CONTROLLING POLYESTER CURING — A SIMPLIFIED VIEW

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Why worry about curing?

If someone in your plant doesn't worry about curing (or crosslinking), good composite parts cannot be made. Oh, you may be lucky for a time and make parts that are acceptable without controlling curing, but the chances of making good parts over the long term are nearly nil. Curing is not the only thing to worry about in making composite parts, but there is nothing in the entire process that is more important. You may think that you don't need to worry about the details of curing because you will simply follow the recipe suggested by the resin supplier, but that too, is short sighted. The curing reaction is a very complicated process that is affected by many different things, some of which cannot be fully covered by any general recipe. Eventually conditions will change (humidity, weather, resin uniformity, conditions of ingredients as they are stored, suppliers, equipment conditions, etc.) and the conditions anticipated by the recipes will not exist any more. You may begin to make parts with poor quality, sometimes without realizing it until the marketplace tells you.

But does this situation require that you must have a PhD chemist to watch over every resin batch to insure quality? No! Fortunately, there is a middle ground between blindly following the general recipes and hiring your own resin chemist. You can take three key steps that will help significantly in controlling the curing reaction and give you an enhanced capability to meet the challenges of long term control over your process. These three steps are:

1. Teach **everyone** in the plant the fundamentals of controlling the curing reaction because almost everyone's work is either associated with controlling the reaction or is affected by what happens in the reaction. Upper management should be especially involved because of the importance of this process to the overall well-being of the company and, therefore, the decisions that must be made to optimize output and profits.

2. Assign someone to become an in-house "expert" who can coordinate this training effort and can interface with outside experts (such as technical service representatives at supplier companies). This person need not be a trained chemist, but should be someone who is willing to learn the terms used in discussing the curing reaction and who is willing to spend some time relating the basic concepts of curing to your particular conditions.

3. Monitor and record key variables which affect curing and then implement good process control methods using the data from the process. This gives you some knowledge of the details of your process and allows you to see trends and to relate changes in product quality to changes in the process.

The purpose of this article is to give a broad overview of the curing reaction and to identify some of the key variables so that you will have a head start on implementing these three steps.

What happens during curing?

Simply put, during the curing reaction, medium-sized molecules link together to form enormous molecules. When that happens, the resulting material becomes solid with dramatic increases in strength, stiffness, hardness, and other desirable mechanical, physical, and chemical properties. This resulting solid material cannot be remelted or reshaped, so any molding (shaping) of the material must be done while curing takes place. Also, reinforcing fibers must be introduced before curing so that the fibers can be wetted by the liquid resin and be properly encapsulated and positioned in the resulting solid product. The creation of the links (bonds) during curing involves a series of chemical reactions. By examining these reactions, you should gain a greater insight into the basics of curing reactions in general and, thereby, understand which variables are important to control and how they should be controlled with the particular resin system you employ.

What are the basics of polyester (and vinyl ester) curing?

For a molder who is going to carry out a curing/molding operation, the starting resin is generally a liquid consisting of medium-sized molecules. These molecules are short-chain polyester polymers which have been synthesized by the resin manufacturer. In making these resins, the resin manufacturers can vary components and conditions to create a wide range of resin grades and types. These various grades and types allow great variations in suggested cure conditions, final part properties, and resin costs. The examination of the differences between the various resin grades and types goes beyond the scope of this paper except to note that in choosing one particular resin or combination of resins for your plant, you should work closely with the resin manufacturer or supplier/distributor to select resins that meet your particular needs and desired product properties.

The basic curing reaction is illustrated in Figure 1 for polyesters. The short polyester polymers are characterized by the existence of carbon-carbon double bonds at several sites along each polymer chain. These carbon-carbon double bonds are called unsaturation sites. Unsaturated sites are present in the polyester molecules because the resin manufacturer uses an unsaturated acid (usually maleic acid) as one of the components from which the polyester is made. Other acids (such as “ortho” and “iso”) might also be used in combination with the unsaturated acid to make the polyester molecules. Several other materials, such as glycols are also added by the resin manufacturer to make the polyester molecules.

