EPOXY RESIN FORMULATION MADE SIMPLE: CASE STUDIES

By William T. McCarvill and A. Brent Strong

What are epoxies and how do they differ from polyester thermosets?

Polyesters and epoxies are both families of thermosetting resins. The fundamental difference is the type of reactive chemical group that is involved in the crosslinking reaction. For polyesters, the reactive group is a double bond between two carbon atoms. For epoxies, the reactive group is a small 3-membered ring of two carbon atoms and an oxygen atom – called the epoxy ring. We can appreciate the differences in crosslinking reactions and conditions without delving into the chemistries involved. Polyesters are crosslinked by adding a small amount of peroxide initiator (catalyst) to a solvent system of the resin. Then, either with heat or at room temperature, and perhaps with the addition of additional chemicals, the resin cures. Epoxies do not use peroxides and are often not solvated. Curing an epoxy is accomplished by adding a curative (hardener), but the conditions for curing can vary widely depending on the natures of resin and the curative, as well as the requirements of the manufacturing operation and the properties of the final product.

When compared with the polyester crosslinking process and the properties of polyester products, the epoxy system and product properties are far more versatile. This greater versatility is both good and bad. Good because the molder can select curing conditions and properties that are just right for the product and manufacturing application. Bad because the system can become so complex that specialists are required to choose the proper components of the resin mixture, the type of curative, and the molding conditions. These specialists are called epoxy resin formulators. The purpose of this article is to give you insight into the capabilities of epoxy resin systems and to simplify the concepts of formulation so that you can see what the formulators are doing and, perhaps, do some simple formulating yourself.

The formulation of epoxy resins requires the optimization of cost, performance, and processing aspects. Typically ingredients are selected for their chemical and physical attributes and then various formulations are tried in small test mixes until the desired properties are achieved. But it is not just what is put together that matters, how the ingredients are assembled and used affects the consistency of properties, the processing characteristics, safety in scale up, and full-scale production practice. The discussion of fundamentals and the case studies in this article illustrate the principles which, we believe, will give the results desired. The case studies link the chemical and physical properties desired for a part with common sense ways to mix and use resins in actual plant conditions. This article explains the "why" behind the mixicology (our new word) of epoxy resins.

Epoxy resins formulating

Thermoset chemistries such as epoxy resin technologies are generally mature and well understood. A whole industry has developed in supplying resins, additives, curatives, thickeners, diluents, wetting agents, impact modifiers, fillers and resins pre-dissolved in a variety of solvents. Custom versions of any of these can be available should the supplier decide the market justifies it. This vast number of compounds enables the formulator to devise mixtures that closely fit process and cured material requirements (and bewilder the non-formulator). Various philosophical approaches have been taken to expedite the development of the optimum mixture but, for all of them, the key is to reach the combination of ingredients that will meet all requirements in an efficient manner. As with all engineering endeavors, perfection is never achieved. Compromises will be made.

It is necessary to have a modest level of fundamental understanding of the chemical and physical attributes of epoxy systems for successful formulation. To select ingredients at random and put them together in a haphazard manner will lead to dissatisfaction with the end product, and a risk of injury and property damage. Here are a few general fundamentals.

A given manufacturing/molding process has physical and chemical requirements. For instance, highly fluid resins are needed for wet layup, filament winding and resin transfer molding. High viscosity, solid resins are needed for powder coating. A resin to be used for a painted or a trowelled application will have an intermediate viscosity and must be easily spread to wet the surface, but must not run off the surface. In some processes the resin is heated to reduce its viscosity during the pumping and wetout steps, but then must become a high viscosity liquid or semi-solid for subsequent processing; thus, both high and low viscosity requirements must be met.

