

UNDERSTANDING EPOXIES

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What are epoxies?

Just as polyesters are a family of thermosetting resins with some basic similarities, epoxies are also a family of thermosetting resins with characteristics unique to themselves. The differences in characteristics between polyesters and epoxies arise from many features of the polymers, but the root of the differences is the presence of one or more epoxy chemical groups (also called oxirane groups) in epoxy resin molecules and, in polyesters, the presence of the polyester and carbon-carbon double bonds.

The epoxy chemical group is pictured in Figure 1a. Epoxies crosslink at the epoxy sites as illustrated in Figure 1b. Note that the epoxy molecule is combined with a hardener material to effect crosslinking (curing or hardening) whereas polyesters crosslink at the carbon-carbon double bond (unsaturation) using styrene and a peroxide. No styrene or peroxides are needed for epoxies. Several types of hardeners are available for curing epoxies, and the nature of the hardeners will be discussed later in this article. The type of hardener can have a major effect on the properties of the cured material.

This article will explore the molding characteristics of epoxies, generally in comparison with polyesters and will then look at properties and some of the uses of epoxies, especially where epoxies are dominant in that use. We will explain why epoxies are the most widely used matrix material in the field of advanced performance composites and what value epoxies might have in

general FRP materials. Some of the molding considerations for epoxies will also be explored and compared to polyester molding methods.

Comparison of epoxy and polyester molding conditions

One of the great advantages of epoxies is the wide variety of cure conditions that can be used to achieve a good cure. This variety of conditions arises because epoxies cure by the reaction of two materials — resin and hardener (curing agent) — both of which can have a wide variety of properties. Polyesters, too, have a wide variety of resin choices available, but the curing agent is almost always limited to peroxide catalyst with styrene. Therefore, in considering epoxy curing conditions and comparing them to polyester cure conditions, both the type of resin and the curing system need to be considered with epoxies.

The processing of epoxies and polyesters are compared in Table 1. As already indicated, the active site for crosslinking in the epoxy molecule is the epoxy ring, whereas the active site in polyesters is the carbon-carbon double bond. The shelf lives of the two materials are directly related to the nature of the crosslinking reactions. With epoxies, the crosslinking reaction does not begin until the hardener is added. Even then, because the reaction requires a hardener molecule for every epoxy reacted, the reaction proceeds slowly and only to the extent that hardener is available. With polyesters, any source of free radicals (peroxides, sunlight, contaminants) can initiate the reaction and the reaction can proceed extensively because, once the reaction begins, it will continue through a chain reaction mechanism. This tendency to proceed by a chain reaction mechanism is why inhibitors are needed for polyesters. Inhibitors are not needed with epoxies.

The styrene in a polyester system acts as both a solvent for the materials and as a participant in the crosslinking reaction. The styrene facilitates the speed and the extent of the crosslinking reaction in polyester system. Usually epoxies have no solvent, although in some cases where the epoxy or the hardener is a solid or the viscosity is very high, a solvent can be used. In these cases, the solvent chosen usually contains a single epoxy ring, thus allowing it to participate in the crosslinking reaction and become part of the final material, much like occurs with styrene.

Although some accelerators are available for epoxy systems, they are rarely used. This reflects the predominance of high temperature curing for epoxies where the acceleration of the cure is provided by thermal energy. Because of the need for high temperatures for curing most of the epoxies, the pot life can be adjusted based on the temperature used. When room temperature epoxies are used, accelerators are common, especially with some of the hardener systems.

Viscosities are a major problem with many epoxy systems. The resins and hardeners are often chosen to provide stiffness, strength, toughness, and high thermal stability. These properties are usually achieved by using higher molecular weight polymers in the resin, hardener, or both. The higher molecular weights mean more entanglement at the molecular level and this causes higher viscosities. Hence, fiber wet-out using these high viscosity systems is more difficult than with low viscosity resins.

