PHENOLIC RESINS

1. Introduction

Phenolic resins are a large family of polymers and oligomers, composed of a wide variety of structures based on the reaction products of phenols with formaldehyde. Phenolic resins are employed in a wide range of applications, from commodity construction materials to high technology applications in electronics and aerospace. Generally, but not exclusively, thermosetting in nature, phenolic resins provide numerous challenges in the areas of synthesis, characterization, production, product development, and quality control.

As a family of resins originally developed in the early twentieth century, the nature and potential of phenolic resins have been explored thoroughly to produce an extensive body of technical literature (1–9). A symposium sponsored by the American Chemical Society commemorated 75 years of phenolic resin chemistry in 1983 (10), and in 1987 the Phenolic Molding Division of the Society of the Plastics Industry (SPI) sponsored a conference on phenolics in the twenty-first century (1). Exciting new developments continue as new systems are developed for carbon–carbon composites, aramid honeycombs, and new derivative chemistries such as cyanate esters and benzoxazines. New U.S. patents with phenolic resins in the claims are growing at about 150 patents per year.

Phenolic resins are prepared by the reaction of phenol or substituted phenol with an aldehyde, especially formaldehyde, in the presence of an acidic or basic catalyst. Their thermosetting character and the exotherm associated with the reaction presented technical barriers to commercialization. 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 (11).

Work on the first commercially viable product was initiated by Baekeland in 1905. Using phenol and formaldehyde as starting materials, he established not only the differences between acid- and alkali-catalyzed products, but also the importance of excess phenol or formaldehyde made in producing intermediates. However, producing the resin was only part of the challenge. Baekeland also developed the technology to convert the reactive resins, which had a severe tendency to foam and cure to a brittle product, into useful molded articles by adding wood or mineral fibers and molding under heat and pressure. The final molded parts were tough, temperature resistant, and had a low void content (12). The first commercial phenolic resin plant was Bakelite GmbH, started in Germany in 1910; in the same year, the General Bakelite Co. was founded in the United States.

Early phenolic resins consisted of self-curing, resole-type products made with excess formaldehyde, and novolaks, which are thermoplastic in nature and require a hardener. The early products produced by General Bakelite were used in molded parts, insulating varnishes, laminated sheets, and industrial coatings. These areas still remain important applications, but have been joined by numerous others such as wood bonding, fiber bonding, and plywood adhesives. The number of producers in 2001 is approximately 15 in the United States and over 50 worldwide. Overall the number of producers is declining as the industry continues to undergo consolidation.

2. Monomers

2.1. Phenol. This is the monomer or raw material used in the largest quantity to make phenolic resins (Table 1). As a solid having a low melting point, phenol, C_6H_5OH, is usually stored, handled in liquid form at 50–60°C, and stored under nitrogen blanket to prevent the formation of pink quinones. Iron contamination results in a black color.

The most widely used process for the production of phenol is the cumene process developed and licensed in the United States by Honeywell (formerly AlliedSignal). Benzene is alkylated with propylene to produce cumene (isopropylbenzene), which is oxidized by air over a catalyst to produce cumene hydroperoxide (CHP). With acid catalysis, CHP undergoes controlled decomposition to produce phenol and acetone; α-methylstyrene and acetophenone are the by-products (13). Other commercial processes for making phenol include the Raschig process, using chlorobenzene as the starting material, and the toluene process, via a benzoic acid intermediate. In the United States, ~35–40% of the phenol produced is used for phenolic resins.

2.2. Substituted Phenols. Phenol itself is used in the largest volume, but substituted phenols are used for specialty resins (Table 2). Substituted phenols are typically alkylated phenols made from phenol and a corresponding α-olefin with acid catalysts (14). Acidic catalysis is frequently in the form of an ion-exchange resin (IER) and the reaction proceeds preferentially in the para position. For example, in the production of *t*-butylphenol using isobutylene, the product is >95% para-substituted. The incorporation of alkyl phenols such as cresol into the resin reduces reactivity, hardness, cross-link density, and color formation, but increases solubility in nonpolar solvents, flexibility, and compatibility with natural oils.

2.3. Formaldehyde. In one form or another, formaldehyde is used almost exclusively in the production of phenolic resins, regardless of the type of phenol (Table 3). It is frequently produced near the site of the resin plant by either of two common processes using methanol (qv) as the raw material. In the silver catalyst process, the reaction takes place at 600–650°C and produces water and hydrogen as by-products. The more common metal oxide process operates at 300–400°C. The gaseous formaldehyde is absorbed in water, and the final product is a formalin solution containing 36–50% formaldehyde. Of the various chemical forms of formaldehyde, the aqueous form is preferred for making phenolic resins, even though at least half of this form is water. The water serves to moderate the reaction and is readily removed in processing equipment (15).