All thermoset resins are reactive and exposure to time and temperature will result in their thickening and solidification. Resins designed to cure at room temperature have very short pot lives. The various reactive components are kept separate until just before use when they are combined and allowed to react, usually just before molding. Their viscosity rapidly builds until they are no longer processable. Conversely, resins that require elevated temperatures to reach full properties will have long pot lives and long storage times at lower temperatures. Sometimes they are supplied as a one-part mixture. Incomplete and inadequate cure conditions will result in less that anticipated performance.

Resins designed for cure at low temperatures will not have the thermal resistance of resins formulated for high temperature capability, even if cured at high temperature. Conversely resins formulated for high temperature capability will cure very slowly or not at all at room temperatures.

General Rules for Mixing

Epoxy resins themselves, that is, without the curative, are relatively unreactive. They can be subjected to elevated temperatures to dissolve additives and, if required, conduct reactions with those additives. This is not to say that long times at elevated temperatures are always allowable and are safe. Care must be taken to ensure that the conditions are acceptable from a quality and safety aspect. However, epoxy resins without the curative can be mixed under conditions that would be unsafe if the curative was present. When the epoxy resin is mixed with the curative, chemical reactions begin when subjected to time and temperature. Therefore, it is necessary that the blending of epoxy resins, dissolution of thermoplastic components, pre-reactions with rubber, and other additive reactions be done before the curative is added to the mix.

If a material is a solid in the form of a powder, transfer and weighing is straight forward. This is also true if the material is a pourable liquid. Some resins, curatives and modifiers fall into these categories and are easily handled. However, the physical form of many epoxy resins can make them difficult to measure and mix. These resins range from honey-like consistency to materials that are semi-solids. Unlike crystalline solids which can require a high temperature to become molten, resins demonstrate high sensitivity to moderate temperatures. For instance, the viscosity of some resins can drop dramatically with relatively modest increases in temperature. This high thermal sensitivity means that many resins can be easily heated by placing them in a hot box or using a drum heater. However, it should be remembered that resins have poor thermal conductivity and their high viscosity makes convection inefficient for heat transfer so heating times might be quite long. The fully preheated resin can be dispensed from the drum as a liquid and weighed and transferred as needed. A safe effective temperature and time for heating can usually be recommended by the supplier.

One side effect of resins that are semisolids is that it is very difficult to keep the work environment clean. The tacky nature will result in resin transferring onto whatever surface the resin might contact. Therefore, strict housekeeping rules should be followed. Once transferred to a surface, solvent will likely be required to remove the resin. Low toxicity, low volatility solvents such as n-methyl pyrrolidinone (NMP) or γ-butyrolactone (BLO) are generally used. The use of disposable containers can go a long way towards keeping the workplace free from contamination.

The mixing of resins must overcome several impediments associated with resin viscosities. As mentioned above, just as semi-solid resins are preheated to lower their viscosity for transfer and weighing, they must be heated for mixing. Although solid resins in powder or pellet form can be easily weighed and transferred, they must be converted to a liquid by heat, or added carefully to a low viscosity resin otherwise they will go through a high viscosity unstirrable condition. If a mixture of resins is to be blended, it is preferable to start with the lowest viscosity component charged to the mixer first and brought up to the mix temperature. It is followed by the slow addition of solid resin components, or the addition of heated semi-solid ingredients.

It is clear that the mixer must be able to have sufficient power to handle a wide range of viscosities. One type of batch mixer that has been applied to mixing resin uses two blades. A slow speed blade that can scrape material from near the wall of the container overcomes the problems of heat transfer into a viscous medium. By turning over the bulk of the mix, hot spots and dead zones can be avoided. A second blade spins rapidly to provide high shear for thorough blending and dispersal of solid ingredients. When making test batches, adapting the blades and the machine configuration to use disposable paint cans for mixing avoids cleaning and housekeeping issues. Remember that the use of a high speed blade can add additional heat to the mix, especially in small test batches. Due to the relative stability of neat epoxy resins, large mixers can be used to make the unreactive blends. Mixer sizes of 50 to 100 gallon are not uncommon. After the blend is prepared, it is drained into smaller containers.

