

# STRATEGIES FOR LOW STYRENE RESINS

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## **Purposes of Styrene**

Styrene is added to unsaturated polyester resins and vinyl ester resins for two major purposes — (1) to dilute the mixture for effective viscosity control so that the fibers can be wetted; and (2) to serve as a crosslinking agent and promote the ease of crosslinking of the resin. Materials, like styrene, that simultaneously accomplish both of these purposes are called “reactive diluents.” Other active diluents exist, such as methyl methacrylate, but because of the predominance of styrene in the unsaturated polyester and vinyl ester resin market, our focus will be almost exclusively on styrene.

The ability of styrene to accomplish these two purposes has resulted in lower costs overall and improved performance and manufacturing efficiencies. Imagine, for instance, a diluent that was non-reactive. This would require that the diluent be removed during molding. Several epoxy and other high performance resins have this problem and, as a result, are difficult to use and are more costly.

The excellent reactivity of styrene means that the styrene is generally used up in the crosslinking reaction. Styrene forms a part of the cured polymer, generally at a lower cost than the backbone resin system itself. When it has been crosslinked, styrene imparts stiffness to most cured systems (and also some brittleness), but generally enhances the physical properties of the finished product.

Styrene is also an effective and relatively inexpensive diluent. It is able to easily dissolve most of the important resins and, thus, allow easy wetout of the reinforcement. Hence, styrene is nearly ideal from a functional standpoint. However, as you all know, styrene is listed as a hazardous air pollutant (HAP) which emits a potentially dangerous vapor. Therefore, the amount of styrene emitted in the manufacture of FRP parts must be reduced. We will now examine some of the strategies being pursued by the resin manufacturers to reduce the styrene content of their products.

The chemistry of making these changes to reduce styrene content is complex. Therefore, the discussion which follows on the various strategies to low styrene content will be simplified. The focus will be on the direction and concepts behind the changes rather than the details.

### **Strategy One — Modifications of existing polymer systems**

The initial effort by almost all of the resin manufacturers, unsaturated polyesters and vinyl esters, was to modify their existing resin systems so that less styrene would be needed. This strategy was not only prudent commercially, it also gave quick results.

The resin manufacturers realized that if the viscosity of the base resin were lower, the amount of styrene needed to achieve a good viscosity for fiber wet out could be reduced. The first method to reduce the viscosity of the base resin was to shorten the molecular chains, that is, to reduce molecular weight of the resin. Shorter chains have less intermolecular entanglement and, therefore, flow more easily. This means that the viscosity is lower.

The amount of styrene needed in these lower molecular weight resin systems has been successfully reduced. That reduced level of styrene, which was dictated by viscosity control requirements, has also reduced the amount of styrene available for crosslinking. Therefore, the

nature of the crosslinking also changed. The question is, “How has crosslinking changed the resulting polymer properties?”

Two different crosslink characteristics (lower overall styrene content and higher crosslink density) occur simultaneously with these low molecular weight resin systems. The lower amount of styrene available for crosslinking results in a “starved” situation during crosslinking. This starving means that the number of styrene molecules in each of the crosslinks is reduced. (Under excess styrene conditions, multiple styrene molecules join together to form long crosslinks. Under starved conditions, each crosslink would be formed with only one or two styrene molecules.)

The reduction in the total amount of styrene contained in the crosslinks, and therefore, in the cured polymer, would normally lead to lower overall brittleness since styrene is inherently brittle. However, the shorter polymer chains means that the carbon-carbon double bonds occur more frequently and this results in a higher number of crosslinks being formed overall. This higher crosslink density would normally increase brittleness. Therefore, the effects on brittleness from the reduction in styrene content and from the increase in crosslink density approximately cancel and the brittleness is about where it would be in the unmodified resin system.

Generally heat distortion temperature and solvent resistance will be increased by higher crosslink density. Other properties, such as blister resistance, ultra-violet light resistance, chalking, cracking, and surface smoothness, may also be affected but the extent of these effects must be evaluated on a case by case basis with each resin and application. These effects are much more important in gel coats than in laminating resins and should, therefore, be examined closely before any change in gel coat resin is made.

Another modification in current resin systems is a change in molecular weight distribution. This is not just a shift to lower molecular weights but, rather, a change in the statistical spread of the molecular weights of the polymers. Even when the average molecular weight is still quite high, the presence of a significant quantity of low molecular weight molecules has a tendency to make all the molecules slide over each other more easily, thus lowering the viscosity. This lower viscosity allows less styrene to be used.

### **Strategy Two — Developing new polymer systems**

Polyesters are made from the reactions of di-acids and glycols. Resin producers have found that by varying the types and quantities of di-acids and glycols, the resin properties can be significantly changed. (For instance, the differences between ortho and iso resins are just in the choice of acid that is reacted.) Therefore, many possibilities exist for changing the nature of the base polyester resin.

In addition to different combinations of previously used components, some completely new di-acids and glycols are being tried. (Some resin manufacturers call this the clean-slate approach.) The resin manufacturers are reluctant to disclose the details of these changes because of competitive reasons, but it is safe to say that all of the major resin manufacturers are working on innovative new resin structures that will enable the styrene content to be reduced. We should anticipate that within the next few years, many new products will be announced.

Without disclosing any proprietary information, a few basic concepts can illustrate some of the directions that the resin producers are investigating. Some of the acids and glycols (like neopentyl glycol) are known to be more soluble in styrene than the other common components. This increased solubility comes from both molecular shape and chemical polarity effects. At the

same time, these alternate components might give additional benefits such as increased toughness or heat distortion temperature. Therefore, the new resins might have both reduced styrene content and improved physical properties, or at least no major reduction in properties as a result of the decrease in styrene.