Aqueous Formaldehyde. Water solutions of formaldehyde consist mainly of telomers of methylene glycol having <100 ppm of the formaldehyde as CH_2O (5). Alcohols form hemiformals with aqueous formaldehyde according to the following, where $n = 1, 2, 3$, etc.

$$\mathrm{ROH + HOCH_2OH \rightleftharpoons ROCH_2OH + H_2O}$$
$$\mathrm{RO(CH_2O)_{\mathit{n}}H + HOCH_2OH \rightleftharpoons RO(CH_2O)_{\mathit{n}+1}H + H_2O}$$

However, a second mole of alcohol or hemiformal does not add at the ordinary pH of such solutions. The equilibrium constant for hemiformal formation depends on the nature of the R group of the alcohol. Using NMR spectroscopy, a group of alcohols including phenol has been examined in solution with formaldehyde (16,17). The spectra indicated the degree of hemiformal formation in the order of methanol > benzyl alcohol > phenol. Hemiformal formation provides the mechanism of stabilization; methanol is much more effective than phenol in this regard.

The large value for the hemiformal formation constant of methanol and its low molecular weight explains the high efficiency of methanol in stabilizing formalin solutions. Phenol, on the other hand, is inefficient, and phenol hemiformals are only formed by careful removal of water (18).

2.4. Other Aldehydes. The higher aldehydes react with phenol in much the same manner as formaldehyde, although at much lower rates. Examples include acetaldehyde, CH_3CHO; paraldehyde, $(CH_3CHO)_3$; glyoxal, OCH−CHO; CHO; and furfural. The reaction is usually kept on the acid side to minimize aldol formation. Furfural resins, however, are prepared with alkaline catalysts because furfural self-condenses under acid conditions to form a gel.

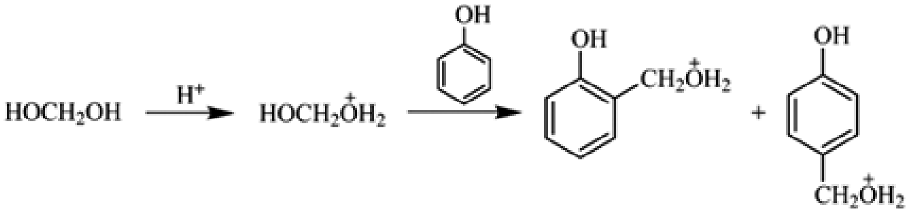
2.5. Hexamethylenetetramine. Hexa, a complex molecule with an adamantane-type structure, is prepared from formaldehyde and ammonia, and can be considered a latent source of formaldehyde. When used either as a catalyst or as a curative, hexa contributes formaldehyde-residue-type units as well as benzylamines. Hexa [100-97-0] is an infusible powder that decomposes and sublimes above 275°C. It is highly soluble in water, up to ca 45 wt% with a small negative temperature solubility coefficient. The aqueous solutions are mildly alkaline at pH 8−8.5 and reasonably stable to reverse hydrolysis.

2.6. Other Reactants. Other reactants are used in smaller amounts to provide phenolic resins that have specific properties, especially coatings applications. Aniline had been incorporated into both resoles and novolaks but this practice has been generally discontinued because of the toxicity of aromatic amines. Other materials include rosin (abietic acid), dicyclopentadiene, unsaturated oils such as tung oil and linseed oil, and polyvalent cations for cross-linking.

3. Polymerization

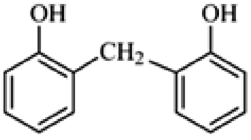
Phenolic resins are prepared with strong acid or alkaline catalysts. Occasionally, weak or Lewis acids, such as zinc acetate, are used for specialty resins.

3.1. Strong-Acid Catalysts, Novolak Resins. Phenolic novolaks are thermoplastic resins having a molecular weight of 500−5000 and a glass-transition temperature T_g of 45−70°C. The phenol−formaldehyde reactions are carried to their energetic completion, allowing isolation of the resin; formaldehyde−phenol molar ratios are between 0.5:1 and 0.8:1. Methylene glycol [463-57-0] (**1**) is converted to the corresponding hydrated carbonium ion **2**, which adds to the ortho and para positions of phenol with the elimination of water to form the corresponding ortho (**3**) and para (**4**) benzylic ions. The benzylic carbonium ions are in equilibrium with the corresponding benzylic alcohols, observed by NMR as transient species in the formation of novolak resins (16).