Heat sources can be either electric or heated water/steam jackets. It is critical that the internal temperature be monitored at all times. It is not sufficient that the surface temperature be monitored as the bulk temperature may be much hotter.

Simple blends of resins or resin solutions of thermoplastics or rubber can be treated much like resins themselves. They can be safely inventoried at room temperature or under refrigeration depending on shelf life studies. They can be reheated in the same way as neat resins. To reduce the time and temperature for dissolution, thermoplastics such as polyether sulphone, phenoxy, and formvar are ground to a small particle size. When adding the thermoplastic, it should be added slowly to prevent the formation of a large sticky mass. These polymers are not soluble in all proportions in all types of epoxy resins. Either the recommendations of the supplier should be followed, or a systematic study should be conducted to determine if the desired addition level into the desired epoxy components can be achieved. One way of determining if the thermoplastic is dissolved is to dip a spatula or tongue depressor into the mix, withdraw a small sample, and press another tongue depressor into the resin on the first sample. After allowing a few moments to cool, the two are pulled apart and the filaments of resin are examined. If the resin filaments are smooth and consistent, the thermoplastic is dissolved. If the filament has fat droplets like pearls in a necklace, the thermoplastic is not completely dissolved. The addition of thermoplastics will drastically increase the viscosity of the mixture over all temperatures. It will be necessary to heat these epoxy/thermoplastic mixtures to a higher temperature than the epoxies alone.

The curative (catalyst) must be added at an appropriate temperature. The mix must be fluid enough to allow dispersal or dissolution of the curative, yet not be close to the onset of polymerization. Keep in mind that catalyzed resins are active and so you should never neglect them. They should be stirred continuously to prevent hot spots and to prevent dead zones where no mixing is occurring. If an elevated temperature step has been used to mix resins and additives, then the resin should be well cooled prior to addition of the curative. Once the curative has been incorporated into the mixture, it should either go immediately to the next process step, or be cooled. Cooling should be done quickly to minimize reactions that could affect safety and quality. If catalyzed resin is to be inventoried, it must be in a container that will facilitate quick cooling and reheating when it is to be used.

It is usually unwise to collect left over catalyzed resin and blend back into fresh resin. Although this is prudent on a material use basis, the eventual loss of control of the heat and time history of the resin blend will introduce variable viscosities and cure characteristics into the part fabrication process. It is best to discard left over resins. Contamination of the resin batch can be minimized through use of disposable handling equipment and thorough cleaning.

The choice of the physical form of the ingredients should keep in mind the end application. For composites this means that the particle size of dispersed ingredients must be small enough to be carried into the fiber bundle by the general resin flow. Solid catalysts and curatives such as dicyandiamide (DICY) and 4,4′-diaminodiphenyl sulfone (DDS) are pulverized to ensure that the concentration in the fiber bundle is the same as between the plies, thus ensuring a dependable reaction throughout. In some cases, the particle size is selected to be filtered by the fiber bundle, such as impact modifiers.

Safety

Exotherms must simply not happen until the material is finally cured in the final shape. Most epoxy resin formulations are autocatalytic which means the rate of reaction goes up as the degree of reaction increases. The reaction is exothermic which means it produces heat. Due to the poor heat transfer of resin, this heat is trapped and since the rate of reaction also increases with increasing temperatures, the reaction quickly goes into a runaway condition. Large exotherms will burn a plant down. Smaller exotherms will destroy equipment and subject workers to toxic fumes and dangerous conditions. The smell of an epoxy exotherm is sickening and is difficult to get rid of. The copious fumes, smoke and smell of even a small exotherm will affect neighboring businesses and homes. Due to the scaling factor, the risk of exotherm goes up dramatically as the volume of catalyzed resin increases. Mixes that were safely carried out on the lab scale can become dangerous when scaled up. Minor changes in process equipment and process conditions can lead to unsafe conditions for a system that has been safely used for many years. The avoidance of runaway reactions is the subject of articles and books and is beyond the scope of this article. There some general rules that will identify risky situations. A new formulation should be compared to an existing one in terms of gel time versus temperature, onset of polymerization by differential scanning calorimeter (DSC) and if possible, time to exotherm at the process temperatures. Batch sizes for catalyzed resin should be as small as possible to foster quick consumption and increase surface area to volume. Temperature control and monitoring is an absolute necessity. Provisions should be made to be able to pump resin out of the vessel and to an outside facility designed to spread the resin into a thin layer. Workers should be trained on how to identify the onset of an exotherm and how to take corrective actions to prevent it.

