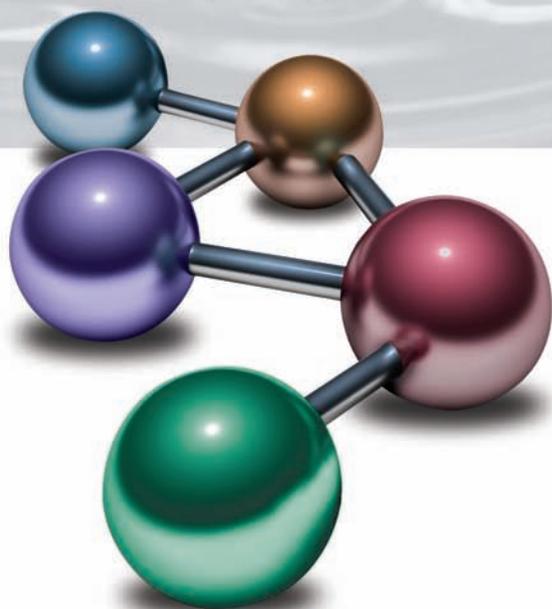




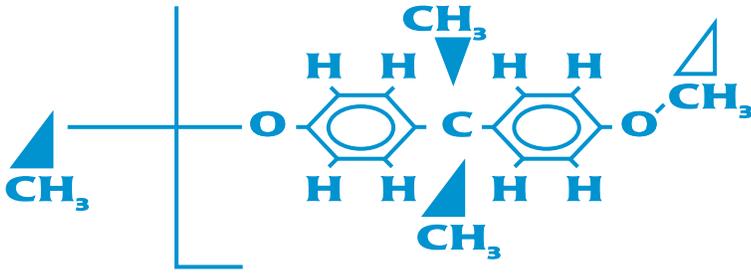
INTERPLASTIC CORPORATION  
Thermoset Resins Division



The Right Chemistry.  
That's What We Bring  
To Vinyl Ester Resins.



CoREZYN<sup>®</sup>  
Vinyl Ester Resins



## All You Need to Know About Vinyl Ester Resins

Vinyl ester resins are epoxy-based, thermosetting resins that are cured by free-radical initiation of polymerization, similar to the curing mechanism of conventional polyester resins. There are numerous types of reactants that make up the vinyl esters so that each resin has its own characteristic properties. However, the chemistry can be typified by the most versatile of these resins. This vinyl ester is the reaction product of a Bisphenol-A (BPA) epoxy and methacrylic acid.

The terminal carbon-carbon double bonds cross-link in a free-radical initiated polymerization. In effect, this structure allows an epoxy to react like a polyester. This by itself is very important since epoxy reactions in general are very sluggish compared to the polyester free-radical reactions. Another important feature of this structure is that it is styrene soluble; the styrene also enters into the free-radical reactions. Since styrene solutions of vinyl ester resins have low viscosity, the resultant resin solution is easily worked in the reinforced plastic processes. Epoxy resins, on the other hand, are high-viscosity materials and require more difficult and expensive processing methods.

Compared to epoxies, the vinyl esters are fast and easy to work with, quick curing and versatile. At the same time, they have been designed to retain most of the desirable properties of epoxy resins. Tensile strength, elongation and fatigue resistance of BPA vinyl esters, for example, are very close to that of the premium aromatic amine-cured epoxies, and are significantly greater than a typical orthophthalic resin, as shown in Graphs 1–4.

Because of the versatility when building from an epoxy molecule, other useful modifications become obvious when building vinyl esters for composite use.

## Novolac Epoxies

Beginning with a Novolac, in contrast to the BPA epoxy, gives (after proper design of the molecule and manufacturing in sophisticated resin reactors) a vinyl ester with superior properties at elevated temperatures, and higher capabilities in resistance to solvents and corrosive blends or mixtures of chemicals. These Novolac vinyl esters, while more costly compared to the BPA vinyl esters, are among the most corrosion-resistant unsaturated polymers available with the unbeatable vinyl ester capabilities of relative ease of gel and cure.

# Fire-Resistant and Corrosion-Resistant Vinyl Esters

These are designed from intermediates already containing the halogen (fire-resistant) component. Hence, when the scientists are "building" the vinyl ester from a BPA epoxy, they can build in the fire-resistant component by reacting it to the epoxy. Of course, the familiar additives, such as antimony compounds and halogenated waxes, also work similarly in these fire-resistant vinyl esters, as they do in fire-resistant polyesters.

