

MOLECULAR DESIGN —

ADVANCES IN RESIN CHEMISTRY

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A hotbed of change

Of the three largest components in composites — resins, fibers, and additives — the resins seem to be changing most dramatically. Almost every resin supplier has significant new products that are being introduced to meet a new market demand, to counter an industry problem, or just because the new product performs better or is less costly. These changes in resins are generally the result of significant changes in the design of the molecular nature of the resins. Many of these molecular design changes represent significant breakthroughs in basic resin chemistry. Most can be explained adequately (though not fully) in layman's terms so that the basic nature of the change and its significance can be readily understood and its advantages and limitations understood at a fundamental level. In this article we will explore the innovative nature of some of these new resins and attempt to explain the changes in basic terms. Each of the major resin groups will be discussed separately.

Polyesters and vinyl esters

Polyesters and vinyl esters have been limited in their applications because of the inherent brittleness of the systems, especially when styrene is used as the reactive solvent. On the other hand, the use of conventional urethanes has been increasing rapidly in many key markets because of their inherent toughness and abrasion resistance, but their use in structural applications has

been slow, largely because of their relatively low modulus. Now, by combining urethanes with polyesters, the best properties of both systems seem to have been selected to give excellent modulus and excellent toughness at the same time. A further advantage is a reduction of styrene emissions when using the polyester/polyurethane hybrid product.

The polyester/polyurethane hybrid system is quite unique because two chemical reactions go on simultaneously as shown in Figure 1. In one reaction, the peroxide reacts with the unsaturation in the polymer and with the styrene in a reaction that is typical of polyester and vinyl ester crosslinking. However, because the basic polyester contains OH groups, these groups are available for additional reactions. In the other reaction, the isocyanate material, which is added to the mix, reacts with these OH groups on the polyester resin to create a very long urethane-like polymer. Although shown as sequential in the Figure, these reactions actually occur simultaneously. The result is a styrene-stiffened network that still has some flexibility from the polyurethane backbone.

Some have identified this technology as reaction spray molding (RSM) when it is used in an open molding operation. The RSM systems have very fast reaction times, often allowing the part to be demolded in a matter of minutes compared to the 3-4 hour cycles of conventional polyesters.

Futura Coating, Inc., a supplier of the polyester/polyurethane hybrid systems reports that the RSM systems can be used to substantially improve gel coats by spraying the hybrid system directly behind the gel coat or by substituting the hybrid for a gel coat to give a high surface quality, lower incidence of roll-out defects, and improves blister resistance while reducing overall cycle time.

Epoxies

Several epoxy resins use new molecular concepts that might prove valuable for your consideration. One of these is the system of waterborne epoxies that are now available.

Waterborne systems, like those sold by Shell Chemical Company, utilize proprietary surfactants to keep the epoxy resins in suspension in a water emulsion. The surfactants modify the surface of the resin so that the resin particles remain widely separated and suspended. These waterborne systems have the obvious advantage of eliminating solvents, many of which are highly restricted. In addition, the waterborne systems are easy to clean-up with water, can be easily blended with many other waterborne resin systems for optimum performance, are easily mixed with water to achieve the desired viscosity, have a long (1 year) shelf life, and can be crosslinked by a wide variety of hardeners. When cured, the waterborne systems give nearly identical properties as the analogous solvent-based system.

Another new wrinkle in epoxy resins involves the combination of the epoxy with a polyurethane resin. Dow Chemical reports that by capping an aliphatic polyglycol (a normal urethane pre-polymer) with an aromatic epoxy endgroup, a blend of the most desirable properties of the urethane and the epoxy can be achieved. (This concept is similar to the combination of polyester and polyurethane discussed previously in this article.) The urethane gives high elongation, flexibility, and toughness while the epoxy gives barrier properties and physical strength as illustrated in Figure 2. The properties of the new resin can be further modified by simple blending with more traditional, and fully compatible, bisphenol-A and bisphenol-F epoxies. Curing can be done with conventional amine-based hardeners but cure is generally slower than conventional, unmodified epoxies.

Polyurethanes

The use of urethane chemistry to modify polyesters and epoxies has already been discussed. Another new concept for polyurethanes is the creation of a class of polyurethanes that seems to have low temperature properties like a thermoset and high temperature properties like a thermoplastic. This combination of properties seems to imply that the crosslinks (bonds between molecules) that are the unique features of thermoset, somehow disappear at high temperature. When this happens, a thermoplastic material is created in which the molecules are free to move about and be formed by traditional thermoplastic molding processes like extrusion and injection molding. Then, as the molded material cools, the crosslinks again form to create the strength and rigidity characteristic of a thermoset. The scientists at Batelle claim exactly that unusual combination of properties for their new resin.