As shown in part b) of Figure 1, peroxides can combine with carbon-carbon double bonds to form a bond with one of the carbons and to form a free-radical (unpaired electron) on the other carbon. This free radical is very reactive and will aggressively seek to bond with some other material. As shown in part c) of Figure 1, the free radical can react with styrene to form a bridge to another polyester chain. In forming this bridge, a free radical is created on the second polyester molecule. This new free radical can then form a styrene bridge to yet another polyester molecule, as shown in part d). Because each step in the reaction creates a free radical, this crosslinking process proceeds like a chain reaction.

The process is finally terminated when the free radical reacts with something other than styrene or a carbon-carbon bond in another molecule. Some of these other reactants can include oxygen, contaminants, and other peroxide molecules. Hence, if these other reactants are present in large concentrations, the crosslinking reactions could be terminated prematurely and the desired number of crosslinks might not be formed. This is one of the reasons that it is so critical to control the concentration of peroxide and any other material that might react with free radicals.

In actual practice, several peroxide molecules will react with several carbon-carbon double bonds to begin these crosslinking reactions throughout the mix. Only a few peroxides are needed to get the reactions started. Hence, the peroxides are only needed in small quantities, usually 1 to 2% of the total resin weight.

Heat is evolved with each bond that is formed. This heat will generally cause the polymer mix to increase in temperature. The rise in temperature is called the exotherm. Generally, thick parts have higher exotherms than thin parts because in thick parts the heat is retained by the polymer, thus causing the reactions to occur faster and, consequently, even more heat to be evolved.

Additives

In addition to the basic resin, many other materials are often added to the mix. It is the nature of these other materials and their effect on curing that is important to control if curing is to proceed properly and repeatedly. Some of these additives make the curing reaction go faster, some make it go slower, and with some the effect can be so complicated that it is not possible to predict the effect in general. Some of the materials are usually added by the molder, although some can also be added by the resin supplier. The molder should monitor or control the concentrations of each of these components in the mix, either as received from the resin supplier or added by the molder.

To assist in the analysis of the effect of each of these additives, a chart has been created (Figure 1) which shows each material on a teeter-totter arranged according to whether it generally makes the curing reaction go slower or faster. Some can make the reaction go faster or slower depending upon specific conditions and these are located in the middle of the teeter-totter. Each component will be examined so that its purpose and effect can be understood.

Additives that make the curing reaction go slower:

- **Inhibitors** —These are chemical materials that absorb free radicals. Inhibitors are generally added to the resin mixture by the resin manufacturer to stop or interrupt any crosslinking chain reaction that might be started by the chance creation of free radicals. Because free radicals can be created at carbon-carbon double bonds through several different mechanisms, such as interactions between the molecules with heat and light, the possibility of having chance creations of free radicals is quite high. Should these chance reactions occur while the resin is being stored, the entire batch of resin could be prematurely crosslinked unless protected with inhibitors. When planned curing is to be done, sufficient peroxide catalyst must be added to first react with any remaining inhibitor molecules and then react with the carbon-carbon double bonds in the polyester molecules. Therefore, a knowledge of the amount of inhibitor in the system is needed to determine accurately the amount of peroxide catalyst needed.
- **Styrene** — Two different effects are occurring simultaneously with styrene. The first is the dilution effect. That is, styrene is a solvent for the system. In this regard, increasing the amount of styrene will dilute the total system and will add mass which must be heated in the reaction. Therefore, additional styrene will slow the reaction. However, the second effect of styrene is as the crosslinking agent. In this role the styrene makes the crosslinking occur more quickly and readily. The effect of the styrene in this regard is to speed up the reaction, although this effect is usually seen later in the overall curing cycle. Incidentally, because of the high brittleness of styrene, excess styrene will generally add brittleness to the finished part. Overall, styrene is placed on the teeter-totter on the slower side because of its initial effect.