If the part manufacturer is buying a formulated mixture from a suppler, the appropriate health, safety and environmental information, labels, and information must accompany the resin. If the part manufacturer is mixing and blending the resin ingredients, then the part manufacturer assumes the role and responsibility of complying with local, state, and federal regulations. If pre-reactions are conducted to react in or stage a mix to a desired viscosity, additional regulations may apply, particularly the EPA’s TSCA inventory provisions.

Workers can become allergic to epoxy resins. This sensitizing may take a period of years, but once a worker has become allergic, it is not reversible. Since resins are not highly volatile and for the most part are liquids, it is very easy to use the proper protective equipment when needed. It is a matter of ensuring compliance.

Chemistry

Epoxy resins come in many forms and ability to react or crosslink. More epoxy group per molecule and stiffer molecular connections between the groups lead to a higher temperature capability and lower toughness. Less epoxy groups per molecule and flexible molecular connections lead to higher toughness and lower temperature performance. The reactive group for epoxy resins is the epoxy group and the amount of these groups in a resin is measured by the weight per epoxy (WPE). This is the weight of resin in grams that has one equivalent of reactive groups.

Curatives fall in several main categories. Aromatic amines provide slower reactivity and higher temperature capability. A special case is DDS or diamino diphenyl sulfone (DADPS) where the reactivity is very low and results in prepreg systems with weeks of tack and outlife. Aliphatic amines are much more reactive, but have lower temperature capability. Anhydrides can be low viscosity liquids that show reduced shrinkage during cure and better electrical properties over amines. Specialty hardeners like DICY offer long room temperature stability, yet fast cure rates at elevated temperatures. There are almost as many curatives types as epoxies: each has its own benefits and drawbacks.

Case Study #1 Moderate Temperature Filament Winding Resin

Filament winding combines fibers and resins just before application to the mandrel. The fibers are pulled through a bath of resin and are wound to a specific pattern followed by a cure in an oven. There are two main areas of concern. The viscosity of the resin has to be low enough so that the fiber bundle is quickly and completely wetted by resin. The resin reactivity must be low enough to allow for long pot life (viscosity remains low enough to wind) yet cure fast enough in the oven for economical throughput. Anhydrides have been used for decades to cure di-functional (two epoxy groups per molecule) yielding composites with good physical, electrical, and corrosion resistance properties. The Lindride 6 series of anhydride curatives are liquid anhydrides that reduce the viscosity of the liquid epoxy component so that the final mixed viscosity is around 200 cps. Typically low viscosity versions of commodity epoxy resins are used with the anhydride. Since the amounts of curative and resin are almost equal, this system is ideal for automated mixing equipment. The large amount of the anhydride also means that the cure exotherm is reduced over amine cured systems so that thicker parts can be made. A catalyst level is used to adjust pot life and cure time. Less catalyst will increase pot life, but also increase cure time. The 6V version offers a 17 hour potlife, yet can be cured at 150C in three hours. The mixed resin should be used immediately. The temperature capability is limited by the choice of the flexible bis-A or bis-F epoxy resin. Typical glass transition temperatures are around 130C for this system when cured at 150C. Higher temperature or longer cures will likely not improve the temperature limit as it is determined by the molecular connections. *Contact William Cranford at 803.799.6863 for more details.*