This uniqueness comes from a chemical reaction that is reversible with temperature. In this case, an OH group on a pre-polymer reacts with an isocyanate. This is the normal polyurethane reaction except that when the OH group is directly on some (usually aromatic) molecules, the urethane bond breaks apart at elevated temperatures (typically 200 to 400°F). The urethane bonds then reform when the material is cooled.

The major advantages of this new resin system over conventional thermosets are in processing. The time to mold the product is significantly reduced because the time to solidify through cooling a thermoplastic is much less than the time required to cure a thermoset. The advantages over a traditional thermoplastic are the greater strength and stiffness imparted by the crosslinked structure at normal use temperatures. The main drawback is the limitation on the useful temperature of the part since the material will soften as the temperature goes up. Note also

that as the temperature increases, isocyanate is formed by the reversible reaction and some caution must be taken as isocyanates react with water. Hence, the time at which the resin is at high temperatures should be limited so that the side reactions of the isocyanates are reduced.

Phenolics

Some resin systems seem to fill a niche in the marketplace that no other product can quite fill, but also seem to not be able to break out of that niche into a wider market. Phenolics seem to be just that type of resin. Within the composite marketplace, the niches for phenolics are in flame-retardant applications, ablative/thermal insulation, and the precursor material for carbon-carbon composites. One of the principal difficulties in expanding beyond these traditional markets has been the relative brittleness of phenolics and operational difficulties in curing the material. Now, two new concepts in phenolic resins have expanded the traditional strengths of phenolics and have solved some of the operational problems associated with traditional phenolic resins.

TAMP resins. The new resin systems are called “Thermally Ablative Modified Phenolic (TAMP)” resins by the company that developed them — HyperSonic Resins and Chemicals. The new chemistry involves the addition of nucleating agents to the phenolic material. These nucleating agents cause the formation of regions within the phenolic resin which, according to the type of nucleating agent added, will have either a silica-like or a carbon-like nature. The regions provide enhanced bonding with the reinforcement and improved wet-out, as might be expected from their respective chemical natures. The regions also enhance the strength of the resin, just as dispersed or precipitated regions provide added strength to metals (called dispersoid or precipitation strengthening).

A somewhat unexpected advantage of the TAMP resins is their improved thermal stability. Where typical acid-catalyzed phenolics begin to decompose at about 284°F, the TAMP resins initiate decomposition at 860°F. Also, where catastrophic oxidation of phenolics typically starts at 850°F, for TAMP resins it starts at 1100°F. These data mean that TAMP resins can be used continuously as high as 650°F with short term exposures up to 700°F. The greater thermal stability also means that the time for ignition from a flame is substantially increased, often doubling the time required for conventional phenolics. Ablative properties are also improved because the improved thermal resistance is accompanied with a tenacious carbon surface that improves the erosion resistance of the material. Smoke is also very low.

In carbon-carbon applications, the TAMP resins give solids contents that are about 10% higher than expected, thus reducing the number of cycles required to give a low-porosity part. A further advantage is that the TAMP materials form silicon carbide particles as a result of the nucleation and these particles improve the thermal stability of the carbon-carbon material.

Initial cure of the water-based resin is done at room temperature after adding the proprietary acid catalyst. Pot life at room temperature is 20 to 30 minutes. Then the part should be post processed at 160-180°F for two hours to remove the water, and then a post cure at 300-320°F to achieve optimal properties.

The applications which have been identified for the TAMP resins include composite tooling, piping systems where flammability is a problem, automotive parts, rail and air transportation, rocket nozzles and casings, and petrochemical plant structures.

PT resins. The phenolic-triazine (PT) resin is made using chemical modification of phenolic resins through a cyanation reaction. The resulting product is highly crosslinked and possesses the same high flame retardance and physical properties of a traditional phenolic but has the advantage of curing by an addition reaction rather than a condensation reaction. Hence, no water or other byproducts are created when the crosslinking occurs. As with traditional phenolics, a post cure will enhance the mechanical properties of the composite. Working temperatures can be as high as 570°F.

The PT systems can also be combined with epoxies to improve the thermal performance of the epoxy resin while retaining many of the favorable properties of epoxies. The PT resins can be obtained from AlliedSignal, Inc. or from Stesalit, Ltd.

Silica/silicones

One of the most unusual molecular developments in recent history is the creation of the family of materials called Polyhedral Oligomeric Silsesquioxanes (POSS). A typical POSS molecular group is shown in Figure 3. This large, rigid structure has properties that are intermediate between a silica (a mineral) and a silicone (a polymer), thus suggesting that the material is somewhere between an inorganic and an organic. (What is it?) Even more startling is the way in which these POSS entities can be incorporated into traditional organic polymers like polyesters, epoxies, urethanes, acrylics, and most others. The changes in properties are quite astounding.