- **Filler —** These materials are usually powdered inorganic materials (rocks) such as calcium carbonate, calcium sulfate, and talc. They add mass to the system and absorb some of the heat generated by the crosslinking reactions, thus reducing the exotherm and slowing the overall reaction.
- **Oxygen —** Normal oxygen gas is made up mostly of O_2 molecules but has a small amount of ozone (O_3) molecules present as well. These ozone molecules are like inhibitors in their ability to absorb free radicals. Therefore, if oxygen is present or added to the system, the curing reaction is slowed. Sometimes oxygen is actually used to stop the reaction and in these instances it is called a quench. Since oxygen is almost always present, the amount of peroxide catalyst used is normally adjusted to provide sufficient to overcome the effects of oxygen. Alternately, the oxygen can be excluded from the reaction area by using some surface coating material like wax or a film.
- **Flame retardants —** The action of these materials can be very complicated, depending on the type of flame retardant used. Therefore, the simple designation of them as favoring slowing the reaction is based primarily on their additional mass and assumes that they have little direct chemical interaction in the crosslinking reactions. It is best, however, to check each flame retardant type for specific reactivity in your system.
- **Reinforcements —** The fibers are usually inert to the crosslinking reactions. Therefore, their principal effect is from added mass and the subsequent absorption of heat which occurs.
- **Mold heat capacity —** The mold is a massive material that acts as a heat sink, perhaps the most important mass in the entire system. Because the mold is often at room temperature, heat is absorbed out of the system and thus the curing reaction is retarded. In some cases,

however, the mold is heated. When heated, the mold will accelerate the curing mechanism. Hence, the classification of the mold as slowing the reaction is simply a reflection of the normal, cold state that occurs during open molding.

Additives that make the reaction go faster

- **Initiators (catalysts) —** These materials are generally peroxides. The peroxides are useful materials for this application because they break apart easily to form free radicals. The process of breaking apart occurs either by heating the peroxides or by the action of some other additive, such as an accelerator. Therefore, if the part is to be cured with heat, then a heat-activated peroxide is used. If the part is to be cured without heating, then a combination of peroxide and accelerator system is needed. Consideration should also be given to final part characteristics, such as color, as these can also be affected by the peroxide chosen.
- **Heat —** Heat will increase the reaction rate for almost any chemical reaction for several different, although interrelated, reasons. Since molecules must collide in order to react, when molecules are heated they move more and therefore the chance that they will collide is increased. Also, the viscosity of the mix is reduced by heating and, therefore, the molecules move more freely and colliding likelihood is increased. Higher heat will also increase the energy of movement of the molecules. This means that when the molecules collide, they will collide harder and, therefore, have a higher chance of creating an effective collision. (Not all collisions result in bonding.) The heating of the molecules also increases the overall energy in the system, thus making it easier for the molecules to overcome the energy of activation which is a threshold barrier for effective reactions to occur. Yet another effect of heating is to increase the break-up of the peroxide molecules, thus increasing the number of chains that

are started and therefore the rate of the curing reaction. Heat can also cause direct formation of free radicals at the carbon-carbon double bonds in the polyester molecules. It is this possibility that leads to the addition of inhibitors to prevent crosslinking from occurring prematurely.

- **UV light (sunlight)** — This type of energy will also create free radicals at the carbon-carbon double bonds. To prevent this from happening, resins are usually stored in opaque containers and inhibitors are added. However, in some resin systems, such as those used in dental fillings, UV light is intentionally introduced into the system by shining a special light on the polymer. This UV light can cause crosslinking to occur without the use of peroxides.
- **Accelerators (promoters)** — These materials are added to the system to improve the efficiency of the initiator. The most common accelerators are organic compounds (such as naphthanates) of cobalt or some other heavy metal. Usually only a small amount of these materials is needed to greatly improve the efficiency of the peroxide. With accelerators, some peroxide systems do not need to be heated and room temperature cures can be done. Some accelerator systems, such as MEKP, are further improved with some peroxides by the additional of aniline compounds, which are sometimes called co-accelerators. With other peroxides, such as BPO, the co-accelerators are effective without the cobalt compounds even being present. Because of the sensitivity of the peroxides to the accelerators, great care should be taken to control the accelerator system concentrations.
- **Part thickness** — As already mentioned, when parts are thick, the resin retains heat and therefore increases the overall temperature and reaction rate. This behavior can be a major problem when parts have significant differences in thickness. Not only will the reaction rate

