CHAPTER 2

REVIEW OF PHENOLIC RESINS

Phenolic resins, which can be called phenol-formaldehyde resins, are synthetic polymers that conclude of a wide range variety of products resulting from the reaction of phenol or substituted phenol with aldehyde, especially formaldehyde , under various conditions. Phenolic resins posses many good properties, such as heat resistance, chemical resistance, moisture resistance, etc. Thus the most important uses of phenolic resins relate to the wood working industry, thermal insulation and molding compounds. Moreover phenolic resins are now employed in a wide range of applications from commodity construction materials to high technology applications in electronics and aerospace.

This chapter reviews the history of phenolic resins, classification of phenolic resins, the manufacture of phenolic resins and also its uses.

History

Phenol reacts with formaldehyde under both acid and alkaline conditions to yield isomeric molecules containing from one, two, or three, to a large amount of phenolic nuclei. The first report of the general reaction was made in 1872 by Adolf Beayer(Beayer,1872). He found that phenol and acetaldehye combined in the presence of an acid catalyst to give soluble, amorphous resins of little commercial significance. In 1894, both Lederer and Manasse synthesized o-hydroxybenzyl alcohol by low-temperature alkaline reaction of phenol and formaldehyde (Herman, 1969). In 1900, the first U.S. patent was granted for a phenolic resin, using the resin in cast form as a substitute for hard rubber (Peter, 1988). In 1900, Leo H. Baekeland convinced that the phenol-formaldehyde reaction could give a commercially valuable product. Later, in 1907, he had defined the differences between the catalytic action of acid and alkaline, and between more than and less than one mole of aldehyde per mole of phenol well enough to be able to manufacture a thermosetting resin reproducibly (Herman, 1969). The first commercial phenolic resin plant was Bakelite GmbH, started in Germany in 1910, and in the same year, the General Bakelite Co. was founded in the United States.

The early phenolic resins consisted of self-curing, resole-type products which are thermoplastic in nature. The early products by general Bakilite were used in molded parts, insulating varnishes, laminated sheets, and industrial coatings (Peter, 1988).

Classification of Phenolic Resins

There are many factors which can be deliberately varied to introduce special characteristics of phenol-aldehyde reaction products. The ones which devide phenolic resins into two great classes, novolaks and resoles, are the type of catalyst-specifically whether it is acid or alkaline- and the ratio of phenol to formaldehyde-specifically whether there is more or less than one mole of formaldehyde per mole of phenol.

1. Novolaks

Novolaks are prepolymers which prepared by the reaction of phenol and formaldehyde in a strongly acidic pH region. The reaction is carried out at a molar ratio of 1 mole phenol to 0.5-0.85 mole of formaldehyde. Novolaks are linear or slightly branch condensation products linked with methylene bridges of a relatively low molecular weight approximately 2,000. So these resins are thermoplastic which are soluble, permanently fusible and can be cured or crosslinked only by addition of a hardener (curing agent), almost exclusively hexamethylenetetramine, to form insoluble, infusible and cross-linked thermosetting products (Knop, 1985).

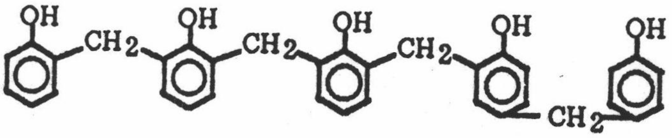


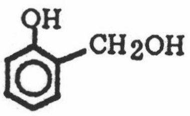
Figure 2-1 Example of a novolak resin molecule

The typical acid catalyst used for novolak resins is sulfuric acid, sulfonic acid, oxalic acid, or occasionally phosphoric acid. Hydrochloric acid, although once is widely used, has been abandoned becaused of the formation of toxic chloromethyl ether by-products. The acid catalyst and reaction conditions affect resin structure and properties. For example, oxalic acid, used for resin chosen for electrical applications, decompossed into volatile by-products on heating above 180 °C. More oxalic acid catalyst is required on an equivalency basis than the sulfonic acid types.