Because of the large cage-like structure of the POSS basic element, when the POSS element is incorporated into a traditional molecule, the properties change as if permanent, large crystalline regions had been added. The decomposition temperature and glass transition

temperatures are increased dramatically, sometimes as much as 200-400°F. Flammability and heat evolution are reduced. Permeability is increased and thermal conductivity is reduced because of the large size and openness of the structure. Stiffness (modulus) and hardness increase while generally maintaining the strength typical of the base resin. In many cases the presence of the POSS group in the resin formulation eliminates the need to add fillers. Hence, the overall weight of the system can often be reduced.

Several companies are working on resins which are enhanced by POSS technology. The basic technology was developed in association with the Air Force Research Lab who have arrangements whereby others can work with this exciting new chemistry.

Thermoplastics

Although thermoplastics have held great promise for tough, solvent-resistant composite parts, when thermoplastics have been used with long fibers, wetout of the fibers has often been a problem. Several systems have been tried to get good wetout and now a new system has been announced by Applied Fiber System, Ltd. The company has licensed the TowFlex process which uses electrostatics to impregnate reinforcement tows with the powdered thermoplastic resin. Because the resin matrix is not fused, the tow remains pliable, thus permitting braiding, weaving, or layup into highly contoured molds. The process has been demonstrated with several thermoplastics including PP, nylon, PPS, PET, ABS, PEI, and PEEK on glass, carbon, and aramid fibers. K2 Corporation has made bike parts supplied by Applied Fiber Systems using the TowFlex process. The parts are press cured at 475°F and then indexed to a cooling station. The total cycle is 12 minutes and glass contents are 53%. Plans call for 5000-8000 bikes a year using the process.

Perhaps the biggest changes in decades in thermoplastic resins are just now emerging. These changes center around the use of new catalysts to make the resins. Metallocene catalysts have already been shown to improve strength and stiffness of many polymers so dramatically that the traditional applications for some polymers (such as polystyrene) are being vastly expanded. DuPont has announced another new catalyst system that is the subject of the largest patent ever filed by DuPont and which they say will substantially affect polymer they now produce.

We can only wait for the results of these catalyst systems to become evident and be ready to change our thinking of what resin will work in a particular application. The future may scramble all existing resin markets, perhaps even including the thermosets.

Cure systems

Some new molecular concepts have been shown to improve or, at least, to present new options for curing polyesters and vinyl esters. These innovative cure systems may not apply to all situations, but you might at least consider them for the unique advantages which they offer. You could evaluate whether they can be applied to your situation or, perhaps, to a new product or manufacturing scheme that might give you a competitive advantage.

Landec Corporation's Intelimer system is a unique heat-activated system that has a very sharp trigger point for commencement of the crosslinking reaction. In this system, one of the key components of the cure system is encapsulated in a special polymer that has a very sharp melting point. Systems with the following encapsulated components are available: cobalt, imidazole, tertiary amine, and dibutyl tin dilaurate. When that melting point is reached, the polymer releases the encapsulated component and the reaction begins. Therefore, the pot life of the system is extended to give essentially infinite shelf life at room temperature. Then, when cure is desired, the

system is heated and cure occurs rapidly at the melting temperature of the encapsulating polymer (which can be chosen to meet specific circumstances). A special catalyst, made by Aztec Peroxides, has been shown to be especially compatible with the Intelimer system. Landec Corporation has also demonstrated similar technologies in epoxies and polyurethanes where the hardener has been encapsulated in a heat-activated polymer.

Photocuring of polyester resins has been given a boost with the introduction of a new family of photoinitiators which hold great promise for making photocuring a viable alternative to conventional curing with peroxide initiators. In announcing the new technology, Ciba Specialty Chemicals pointed out some of the problems of peroxide-initiated systems that can be alleviated through the use of the new photo-initiated system. For instance, the styrene content can be substantially reduced because of less heating and shorter times during cure, the shelf life can be extended, and the limited time/temperature range available for good processing can be expanded.

In the past, photo-initiated cures have had limited success because of problems associated with the photoinitiators. Now, with the introduction of a family of new initiators (bisacylphosphine oxide photoinitiator or BAPO), photo cures are more rapid, more complete, and more efficient than previous photocure systems. A typical photocure can be accomplished with 5 minutes of exposure to 40W fluorescent lamps as shown in Figure 4 which compares a photo-initiated cure with a thermal-initiated cure. Because of the rapid onset of cure in the photo-initiated system, gelation occurs quickly and traps the styrene, reducing the release of styrene to the environment. Physical property results of photo-cured samples showed a generally lower modulus and strength unless the photocured system was postcured, in which case the results were comparable to those of a thermocured system.

Acknowledgments

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- TRAM (phenolic) resins, HyperSonic Resins and Chemicals Co., Dr. Frank Gojny (619/267-3734)