POLYURETHANE COMPOSITES —

TOUGHNESS AND PROCESSING ADVANTAGES

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Overview of Polyurethanes in Composites

Almost everyone in the United States and most of the rest of the world has contributed to the growth of polyurethanes by buying sport shoes made by Nike, Reebok, Adidas, or any one of a multitude of other sports shoe manufacturers. These shoes, made mostly of polyurethane (PUR), have been extremely profitable (just think about the money paid for endorsements) and have contributed to the tremendous surge in the sales of polyurethane resins. But shoes are not the only market for polyurethanes.

Polyurethane resins are used for the finest paints and can even be specially formulated for use as a wall coating that allows graffiti to simply be washed away. Polyurethanes are also used extensively for molded plastic parts. In the medical field polyurethanes are the materials used for artificial heart valves and even complete artificial hearts. In industrial markets, polyurethanes are made into O-rings, seals, and vibration cushions. The newest and most advanced sports clothes are made from Spandex fibers, another polyurethane product. Polyurethanes are also the preferred liner materials under landfills to prevent seepage contamination. With all these new and dynamic uses, is it any wonder that polyurethanes have been combined with fiberglass and other fiber reinforcements to make new and highly innovative composite products?

The automotive industry seems to be at the forefront in the use of PUR in composite structures. Some automotive parts now being made from reinforced PUR include: bumper assemblies, exterior body panels, steering wheels, transmission deadeners, firewall deadeners, belly pans, and in related markets, RV housings and lawn tractor covers. Reinforced PUR is used in these applications because it is tougher than the competing SMC or BMC and yet is still stiff enough to hold its shape during normal use. Most of us have heard of the “dent resistant” side panels for cars and vans and the “5 mph bumper.” Reinforced PUR is one of the most common materials for these applications.

One rapidly growing application for reinforced polyurethanes is in molds, especially when the mold is to be used only a few times. The excellent fluidity of polyurethanes before they crosslink allows the material to flow into small recesses and around details. After crosslinking, the polyurethanes can be tougher and harder than other competitive materials for these “soft” mold applications.

The major questions you might be asking are: What are the properties of reinforced polyurethane that make it so appealing? and What manufacturing methods are used to make these parts? We’ll try to answer these questions for you.

What are the Properties of Reinforced Polyurethane?

The major property of PUR that is driving most of the applications is its toughness. This toughness comes from the high flexibility and elongation of polyurethanes. Although property comparisons between resins are hard to make because of the many grades available, a comparison of elongation of a general casting polyurethane with 55% fiberglass reinforcement shows elongations from 5 to 55% whereas polyester SMC would typically have a maximum elongation of 5%.

PURs can be flexible or stiff. Some specialty grades of reinforced PUR have elongations as high as 600% and are, therefore, considered elastomers. Polyurethanes can have tensile strengths as high as 2000-7000 psi and Shore hardnesses as high as 90D. These properties lead to an ability of some PUR sheets to deflect 6 to 8 inches at -20°F repeatedly. Polyurethanes are, therefore, especially useful for cryogenic applications.

Stiffness, generally measured by flexural modulus, is chiefly a function of the amount of glass reinforcement in polyurethanes, just as it is in polyesters, although the matrix stiffness does have some effect. Polyesters resins are generally stiffer than polyurethanes (polyurethanes have a wider range of stiffnesses including some that are quite flexible), and so the composites of polyesters are, on the average, stiffer than polyurethanes.

What about the thermal capability of PURs. The sag values of PUR reinforced with 20-30% fiberglass are 0.05 inch at normal automotive painting temperatures (325 - 360°F). The sag can be reduced significantly by additional crosslinking, but this results in more brittleness at room temperature. Therefore, reinforced PUR materials are not currently used for horizontal automotive exterior panels because of excessive sag. SMC would be the plastic of choice for these horizontal applications.

Polyurethanes are generally better adhesives than polyesters. Therefore, adhesion to the fiber reinforcements is better across a wide range of reinforcements. This adhesion is also an advantage when the reinforced part is to be bonded into an assembly or covered with another coating.