2. Resoles

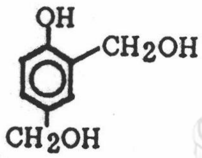
Resoles are prepolymers which prepared by the reaction of phenol and formaldehyde under alkaline condition, pH above 8. The reaction is carried out at molar ratio of 1 mole phenol per 1-3 mole formaldehyde. The results are mono-, di-, tri- hydroxymethylphenols (HMP), these prepolymers are heat reactive and can further react if apply heat, so the reaction must be stopped deliberately befor completion. (Knop, 1985).

The typical basic catalyst used for resoles is sodium, barium, magnesium, potassium and calcium hydroxides, sodium carbonate, ammonia and organic amines (Othmer, 1984).

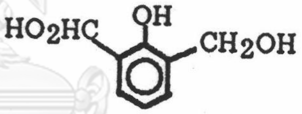


(*o*-hydroxymethylphenol)

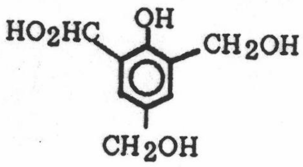
(*p*-hydroxymethylphenol)



(*o,p'*-hydroxymethylphenol)



(*o,o'*-hydroxymethylphenol)



(trihydroxymethylphenol)

Figure 2-2 Species of resole resins

Monomers of Phenolic Resins

1. Phenol

Phenol (C_6H_5OH) is the monomer or raw material used in the largest quantity to make phenolic resins. As a solid with a low melting point (40.9 ^{o}C), phenol is usually stored and handled in liquid form at 50-60 ^{o}C. Storage and transfer tanks for phenol are heated by immersion coils or jackets. (Peter et al, 1988).

2. Substituted Phenols

Substituted phenols used to produce phenolic resins are cresols and alkylphenols. Cresols are important principally for the production of varnish resin (Wolfgang et al, 1991). Alkylphenols are used for the production of coating resins or used as crosslinking agents in the rubber industry. (Knop, 1985).

3. Formaldehyde

Formaldehyde is the most important aldehyde for production of phenolic resins. It is used as an aqueous solution at concentrations between 30-60 %, but 50% is preferred for making most phenolic resins, even though half of the raw material are water. The water serves to moderate the reaction and is readily removed in processing equipmemt (Peter, 1988)

4. Other Aldehydes

The higher aldehydes are less important in producing phenolic resins. They react wiht phenol in the same manner as formaldehyde, although at lower rates. Examples of these aldehydes are furfural, acetaldehyde, butylaldehyde paraformaldehyde, glyoxal and benzaldehyde.

5. Hexamethylenetetramine (hexa)

Hexa is used either as a catalyst or a hardening agent. It forms adducts with phenols and novalaks very easily, which cross-linked on heating. (Peter and Wolfgang).

Manufacture of Phenolic Resins

The process and equipment used for phenolic-resin manufacture depend on resin type and the physical form in which the resin will be used. In general, phenolic resins are produced in small quantities of a great variety of types, so that batch processes are more economic.

The reactors are usually made of stainless steel alloys. Glass-lined reactors are occasionally used for nonalkaline resins. The reactor contains a bottom discharge, which must be large for solid heat-reactive resins. The product can also be discharged to a large cooled surface. Discharge to belt and drum flakers are highly automated; however, they can only be used for less-reactive resins (Peter, 1988).

1. Novolaks Production

Liquid phenol is placed into the reactor, followed by the precise amount of acid catalyst. The formaldehyde solution is added near 90 °C at a formaldehyde-to-phenol molar ratio of 0.75-0.85. For safety reasons, slow continuous of stepwise addition of formaldehyde is preferred because the reaction is exothermic. The heat of reaction is removed by refluxing the water combined with the formaldehyde. When the reaction is completed after 6-8 h at 95 °C, the volatiles, water, and some free phenol are removed by vacuum stripping up to 140-170 °C and 6.2-6.7 kPa (25-27 in.water). Both water and free phenol affect the cure and final resin properties, which are monitored in routine quality-control testing by gc (Peter, 1988). When the desire melting point is reached, the novolak resin is transfered to a heated vessel and then flaked on a continuous cooling belt, blended and pulverized with hexa and additives. Generally, novolaks are used mainly in pulverized form with hexa and additeves(Othemer,1984).