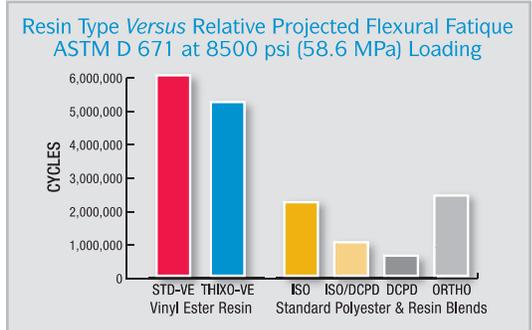
The excellent adhesive characteristics of this BPA epichlorohydrin vinyl ester are the same as the adhesive properties epoxies are well known for. This is demonstrated by the compatibility with and bond strength of vinyl esters to glass, graphite fibers and to the newer high-strength organic fibers such as Kevlar®.

The chemical resistance of vinyl esters represents the best of the two worlds: the excellent alkali resistance of the epoxy, and the acid and oxidizing chemical resistance of the polyester. The alkali resistance is retained since there are relatively few ester linkages – only as terminal groups. These terminal ester groups are made hydrolytically stable by the hindrance afforded by the methyl group of the methacrylic acid. See our award-winning research paper, "15-Year Study of the Effective Use of Permeation Barriers in Marine Composites to Prevent Corrosion and Blistering," which graphically shows the results of water immersion tests on a variety of resins, including the thixotropic marine composite vinyl ester, and dramatically demonstrates this characteristic.

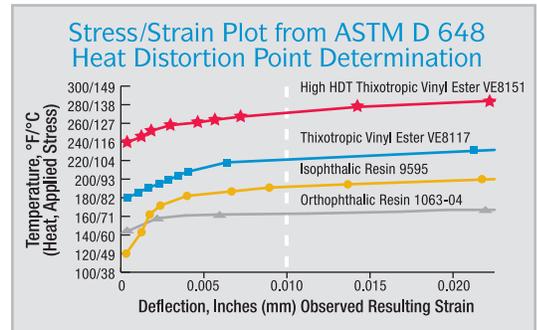
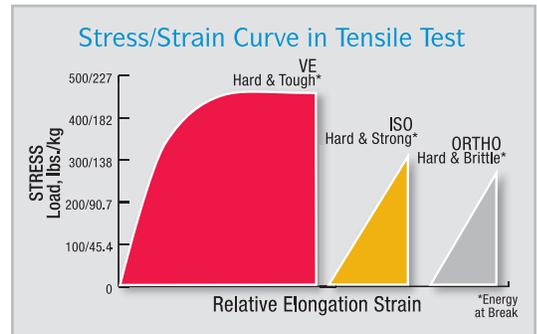
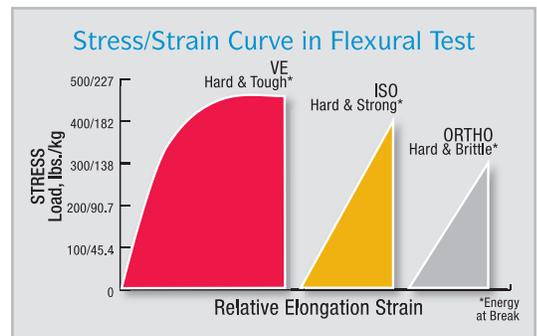
In addition, the copolymerized styrene offers steric hindrance protection to acid and oxidizing chemical attack on the ester groups. Further enhancing the overall chemical resistance of the vinyl ester, the reactive double bond sites are present only as terminal groups. These easily accessible terminal groups leave minimal residual reactive sites that would be subject to attack by corrosive chemicals in service. In contrast, conventional polyester resins have reactive double-bond sites and ester linkages throughout their molecular structure. The resulting widespread structural vulnerability greatly reduces their corrosion resistance when compared to the premium vinyl ester products.

Generally speaking, corrosive attack on unsaturated resins occurs through unreacted double bonds in the resin or through hydrolysis of the ester linkage. The great advantage of vinyl ester is that the only reactive double carbon-carbon bonds are at the ends of the molecule and hence very susceptible to reaction with the double bonds (the "vinyl unsaturation") of the styrene monomer or (another great advantage of vinyl esters over polyesters) to itself. The ester linkages in polyesters occur throughout the molecule, leaving those resins much more susceptible to attack at those sites than are vinyl esters, which only have one ester linkage at each end of the molecule.

In summation, in epoxy-based vinyl ester resins, we have manufactured a polyester-type resin with all the advantages in handling characteristics, plus the superiority in physical properties and corrosion resistance the epoxy molecule imparts. Heat resistance, superior corrosion resistance, fatigue and binding resistance, as well as superior reinforcement adhesion are all obtained when designing with vinyl ester resins.



Graph 1: Vinyl esters for outstanding fatigue resistance.



Graph 2, 3 and 4: Mechanical properties.



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