If many mechanical properties are competitive with polyesters and some much better, what about the surface smoothness and paintability which are so critical for exterior automotive parts? Smooth surfaces are not a problem with PURs. They can be easily molded to a class A surface. Paintability has been a little more difficult to achieve. After 1000 hours in a QUV weatherometer, gloss is significantly lost, but can be regained to near original values with washing and waxing. Paint adhesion is somewhat less than SMC after 1000 hours in the weatherometer.

Another property that is leading to sales of PUR is abrasion resistance. Reinforced PUR materials have Taber resistances far better than most other plastic materials. This advantage is one of the principle reasons PURs are used so widely in athletic shoes.

What Manufacturing Methods are Used to Make Polyurethanes?

Polyurethanes can be both thermoplastics and thermosets and can be both reinforced and nonreinforced. PURs are readily manufactured by almost all of the traditional manufacturing methods including extrusion, injection molding, thermoforming, and blow molding (for thermoplastics) and layup, sprayup, compression molding, and casting (for thermosets).

In addition, some special manufacturing methods have been developed to take advantage of the unique characteristics of polyurethanes. The most important of these unique characteristics is the two-part nature of the reactive liquid components which are mixed in nearly equal volumes. When mixed, these components (usually called the polyol and the isocyanate) will react very quickly, thus allowing short cycles. Pressures are lower than those needed for thermoplastic injection molding because the viscosities of the liquid materials are usually much lower than the viscosities of a molten thermoplastic. The process designed to take advantage of these polyurethane characteristics is called reaction injection molding (RIM). The RIM process uses two storage chambers which contain the polyol and the isocyanate, much like the storage containers in a sprayup system except that for polyurethanes the containers are nearly the same size and have nearly the same pumping volume. These liquids are pumped into a mixing head where the materials are both mixed and metered (pumped) into the mold. The mold is closed during the injection. After a few seconds or, at the longest a few minutes, the reaction of the two components is complete and the part is solid. The mold then opens and the part is removed.

The automotive industry has used the RIM process extensively because of its low emissions (no solvents and closed mold) and its rapid cycle time, especially for thick parts. The automotive industry has also pioneered the use of reinforcements in the RIM process. If the reinforcements are chopped fibers (usually small whiskers), the process is called reinforced reaction injection molding (RRIM) process. In this process, the fibers are mixed into one of the reactants in the storage container and they flow with that reactant into the mold. The pressures required for pumping are somewhat higher than traditional RIM because of the higher viscosity of the fiber-filled liquid, but even then the pressures are less than in thermoplastic injection molding.

Another method of adding reinforcement is to have the reinforcement in the mold prior to the entrance of the reactants. This method allows the use of long fibers, usually in the form of mat or cloth that is wrapped around a foam core for create a preform. This process is called structural reaction injection molding (SRIM). The fibers are wetted by the resins and the reinforcement is therefore encapsulated and held in shape by the polyurethane matrix. Because of the low viscosity of the injected fluids, only low pressures are required in the SRIM process and the molds can be made of a wide variety of materials, usually aluminum or soft steel.

Newer RIM, RRIM and SRIM machines can fill a 40-pound mold in under one second, usually at slightly higher pressures than were common in the past for these processes. Recent studies into mold filling mechanisms have shown that evacuation of the mold cavity substantially decreases fill time. Also, not surprisingly, glass preform density has been shown to be a critical factor in fill time. These studies have led to some interesting optimizations of structural requirements and fill time tradeoffs.

This process is similar to reinforced transfer molding (RTM) that is used to make reinforced polyester and epoxy parts, with a few notable differences. RTM usually does not use a mixing head but, rather, depends on an in-line mixer. To get the mixing desired with only an in-line mixer, the viscosities of the liquid reactant must be very low, and therefore, pressures in RTM can be even lower than those needed in RIM or SRIM. As with SRIM, a preform is placed in the mold prior to the injection of the resin, thus preserving the low viscosity of the reactants. The preform used with RTM is often a chopped fiber preform which has been shaped externally and is then placed in the RTM mold prior to closing it and injecting the reactants. Diagrams of the RTM and SRIM processes are shown in Figure 1.