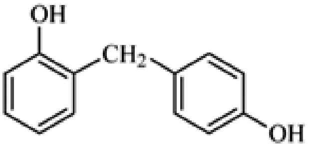


(1) (2) (3) (4)

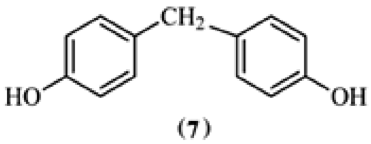
In the next step the hydrated benzylic carbonium ions **3** and **4** react with free ortho and para positions on phenols to form methylene-linked bisphenols, 2,2′(**5**), 2,4′(**6**), and 4,4′(7).



(5)



(6)

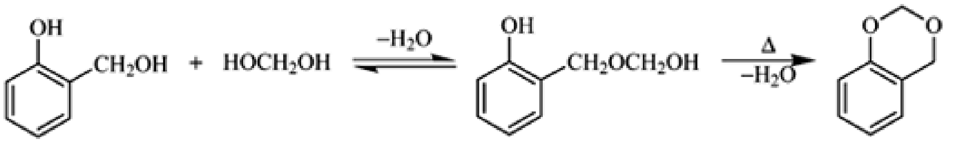


(7)

Continued reaction leads to the formation of novolak polymers having a molecular weight of up to 5000. Acid-catalyzed resins contain 50–75% 2,4′ linkages (**6**). The reaction rate is proportional to catalyst, formaldehyde, and phenol concentrations, and inversely proportional to the concentration of water. The rate of formation of the benzyl alcohol intermediate is 5–10 times lower than the rate to form the methylene-linked bisphenol (**3**). At typical molecular weights of 500–1000, novolak molecules are essentially linear because of the much lower reactivity of doubly-reacted phenolic units. In higher molecular weight polymers, the low concentration of end groups and unreacted phenol causes branching. Above 1000 molecular weight, branching has been observed by ^{13}C NMR; about 20% branching has been predicted in computer simulations (14,19,20).

In the curing process, end groups are more reactive than the backbone groups. Thus a branched resin having a higher content of end groups than a corresponding linear equivalent may gel sooner and cure faster because of the higher resin functionality. The properties of an acid-catalyzed phenolic resin are shown in Table 4.

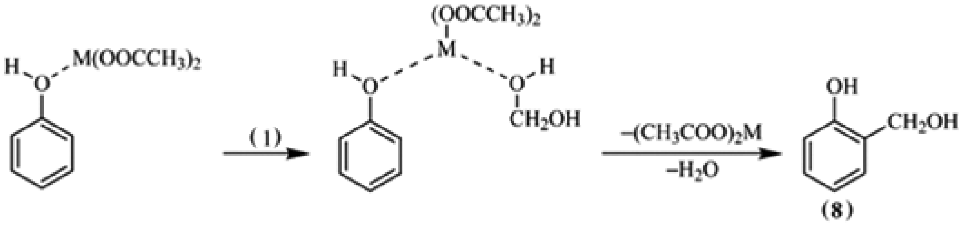
The typical acid catalysts used for novolak resins are sulfuric acid, sulfonic acid, oxalic acid, or occasionally phosphoric acid. Hydrochloric acid, although once widely used, has been abandoned because of the possible formation of toxic chloromethyl ether by-products. The type of acid catalyst used and reaction conditions affect resin structure and properties. For example, oxalic acid, used for resins chosen for electrical applications, decomposes into volatile by-products at elevated processing temperatures. Oxalic acid catalyzed novolaks contain small amounts (1–2% of the original formaldehyde) of benzodioxanes formed by the cyclization and dehydration of the benzyl alcohol hemiformal intermediates.

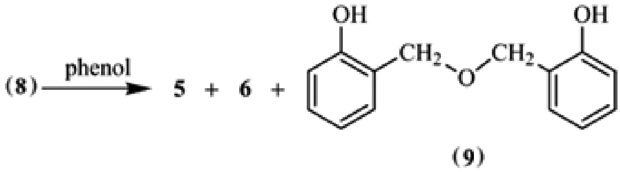


Benzodioxane is reasonably stable at neutral pH, but may decompose when the resin is cured, serving as a source of labile formaldehyde. Benzodioxanes are not found in sulfuric or sulfonic acid catalyzed resins, since the stronger acid readily catalyzes the second step in the reaction sequence.

3.2. Neutral Catalysts, High Ortho Novolaks. In the range of pH 4–7, formaldehyde substitution of the phenolic ring is possible, using divalent metal catalysts containing Zn, Mg, Mn, Cd, Co, Pb, Cu, and Ni; certain aluminum salts are also effective. Organic carboxylates are required as anions in order to obtain sufficient solubility of the catalyst in the reaction medium, as well as to provide a weak base. Acetates are most convenient and economical. Although lead acetate is highly effective because of its excellent solubility properties, it has been largely eliminated because of lead toxicity. Zinc and calcium salts are probably the most widely used catalysts (21).