The acid catalyst has several significant effects at a constant rate of formaldehyde addition. Strong acids,e.g, sulfuric or hydrochloric, promote lower pH and rapid exothermic reaction. These acids normally are neutralized with lime or caustic before final dehydration. Weaker acids, e.g, oxalic or phosphoric, produce a milder reaction and a product of less color compared with products made with mineral acids. Oxalic acid decomposes to carbon monoxide, carbon dioxide, and water at elevated temperatures, about 180 °C, and neutralization or extraction process may be unnecessary.

2. Resoles Production

Most resoles are produced by a batch process. Initially, reaction of phenol and formaldehyde is carried out at a controlled heating rate. For low molecular weight water soluble resins, the product is cooled and neutralized after heating. If resin advancement is required, partial condensation is accomplished in a second step at same pH or at different pH. Finally, water is removed by vacuum dehydration, during which advancement time occurs. The product is recovered as a syrup, or solvent is added and the product is recovered in solution. Additives and modifiers can be added at different steps of the process and their permutations and combinations are almost infinite. The largest-volume uses of liquid resoles are for plywood and insulation applications.

Liquid and solution resole resins are cooled in the reactor using jacket cooling and vacuum refluxing. Discharged products are filtered and pumped to refrigerated, intermediate holding areas of packaging for shipping. The stability of liquid resole products varies greatly from product to product and depends on the storage temperature(Peter, 1988).

Uses of Phenolic Resins

1. Molding Materials

Phenolic molding materials are highly consolidated composites containing particulate and/or fibrous fillers, various additives, and a high concentration of resin binder. Resin functionality and curing conditions are such that a high cross-link density is developed in the finished part. Important properties of the cured product include temperatur resistance, modulus retention at elevate temperatures, good electrical properties, solvent resistance, and a high gloss surface. Cured products are applied to be electrical sockets, switch gear, circuit breakers, and many other devices where good electrical properties. Molding-material properties depend not only on the type of resin but also on the fillers used and their concentrations.

The phenolic resins that are used in molding materials are predominantly novolaks and hardening agent which usually are hexamethylenetetramine. Resin/curing-agent content is 30-50 wt%. Oxalic acid-catalysted novolaks are used in greatest amount.

2. Coatings and Adhesives

Most coating and adhesive applications involving phenolic resins are based on combinations with other thermoplastic or thermosetting polymers. In the area of coating applications are, automotive primers, can coatings, drum linings, anticorrosion paints, printing inks, wire enamels. In all cases, the phenolic is coreactive with the second resin. Phenolic-resin compositions varying depends on the polymer with which the resin is to be combined. All modified phenolic resins that are used in coatings display one or more of the following properties: good solvent, abrasion and corrosion resistance, thermal stability, and insulating properties,etc.

3. Wood Composites

Wood composites include plywood,particle board, fiberboard, wafer board, and macroscopic wood composites such as beams, arches. Plywood manufacture involves adhering three or more layers of wood with a phenolic resin under heat and pressure. Caustic-catalyzed water-soluble resoles are employed. The resin generally is combined with fillers and diluents in order to control wetting and to avoid substrate penetration. Particle board is based on wood chips, shavings, and wood flour rather than on wood sheeting. Liquid resoles are also the principal resin used in particle-board manufacture.

4. Fiber Bonding

In fiber bonding the resin is used as a binder in such products as thermal-insulation batting, acoustical padding, and cushioning materials. All these materials consist of long fibers laid down in a randomly oriented, loosely packed array to form a mat. They are bonded with resin to preserve the special insulating or cushioning quality of the mat. Resole-based resins are the standard for the fiber-bonding industry. They have excellent curing properties and low content of solvent extractables after curing.

5. Laminates

A wide variety of applications that exist for phenolic-bonded laminates are based on paper, cotton, or glass substrates. Commercial items include electronic circuit boards, gears, rods, bearings, furniture, wall paneling, home and office furnishings.

6. Abrasives

Phenolic-based abrasives are of two types; bonded abrasives, including grinding wheels, snagging wheels and coated abrasives, including sandpaper, disks, belts, etc. Bonded abrasives that are based on phenolic resins display greater strength and thermal-shock resistance than those based on ceramic or vitrified compositions. Metal grinding is a principal application for phenolic-bonded abrasives for which surface temperatures are higher than 1000 °C

7. Friction Materials

Phenolic resins are the principle bonding agent for the asbestos used in friction materials. The major categories are automotive brake lining,clutch facings and automatic transmission discs.