™ particles, provides a new structure in the cured resin that helps stop brittle crack propagation and premature composite failure.

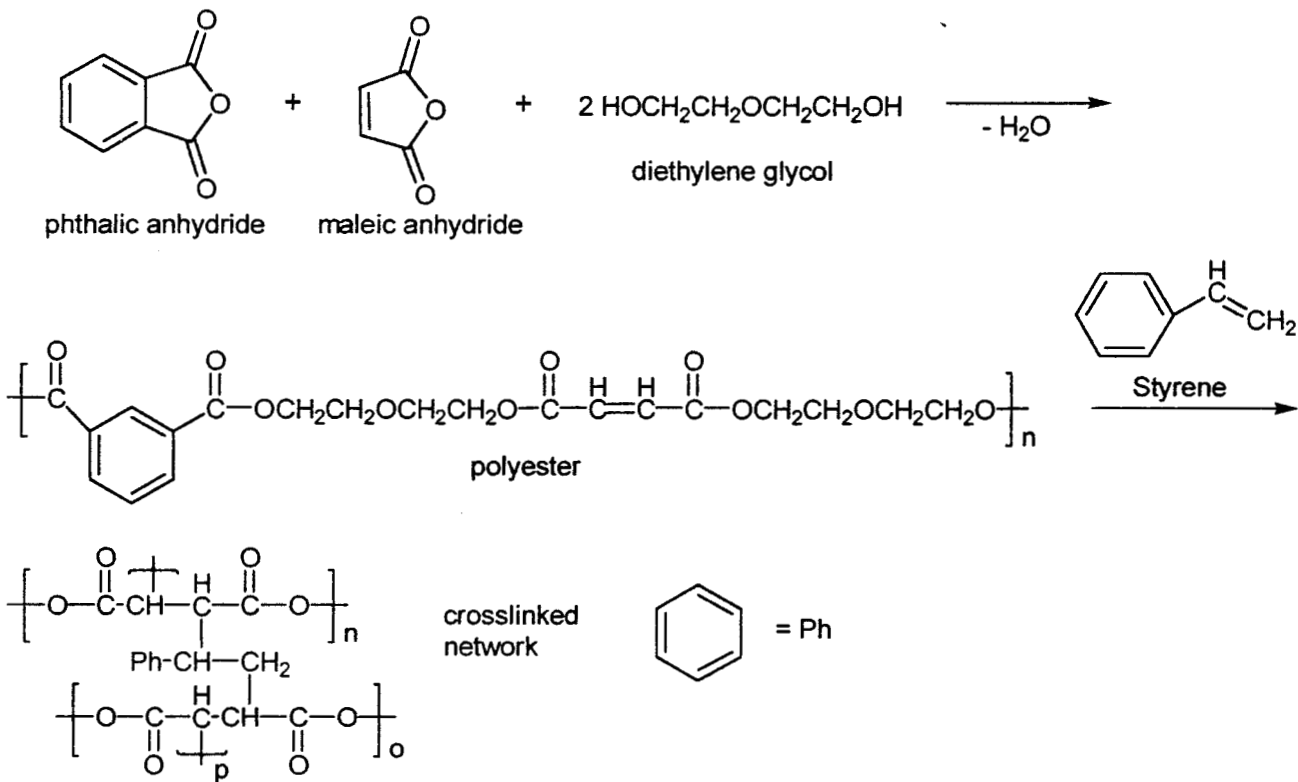
### Unsaturated Polyesters

Polyester resins (1.26 billion pounds produced in 1993) are widely used in construction and marine applications. Network formation distinguishes polyester resins from linear (thermoplastic) polyesters such as PET. Crosslinking is achieved either by use of polyols such as glycerol, as in the case of saturated polyesters (glyptal), or by the use of unsaturated dicarboxylic acids, such as maleic anhydride in the case of unsaturated polyester resins. Glyptal, which is used mainly as an adhesive or modified with natural or synthetic oils (oil-modified alkyds) for coatings, is formed by the reaction of glycerol and phthalic anhydride, as shown in Figure.9.11. The reaction is allowed to continue until a viscous liquid is obtained. The liquid can then be transferred to a mold for further network development hardening).



**Figure 9.11** Formation of glyptal resin by the reaction of phthalic anhydride o glycerol.

Unsaturated polyester resins, which are used as the matrix component of glass fiber composites, may be obtained by copolymerization of both saturated acids (e.g., phthalic anhydride) and unsaturated acids (c.g., maleic anhydride) with a diol such as propylene glycol or diethylene glycol, as shown in Figure 9.12., incorporation of the saturated acid serves to decrease crosslink density and consequently resin brittleness. Fumaric acid may be used in place of maleic acid to increase impact resistance. The low-molecular-weight product is soluble in styrene, which can then participate in a crosslinking step with the double bonds of the prepolymer during initiation by peroxides.



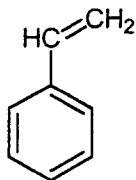
**Figure 9.12.** Formation of unsaturated polyester resin.

Taken From the Network Polymers: Elastomers and Thermosets (pgs. 330-331)

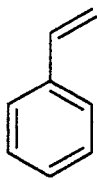
## 2 D Chemical Structures

### STYRENE

CH=CH<sub>2</sub>    C<sub>8</sub>H<sub>8</sub>    <sup>5</sup>HS=171  
STYRENE    CAS=100-42-5



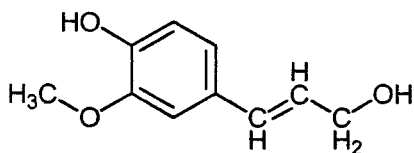
Styrene



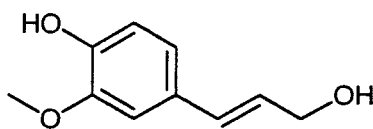
Styrene

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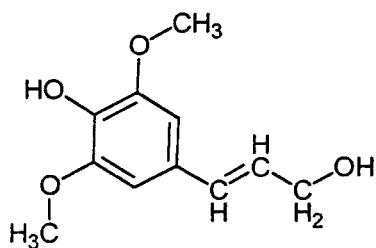
### Primary Precursors of Lignin



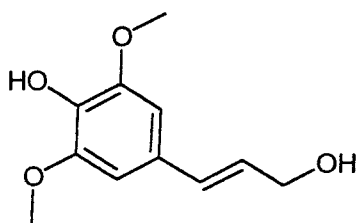
*trans*-Coniferyl alcohol



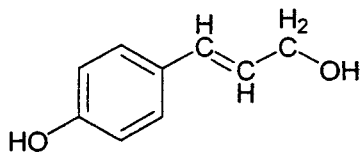
*trans*-Coniferyl alcohol



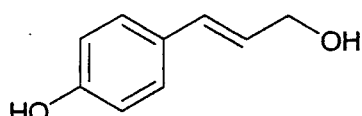
*trans*-Sinapyl alcohol



*trans*-Sinapyl alcohol



*trans*-p-Coumaryl alcohol



*trans*-p-Coumaryl alcohol

Photomicrographs of Fibrous Glass at the break showing Renfil™ chemically bonding to the glass