Case Study #2 High Temperature Filament Winding resin

An example of a filament winding system that will provide a glass transition temperature above 230C is the Lindoxy 190/Lindride 25V combination. Instead of a flexible backbone epoxy resin, a short, stiff ring backbone resin is used (Lindoxy 190). The Lindride 25V is a liquid anhydride that imparts elevated temperature stability. Both components are low viscosity liquids and when combined have a viscosity of 500 cps at room temperature which facilitates wet winding. The combination is slow to react giving long pot life. The basic molecular connections can give high temperature potential, but this requires a high temperature cure. Glass transition temperatures above 230C can be achieved with oven temperature of 230C. Lower cure temperatures will result in lower temperature performance. The anhydride systems show less shrinkage during cure than amines which can be an advantage with thick parts. Moisture can have a deleterious affect on the anhydride curative so care must be taken to prevent absorption of moisture before the part is cured. *Contact William Cranford at 803.799.6863 for more details.*

Case Study #3 Room Temperature Cure Wet Layup Resin

If high temperature performance is not needed and simple quick fabrication techniques will work to make the part, room temperature or low temperature systems are available. In wet layup a fabric is either hand impregnated with the resin and then placed on the tool, or the dry fabric is placed on the tool and resin is worked into it. The resin mixture should have an intermediate viscosity so that the resin does not flow out of the layup, especially on a vertical surface, or alternately, the mixture is too thick to work into the fabric. The PRO-SET 135 epoxy resin is designed to balance these needs with a mixture of flexible low functionality resins. Aliphatic amines having a high reactivity are suitable as they are liquids at room temperature and cure at room temperature. The PRO-SET 229 hardener mix has some highly reactive amines that allow for room temperature gelation and hardening. This system also contains some aliphatic amines that provide better mechanical properties and, after a cure up to 82C, a glass transition temperature suitable for less demanding applications. When combined, the resin and hardener have a viscosity of 950 cps and the pot life is around an hour at room temperature. Several days may be needed for the cure reaction to proceed far enough to handle the part. It is a requirement that both the epoxy resin and curative be liquids at room temperature to facilitate mixing since the amines are too reactive to be blended at elevated temperatures. In this case the epoxy or epoxy blend is made up by simply stirring at room temperature. Batch size should be kept to the minimum that facilitates the wet layup operation and the mix must be used immediately. Room temperature can be very different in the summer versus the winter. It would be prudent to determine the pot life at these temperatures. Epoxy laminating resins do not have noxious volatiles like polyester resins and can be worked in an open situation. The fatigue life of epoxy composites also tends to be better than provided by polyester resins. *Go to www.prosetepoxy.com or call Brian Knight at 989.671.4079.*

Case Study #4 Room Temperature Cure VaRTM Resin

Resin infusion processes depend on very low resin viscosity to impregnate a fabric perform using only vacuum to help the resin flow into the preform. This process is less messy than hand lamination. A dry perform is placed into the mold, sealed with a vacuum bag and the liquid resin is allowed to flow inside the bag. The increased compaction afforded by the vacuum produces a higher quality laminate as compared to hand lamination. The same PRO-SET mixtures of reactive liquid amines are used with an epoxy blend. The blend consists of low viscosity base resins combined with a very low viscosity compound that reduces the overall mix viscosity substantially. This type of compound is called a reactive diluent. It has an advantage over the use of a non-reactive solvent in that the reactive diluent becomes chemically combined with the resin and usually requires little or no ventilation like solvents do. The mixture of PRO-SET 117LV very low viscosity resin and the PROSET 229 hardener will yield a 110 minute pot life. Its 310 cps viscosity is one-third that of the combination of resin and curative suitable for wet lamination. *Go to www.prosetepoxy.com or call Brian Knight at 989.671.4079.*

