# Phenolics (PF)

**Phenolics** were the first thermoset materials to be synthesized (under the name of Bakelite™ by Leo Bakeland in 1907). They are still among the most widely used thermosets, undoubtedly because they are some of the lowest-cost engineering materials on a cost-pervolume basis. Phenolics are formed from the condensation polymerization reaction between phenol, an aromatic molecule, and formaldehyde, a small organic compound often used as a solvent or as a preservative. As discussed previously, crosslinking requires that at least one of the reactants have more active reaction sites than the minimum needed for just polymerization. Phenol has three active sites, as indicated in Figure 9.4, which is one more than condensation polymerization requires and therefore permits crosslinking to occur.

**Figure 9.4 Phenol showing (a) the reactive sites and (b) the crosslinked phenolic thermoset.**

        The condensation reaction for phenolics can be carried out under two different conditions, which produce very different intermediates (B-stage materials). The intermediates, called **resoles** in one case and **novolacs** in the other, are the materials usually sold to molders. In the resole process, the condensation polymerization is performed in an alkali solution with excess formaldehyde and is carefully controlled so that a linear, non-crosslinked polymer liquid, a resole, is produced. The resole can be stored or shipped for subsequent molding operations. When molding, the crosslinking is accomplished by simply heating the viscous liquid. Since the molder can form the crosslinked part by simply heating without needing to add any other materials, resoles are also called **one-stage resins**.

        The uncured resole is a viscous liquid that is water soluble and is widely used as a coating and impregnation material to give strength and body to paper when subsequently cured. Resoles can also be stirred vigorously to form a foamed material, about the consistency of whipping cream, which can then be molded and cured into a rigid foam. These foams will readily absorb and hold water and are used widely by florists as embedding forms for making floral displays. This and other phenolic products are shown in Photo 9.2.

(a)

(b)

**Photo 9.2(a) Phenolic handle. (b) Various phenolic products.**

        The novolacs are formed by reacting phenol and formaldehyde in an acid solution but with insufficient formaldehyde to complete the reaction—the opposite conditions from those used to form resoles. The resulting novolac material is a non-crosslinked polymer in the form of a powder. Novolacs will not crosslink with just the addition of heat, but require a curing agent, the most common of which is hexamethylene tetramine or, simply, **hexa**. Hexa is heat activated and so molding is usually done with pressure to compress the powder and with heat. Because a second material (hexa) must be added to novolacs, they are called **two-stage resins**.

        Most molded phenolic parts are made from novolacs. If molded without fillers or reinforcements, the parts are brittle and have high shrinkage in the mold, as would be expected from the highly aromatic and multiple crosslinked nature of the cured resin. (See Figure 9.4.) Novolac powders are therefore usually blended with fillers and reinforcements, called phenolic molding powders, to increase strength and toughness. The cost of the part is also reduced by the addition of the fillers. The most common filler is wood flour, which is a purified sawdust. Other common fillers and reinforcements are cotton fibers, fiberglass, and chopped thermoplastic fibers such as nylon.

        The high number of OH groups in the polymer gives it excellent adhesive qualities. Phenolic adhesives are used for plywood, printed circuit boards, foundry shells and cores, sandpaper, brake linings, and grinding wheels (where the grit is mixed with phenolic powder and molded to the desired shape).

        However, this highly adhesive nature of phenolics causes molding problems: They tend to stick to the mold. Mold releases can be sprayed onto the mold surface or the hot mold can be coated with beeswax. Alternatively, materials such as waxes can also be blended into the molding powder. Materials added to the resin for this purpose are called internal **mold releases**. A typical formulation for a phenolic molding material is given in Table 9.1.

**Table 9.1 Typical Formulation for a Phenolic Molding Compound**

        An important property of phenolics that leads to many applications is nonflammability. When phenolics are subjected to a flame, they char rather than melt or burn. Many applications in which avoiding flammability and smoke is important, such as the interior of airplanes, require that phenolics be used for coatings and many molded parts. Rocket nozzles are another application for which these properties are important. Most materials cannot withstand the tremendous heats of the exhaust gases from rockets. Because phenolics form a rigid and stable char that is only slowly eroded away by the action of the exiting gases, they are used for this application. Furthermore, the char has a very low thermal conductivity so that surrounding materials are protected by the decomposed phenolic (**char**).

        Low thermal conductivity is a property characteristic of phenolics that promotes their use as pan handles, bases for toasters, knobs for appliances, and motor housings. Most people recognize the dark handles characteristic of phenolics. The dark color is inherent to phenolics and limits their use in some applications. A dark pigment is often added to phenolics to standardize the color and to decrease the sensitivity of the material to UV radiation. (See Photo 9.2.) Phenolics also have very high electrical resistance, and so are used extensively for electrical switches, circuit breakers, connectors, and for commutators, radio cabinets, and automotive electrical parts. These latter applications are decreasing, however, because of the more rapid processing and inherent impact toughness of engineering thermoplastics.

        Solvent sensitivity of phenolics depends strongly on the nature of the filler. It is generally good for organic solvents but is poor for acids and bases.

        Phenolic powders are usually compression molded in matched metal molds, although they can also be transfer molded and injection molded. (When injection molded, care must be taken not to allow the thermoset material to set up in the barrel of the extruder, as might occur during an interruption in the molding process.) Because the crosslinking occurs by condensation polymerization reactions, water is a by-product of the process. If not allowed to escape from the part while crosslinking is occurring, this water can create part defects and surface blemishes. Therefore, when molding phenolics, the mold is often cracked open during the molding cycle to allow the water vapor (usually steam) to escape. This process is called **breathing the mold** or **bumping the mold**. Use of a dielectric preheater can help reduce the amount of water condensate.

        After the parts are molded, machining is rather difficult because of the abrasive nature of the filled phenolic resin. Fortunately, most phenolic parts are molded to near net shape, so extensive machining is not required.

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