The volatiles from the polyester system are, of course, from the styrene. Although epoxies do not use styrene and can, therefore, be expected to have lower volatile organic compounds (VOC), it should be noted that some of the hardeners used with epoxies have

relatively high vapor pressures (although still less than styrene) and can, therefore, have moderately high volatiles. Some of these volatiles may be toxic or skin irritants.

Because epoxies cure through direct reaction of the hardener molecules with the epoxy rings, mutual migration of the epoxy and hardener molecules is required for them to get close enough to react. This migration is facilitated by high temperatures, but even then takes more time than the reactions of polyesters which require far less migration of molecules. Therefore, the reaction rates of epoxies are usually longer than polyesters. Furthermore, as the polymers become crosslinked, the ability of the molecules to migrate is diminished. This results in lower crosslinking and, therefore, the frequent need for post curing.

The lower shrinkage of the epoxy is related to the low overall crosslink density. Most epoxies have only a few crosslink sites per molecule — typically 2 to 4. Polyesters, on the other hand, can have many carbon-carbon double bonds per molecule and, therefore, higher crosslinking. This higher crosslinking in polyesters draws the molecules together and causes shrinkage.

Comparison of epoxy and polyester properties

A comparison of several key properties of epoxies and polyesters is presented in Table 2. The comparisons are quite general, showing mostly trends and relative values, because both epoxies and polyesters are families of resins with many different materials and much overlap between the two groups. However, the basic characteristics of the two groups are different enough that the comparisons given in Table 2 can be quite useful.

Probably the most widely recognized property of epoxies is their excellent adhesion to a very broad range of substrates, including reinforcing fibers. Hence, one of the major uses for

epoxies is as an adhesive and as a matrix for composite materials. The superior shear strength of epoxies, compared with polyesters, further adds to the value of epoxies as adhesives and a matrix for composites.

Epoxies, especially the aromatic polymers with aromatic hardeners, have excellent resistance to water and most organic solvents. The polyester group is, on the other hand, susceptible to water absorption and chemical attack, especially at elevated temperatures. This resistance to water and chemicals is another reason that epoxies are used so widely for aerospace composites.

Data from Shell Chemical Company indicates that epoxies have superior retention of flexural strength after 1 million cycles compared to polyesters and vinyl esters and higher flexural strength to begin with. This properties may be related to the superior ability of the epoxy resins to adhere to the fibers in the composite material.

Flammability and smoke generation can be problems with both epoxies and polyesters. The methods for reducing flammability and smoke are similar in the two systems. Typically, the resin can be brominated and/or a flame retardant filler can be added. Because of the highly aromatic character of many epoxies, the flammability is often reduced compared to aliphatic epoxies and polyesters. These conditions will, however, often result in higher smoke values.

In some cases, the most important consideration is cost. Epoxies are almost always higher priced than polyesters, although some overlap exists. Where cost is an overriding consideration, polyesters are favored even though epoxies have superior properties. In applications where performance is more important than cost, such as aerospace, epoxies predominate. It is probably worthwhile, however, to examine a specific epoxy resin and to

calculate total part cost since some savings in total resin weight may be made using epoxies or the resulting superior properties may allow for higher overall costs.

Comparison of hardeners

The most common hardener types are listed in Table 3 along with their relative advantages and disadvantages. Epoxies cured with aliphatic amines are the most common and the lowest in cost. The others are used for special applications or when some specific property needs to be enhanced over the amine-cured value. The polyamides are made from the amines through addition reactions (adducts) and are a method of solving the potential toxicity problems from the volatile amine materials. The polyamides have a higher viscosity and higher cost but give good flexibility and toughness.

The cyclic aliphatic amines are used when higher temperature performance is needed. The aromatic amines give even higher temperature stability and add to that high resistance to solvents and electricity. The aromatic amines and cyclic aliphatic amines are usually cured at elevated temperatures.

Anhydride hardeners are especially useful when amines are to be avoided, as for instance, when improved chemical and electrical resistance are sought (versus aliphatic amines) but the aromatic amines are not appropriate, usually because of cost. Anhydrides are the second most common hardener systems with epoxies.