Case Study #5 A High Temperature Amine Cured Filament Winding Resin

The combination of a liquid bis-A epoxy and a liquid amine curative makes an ideal combination for a high temperature filament winding resin. The Resolution Performance Products combination of Epicote Resin 862 (a liquid epoxy), Epikure Curing Agent W (a liquid aromatic amine) and an accelerator Epikure Curing agent 537 will deliver glass transition temperatures around 300C when cured at 177C. The mixed viscosity is around 2,200 cps. It may be preferred to wind with a heated cup to increase the rate that fiber can be pulled through and still be completely wetted with resin. The aromatic amine is much less reactive than the amines used for room temperature cure. This system gives a pot life of 25 hours at room temperature and cure rates would be slow even at elevated temperatures. The use of an accelerator reduces the cure time without seriously affecting pot life at room temperature. Amines are preferred over anhydrides in situations requiring a different resistance to the chemical environment. *E-mail tec.epon@resins.com for more information and www.resins.com for other starting formulations.*

Case Study #6 A high temperature capable prepreg resin

Diaminodiphenyl sulfone (DDS) in conjunction with multifunctional epoxies are the basis for high temperature capable prepreg systems. The DDS curative is latent, providing long freezer and out life. Its slow reactivity also allows for moderate temperatures when it is mixed into the resin. Since it only partially dissolves during a typical hot melt resin mix, it is necessary that it be micropulverized so that it does not become filtered out during the prepreg step. As in the case of the moderate temperature prepreg resin, the epoxy components must be selected on the basis of their ability to meet the temperature requirements as well as the ability to have a low viscosity at elevated temperatures to facilitate mixing, filming and prepregging, but also the right rheology at room temperature for good tack and drape. Multifunctional epoxies can deliver the temperature performance, and they come in a wide variety of viscosities so that the right tack and drape can be achieved.

Huntsman Araldite MY720 (multifunctional epoxy) combined with Aradur 976-1 (DDS) is a classic mixture for high performance composite applications. This resin yields a 254C Tg after a 2-hour cure at 177C cure with impressive retention of properties under hot wet conditions..

The multifunctionals are solids and semi-solids at room temperature. It is customary to heat them to a pourable viscosity in a hot box or with a drum heater so they can be dispensed and weighed. The components are dispensed into a can equipped with a high speed and a low speed blade and heated to a viscosity adequate to disperse the DDS. Once the DDS is dispersed, it is taken to the film-making machine or it is cooled.

Contact Mark Bialy at 949.854.3998 for more information.

Case #7 Industrial/Sporting goods Prepreg

Typical sporting goods or industrial composite applications do not require the high temperature capability of the DDS/multifunctional epoxy blend. Resins that cure rapidly at lower temperatures are desired. DICY is a very latent curative at room temperature due to its insolubility in resins. If uses alone it requires cure temperatures over 150C. The use of a co-accelerator can lower this schedule to 30 minutes of less at 121C. In contrast to the almost equal amounts of resin and hardener found for anhydride cures and the 20-30% hardener to resin found for aromatic amine cures, DICY is used at the 3-8% level and co-accelerator is used at the 2-5% level based on resin.

Air Products CG-1200 is a micro pulverized DICY in granular form and is added to the mix followed by the URS or UR-2T substituted urea co-accelerator. It offers months of pot life at room temperatures and is found in one-part adhesives due to this stability. A high shear mixer should be used to disperse both components. The mix should be free from agglomerates but it will not be clear due to the solid DICY. If an adequate mix blade configuration and speed is used, it should not be necessary to filter the mix. The DICY is not dissolved in this step, rather, it remains as a crystalline solid which contributes to its stability. Since the DICY is not dissolved, it has to micropulverized so it is not filtered out by the fiber bed during prepregging. If it is filtered out, the region between the plies will be enriched in curative and the region within the fiber bundles will be curative lean. This can result in erratic cured properties. Once DICY reaches the temperature of reaction, it polymerizes rapidly. Under that temperature the reaction rate is very slow, this makes it difficult to stage thick DICY laminates to keep the part exotherm under safe levels.

Contact Product Information Center at 800-345-3148.

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