Some resin manufacturers have found that new resin systems requiring lower styrene concentrations can be made by varying the sequence of addition of the di-acid and the glycol components. These changes occur because mixtures of multiple types di-acids and glycols are often used in making the polyester resins which have different reactivities. An example of such a change would occur under these two scenarios. If two di-acids are mixed together and then added to the glycols, the distribution of the acids could be random. However, if one of the di-acids is added to the glycols and then the second added later, the result could be a preferential positioning of the second di-acid at the ends of the polymer. Hence, two very different polymers could be formed.

The sequence of components along the backbone resin can also be altered by changing the addition sequence because of differences in reactivities of the components. A particular component could be forced to group together or to be dispersed to the ends depending on its relative reactivity with respect to other components and when they are added. Some have called these changes one-stage and two-stage additional polymers.

Using known principles and new technologies, the resin manufacturers are attempting to create shapes and chemical natures that favor lower styrene contents.

Occasionally a polyester is made using a component other than a di-acid and glycol, such as dicyclopentadiene (DCPD). This material can be used to react with maleic acid and glycols to

form a low molecular weight chain of only a few units. Such units are often called “adducts” because a few units are “added together.” The net result of mixing DCPD with maleic acid and ethylene glycol is an adduct of DCPD—maleic—glycol—maleic—DCPD. This adduct has low molecular weight and, therefore, low styrene requirement. The net result is a resin with fast cure cycles, good reinforcement print hiding, good fiberglass wetout, good moisture resistance, good stiffness, and good air bubble elimination when compared with many conventional resins.

Vinyl esters properties can also be changed significantly by modifying the nature of the backbone. Vinyl esters tend to have more options available for these modifications of the resin backbone and, of course, the specific natures of the changes are different, but the concepts discussed in this section are similar between vinyl esters and unsaturated polyesters.

Another major area of focus is the blending of unsaturated polyesters and vinyl esters with other polymer types. These blends can be done as monomers (in which case they are often referred to as copolymers) or as blends after full polymerization has been done (in which case they are referred to as mixtures). Some of the interesting blends with unsaturated polyesters include: polyurethanes, melamines, phenolics, epoxies, and vinyl esters. In general, these blended polymers are higher in cost than the basic polyester, but the properties of the blend can be substantially better, thus allowing for the use of less resin or of entering new markets.

### **Strategy Three — Other monomers**

Styrene is not the only monomer that acts as a reactive diluent for unsaturated polyesters and vinyl esters. Therefore, some alternate monomers which have lower vapor pressures are being investigated as styrene alternatives. One approach is to choose monomers that are similar to styrene in chemical reactivity but have a higher molecular weight and, therefore, a lower vapor

pressure. For instance, vinyl toluene is very similar to styrene (having just an additional methyl group on the benzene ring) but has a lower vapor pressure and, therefore, lower air pollution potential. Another example is t-butyl styrene. The major problem is the higher cost of these alternate monomers.

Another approach is to simply combine two or three styrene molecules together and then use these dimers and trimers as the reactive diluents. (Very short chains such as these are sometimes called oligomers.) Performance of these materials is almost the same in the cured product, and wet out of the fiberglass is still excellent since only enough of the dimers and trimers is added to achieve the same viscosity used with the monomer. However, the cost of producing the dimers and trimers is significant.

Some have been looking at using completely new monomers that are not like styrene at all. The prime example is methyl methacrylate (MMA), sometimes known as acrylic. This material also has a high vapor pressure and so it is also considered a hazardous air pollutant (HAP) but may be more compatible with some polymer systems and, therefore, allow lower concentrations to be used to achieve acceptable viscosities. MMA can also give some improved properties (such as lower smoke generation). Again, cost is a problem.

#### **Strategy Four — Suppressants**

Yet another strategy is to form a surface layer to suppress the emission of styrene. Layers such as this, often formed by adding wax to the resin mixture, have been used for many years to exclude oxygen so that cures can be improved. Hence, this concept is really using an old technology for a new purpose. The problem with this method has always been the potential for poor bonding wherever the wax is present. This adhesion problem has been alleviated somewhat

by creating adhesion-promoting films. These films contain carbon-carbon double bonds, thus allowing crosslinking to occur through the film. Adhesion between materials on both sides of the film is thus promoted.

These film-forming materials work best on horizontal surfaces and when the materials are quiescent (that is, non-turbulent). Hence, if sprayed, they will form best if allowed to sit for some time. Non-horizontal surfaces will form some films, but they are not as effective. To alleviate these problems, some of the film forming systems contain excess thixotropic agents to ensure that the resin stays on the vertical surfaces and becomes quiescent.

The use of highly thixotropic materials can, in themselves, reduce solvent escape. The paint industry has successfully used this technology for some time. (That is why some paints are so thick when in the can but smooth and spread easily when brushed, rolled, or sprayed.) Perhaps there are other lessons that can be learned from the paint industry.

### **Summary**

The resin manufacturers are working very hard to reduce the amount of styrene in their resin systems. Some excellent success has already been achieved and more success is shortly to be announced. Some important new scientific principles are being discovered and, hopefully, these will lead to even greater successes in the future.

Undoubtedly, these new resins will require some changes in product design, manufacturing and molding. Along with the improved techniques in manufacturing, the amount of styrene moving into the atmosphere will surely be significantly reduced.

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