The latent hardener system, which uses a Lewis acid (sometimes called catalyzed), is used when the pot life and the shelf life are to be extended. In this hardener system, the hardener is insoluble in the resin and is, therefore, withdrawn from any physical contact except around the edges of the insoluble particles. This withdrawal effectively stops crosslinking from proceeding.

Improving epoxy performance

The major complaint against the use of epoxies is their brittleness. Several methods have been tried to improve toughness. These include: inter-dispersed particles, thermoplastic blends, and changes in the basic resin or hardener to give more aliphatic regions and thus more elongation. Several types of toughened epoxies are commercially available, although a problem with some of these products is phase separation and a resulting loss in properties. On the whole, however, toughened epoxies have proven their worth and their use is increasing rapidly.

Summary

Epoxy resins are as common as the two part adhesives that are readily available in hardware stores. They are also used in some of the most sophisticated aerospace applications. The breadth of these applications shows the variability of formulation that can be achieved with epoxy resin systems. This family of resins has many advantages over polyester and other resin systems. In fact, the vinyl ester resins are often epoxy resin molecules that have had the epoxy ring substituted with a carbon-carbon double bond. Vinyl esters can, in this light, be thought of as epoxies that have been modified so that they will cure like polyesters. Vinyl esters have properties about intermediate between polyesters and epoxies. If you have an application where improved properties are important, you might consider epoxy resins.

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Figure 1 A typical epoxy resin