Table 1 is a comparison of the RIM-like processes which can be used to make reinforced PUR and polyester parts. As noted in Table 1, the processes employing PUR resins contain no volatile solvents and require no peroxide initiators or accelerators. Mixing of the PUR materials is generally easier than with polyesters because the PUR components are mixed nearly 1:1, thus simplifying the mixing scheme. Reaction times for the PUR processes are generally much faster than for polyesters. If needed, catalysts (non-peroxide) can be added to the PUR materials to make the cure faster, but some difficulty is encountered when trying to slow down the reaction of the polyol and isocyanate. Wet-out of the fibers is relatively easy in all cases. Pressures are highest among these processes in the RRIM process and lower in the others which pump only neat liquids (without reinforcements).

Reinforced polyurethane parts can also be made by spray-up and wet lay-up techniques. In both of these manufacturing methods, normal mixing and spraying equipment is used, with some minor alterations to allow for the nearly equal mixing of the two polyurethane components. The molds for PURs would be about the same type as used for reinforced polyesters. Parts made by spray-up of polyurethanes include tailgates for salt-spray trucks (where the superior salt resistance of PUR over polyester is the consideration) and several parts which come into contact with gasoline (superior solvent resistance).

Reinforced polyurethanes have been successfully pultruded and filament wound, again without many modifications in the manufacturing apparatus except to inject the reactive components into the die rather than use a resin bath. Neither pultrusion nor filament winding have, however, gained the acceptance of RRIM or spray-up.

Polyurethanes can be easily cast. Some of the important applications for this method would be conveyor belts and other rubber replacement applications where the higher abrasion resistance and chemical resistance of PUR are desired properties, such as liners for hopper cars and belts and liners for mining applications. Some PUR belts have met FDA approval for food contact applications and there use as a matrix over flexible cloth or fibers for food processing belts is growing rapidly.

In all of these manufacturing methods, one major difference in handling of the materials should be noted. One of the components used to make polyurethanes is isocyanate. This material is reacts with water and therefore can be hazardous. It should not be allowed to come in contact with skin or eyes. Normal precautions are usually sufficient (goggles, gloves, long sleeves, etc.) but the high reactivity should be a constant safety consideration.

Polyurethanes can be both thermosets and thermoplastics. As thermosets, two components (isocyanate and polyol) are reacted. Both components are available in a wide variety of types and grades to provide an extremely wide range of properties. The thermoplastic material are available, as are most thermoplastics, in pellet form. Both non-reinforced and reinforced pellets can be purchased commercially. The reinforced pellets contain very short fibers at up to about 35% loading, typical of other reinforced thermoplastics.

What are the Major Limitations to Reinforced Polyurethanes?

The most serious limitation is simply cost. Polyurethanes cost from $0.75 to $1.00 per pound in the least expensive grades and are more typically $1.80/pound in the grades that would be used with fiberglass reinforcement. Some highly weatherable grades would cost over $3.00/pound.

Some authorities have suggested that polyurethanes have some problems in flammability that are not present in polyesters. Two issues have been raised. One is the possibility of formation of HCN, a highly toxic gas. Although this gas may be present in smoke from PURs, the levels detectable are quite small and are generally lost amidst all of the other off-gases and combustion products. Another issue raised against PUR flammability characteristics is the low amount of internal oxygen compared to many other plastic resins, such as polyesters. The critics suggest that this lower oxygen content will lead to the formation of more carbon monoxide, which is poisonous, rather than the harmless carbon dioxide. However, little evidence to support these suppositions has been widely distributed and accepted. Therefore, although some concerns have been raised with PUR flammability characteristics, they have not been carefully demonstrated. PUR materials will, however, burn, as do many plastics. Some progress has been made in reducing the flammability of PUR, chiefly by combining PURs with other polymer systems, but as yet, no common reinforced PUR material can meet the stringent flammability requirements for US Navy applications.

In general, polyurethanes are not going to replace polyesters except where the unique properties or processing advantages are very significant. The most important properties are flexibility, toughness, abrasion resistance, solvent resistance, and good adhesion. The advantages in processing are shorter cure cycles, some unique processing methods, and the lack of volatile solvents or co-reactants. With these advantages, applications for reinforced polyurethanes will continue to develop. Some will be as replacements for polyesters, but the majority are more likely to be as replacements for other materials or as totally new applications. This latter consideration is one of the challenges for the reinforced plastics industry. Can the industry expand by using current manufacturing technologies and new materials to enter new markets? Reinforced polyurethanes may have just the combination of properties that leads to some of these new markets.

Additional Reading and References

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