be higher in the thicker areas, but the amount of crosslinking that occurs will be higher in the thicker areas. This could cause embrittlement in the thick areas and internal stresses in the part because the of increases in part shrinkage that occur with higher degrees of crosslinking. Furthermore, the higher heat in the thicker regions can cause greater thermal shrinkage and result in cracking. Hence, parts must be carefully designed to minimize thickness variations.

- **Wax or films** — These materials are added to exclude oxygen and prevent the inhibition effect that oxygen brings. Since the greatest inhibition effect is usually on the surface exposed to the oxygen, the wax coating or film can be added only to that surface to prevent a decrease in surface properties (such as hardness or gloss).
- **Post cures** — Adding heat after the part is formed is called post curing. This is done to give additional movement of the molecules and greater efficiency of molecular collisions, thereby resulting in the formation of more crosslinks. The heating can also cause any residual peroxide to break apart and initiate some additional chains.

<u>Materials that can make the system go either faster or slower</u>:

- **Resin grade/type** — The resin is the most complicated component in the entire mixture and is, therefore, so variable that it cannot be classified on either side of the teeter-totter. Some resins, especially those with a high degree of unsaturation, will cure quickly and result in high exotherms and high crosslink densities. Others, with less unsaturation or with unsaturation sites that are less reactive, proceed more slowly. Some resins are especially sensitive to certain catalysts and therefore proceed rapidly when they are used but more slowly with other catalysts. The length of the chain of the resin before crosslinking can affect the reaction rate. Very long chains can increase system viscosity and therefore slow the reaction rate. Resins might even be mixtures of two or more types of polymers, each with its own reactivity. Therefore, the manufacturer should be consulted about resin reactivity as it might occur in the particular system you intend to use.

- **Water —** Water adds to the total mass in the system, thus slowing the reaction by absorbing heat. On the other hand, water can increase reactivity in some peroxide systems, although it can retard rates in others. Some resins are less reactive when water is present. Water can also affect the action of accelerator systems. The action of water is, therefore, difficult to predict. The best practice is to monitor and record humidity and water content in the system and then attempt to correlate its affect on the overall system.
- **Pigments —** Usually pigments have little effect on the system. However, since some pigments can contain metals (such as iron oxides), they can have an accelerating effect. In contrast to that, however, some metals will interfere with the basic crosslinking reactions. Pigments add mass, thus retarding the system, all else being equal.
- **Contaminants —** Because the nature of the contaminant is not specified, the nature of the effect is not known. However, the fact that the effect is unknown invites variation in the process and, potentially, the production of poor quality parts. Some contaminants are significant parts of the environment in some plants and, therefore, may have a more predictable and repeatable effect. Be aware of the possibility for such contamination and act to control and limit its presence.

Summary

In general, if the reaction proceeds too slowly, the amount of crosslinking is likely to be lower than desired. Long cures will also increase the number of molds that are needed and will result in more money being needed to achieve the same production volumes as could be attained with faster cures. The variables associated with slowing the cure should all be examined for possible effect on the system.

If the cure proceeds to quickly because too much heat is generated, the part could be too brittle. Also, the crosslinking might proceed so quickly that all of the styrene is not used and the resulting part could have residual styrene content. If the cure proceeds quickly because too much peroxide was used, incomplete crosslinking would likely result and that would lead to poor physical properties and poor solvent and water resistance. All of the other variables that may increase reaction rate could likewise cause problems with the part.

Therefore, cures that are too slow and too fast can both be problems. The best situation is to understand, monitor, and control the effects of the various components in the mixture and the variables that control the rate. Remember that the cure reaction is the heart of polyester and vinyl ester molding and must be carefully controlled to make good quality parts over the long run.

Additional Reading and References

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