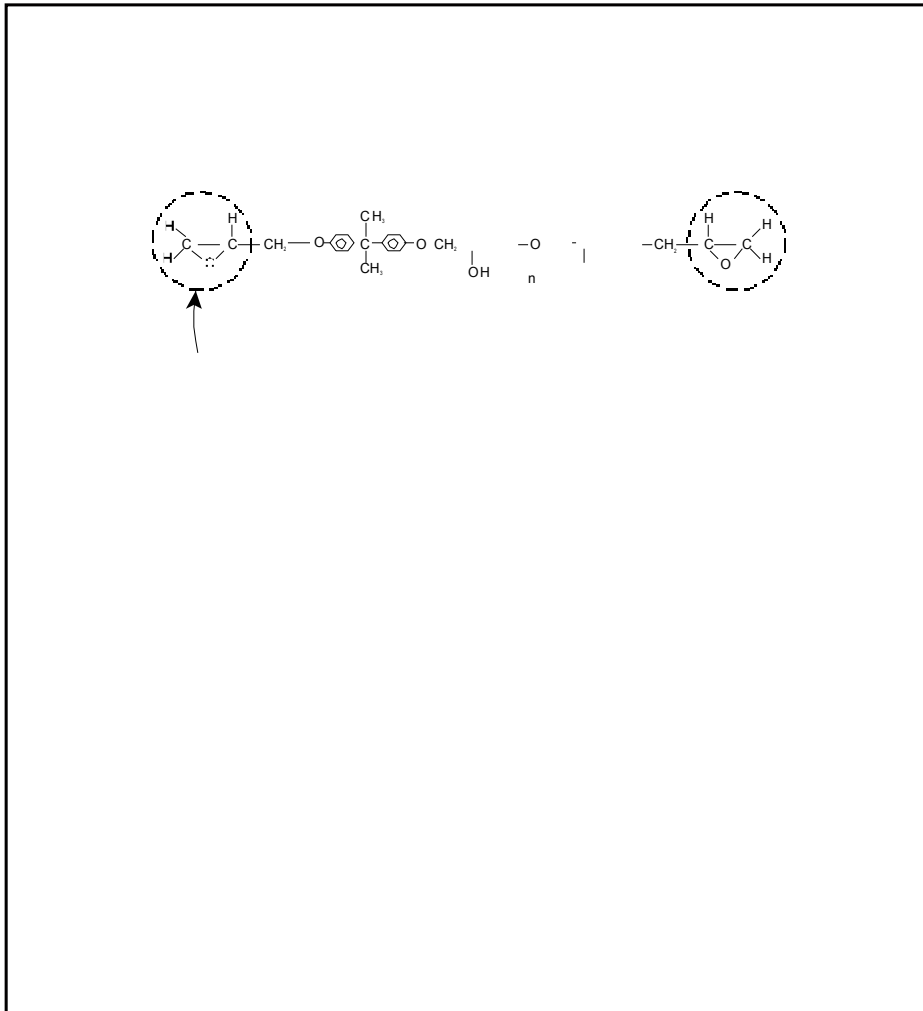


Table 1 Processing Comparison of Epoxies and Polyesters

Processing Parameter	Epoxies	Polyesters
Active site on polymer	Epoxy ring	Carbon-Carbon double bond
Resin storage/shelf life	Generally stable for long periods unless hardener has been premixed	Less stable than epoxies both prior to and after mixing in the catalyst (hardener)
Use of inhibitors	Rare	Frequent
Toxicity of uncured resin or hardener	Some have toxicity problems, especially hardeners	Generally few toxicity problems except with accelerators
Use of solvents/diluents	Most systems have no solvents, diluents can be reactive	Styrene widely used
Use of fillers	Same as polyesters	Same as epoxies
Curing agent	Hardeners (reactive intermediates)	Peroxide catalysts
Typical resin/hardener mix ratios	Resin and hardener often mixed at 1:1	Concentrations are usually about 2% peroxide
Use of accelerators/promoters	Used only rarely	Used often
Pot life	Adjustable from a few hours to many months	Generally not as long as epoxies
Fiber wet out/viscosity	Viscosities generally higher than polyesters	Low viscosities and easy wet-out
Volatiles from the system	Low	Relatively high
Cure temperatures	Some room and elevated temperatures	Mostly room temperature
Cure rates	Adjustable from a few minutes to many months	Generally shorter than epoxies
Byproducts of curing reaction	None	None
Degree of cure	Often needs post curing	Rarely needs post curing
Shrinkage	Very low	High compared to epoxies

Table 2 Comparison of Epoxy and Polyester Properties

Properties	Epoxies	Polyesters
Adhesion	Excellent	Good
Shear strength	Excellent	Good
Thermal stability	Excellent, especially in high temperature cure products	Fair
Water absorption resistance	Good	Fair
Chemical resistance	Good	Fair
Toughness	Fair, can be toughened	Fair
Creep resistance	Good	Fair
Fatigue resistance	Excellent	Fair
Flammability resistance	Smoke can be a problem	Smoke and flammability can be problems
Cost	Typically over \$1.50/pound	Typically under \$1.00/pound

Table 3 Comparison of Several Common Epoxy Hardener Systems (Adapted from “General Guide: Formulating with Dow Epoxy Resin,” Form No. 296-346-1289)

Hardener Type	Characteristics	
	Advantages	Disadvantages
Amines (aliphatic)	Convenience Room temperature cure Low viscosity Low formulation cost	Potential skin irritant/toxic High vapor emission Blushes easily Limited shelf/pot life
Polyamides (adducts)	Convenience Room temperature cure Low toxicity Good flexibility or resilience Good toughness	Higher formulation cost High viscosity Low heat resistance Low vapor pressure
Amines (cyclic aliphatic)	Moderate temperature use Improved chemical resistance	Moderate temperature cures (some room temperature)
Amines (aromatic)	Good electrical resistance Moderate to high heat resistance Good chemical resistance Good pot life Moderate viscosities	Many are solids at room temperature Long, high temperature cure
Anhydrides	Moderate heat resistance Good chemical resistance Low viscosity Long pot life	Long, high temperature cures unless accelerated Critical mix ratios Hardener absorbs water Accelerators commonly used
Latent (Lewis acids)	Very long shelf life Long pot life Moderate to high heat resistance Good electrical properties	Long, high temperature cures Hardener insoluble in resin Often uses accelerators Poor moisture resistance