Novolaks produced from these catalysts exhibit a high content of 2,2′-methylene units. The mechanism proposed for the ortho-directing effect involves chelation of the phenolic unit with the metal ion.

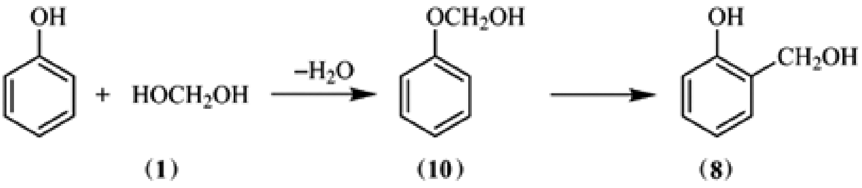




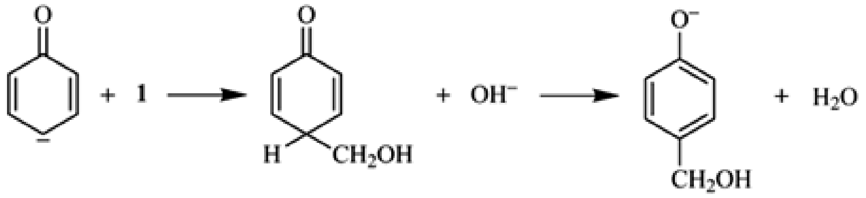
Zinc acetate catalyst produces essentially 100% *o*-methylol phenol (**8**) in the first step. The second step gives an approximately equal quantity of 2,2′- (5, 45%) and 2,4%-diphenylmethylene (6, 45%) bridges, indicating little chelate-directing influence. In addition, a small quantity (10%) of methylene ether units (**9**) (dibenzyl ether) is observed at moderate reaction temperature.

High ortho novolaks have faster cure rates with hexa. Typical properties of a zinc acetate catalyzed high ortho novolak are also shown in Table 4. The gel time with hexa is one-third of that with a strong acid catalyzed novolak.

3.3. Alkaline Catalysts, Resoles. Resole-type phenolic resins are produced with a molar ratio of formaldehyde to phenol of 1.2:1 to 3.0:1. For substituted phenols, the ratio is usually 1.2:1 to 1.8:1. Common alkaline catalysts are NaOH, $Ca(OH)_2$, and $Ba(OH)_2$. While novolak resins and strong acid catalysis result in a limited number of structures and properties, resoles cover a much wider spectrum. Resoles may be solids or liquids, water-soluble or -insoluble, alkaline or neutral, slowly curing or highly reactive. In the first step, the phenolate anion is formed by delocalization of the negative charge to the ortho and para positions. Alkaline catalysts are also effective in the polymerization–depolymerization of methylene glycol. The mechanism of the formaldehyde addition to the phenolate is still not completely understood. The most likely mechanism involves the contribution of phenol hemiformals (**10**) (5).



Rate studies show that base-catalyzed reactions are second order and depend on the phenolate and methylene glycol concentrations. The most likely path involves a nucleophilic displacement by the phenoxide on **1**, with the hydroxyl as the leaving group. In alkaline media, the methylolated quinone intermediate is readily converted to the phenoxide by hydrogen-ion abstraction (22).

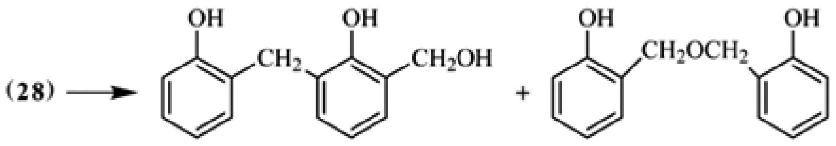


The ratio of ortho-to-para substitution depends on the nature of the cation and the pH. Para substitution is favored by K^+ and Na^+ ions and higher pH, whereas ortho substitution is favored at lower pH and by divalent cations, such as Ba^{2+}, Ca^{2+}, and Mg^{2+} (23).

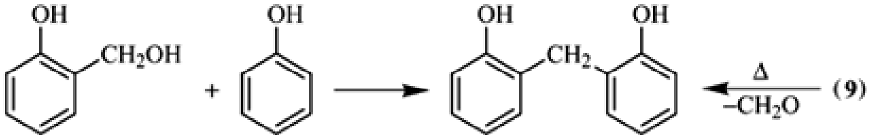
Several extensive kinetic studies on the polymethylolation of phenol have been reported (22,24,25). For the reaction scheme shown in Fig. 1, seven different rate constants must be determined. Despite different solution concentration, temperatures, and methods of analysis, comparing reaction rates (26–28) from each study using an NaOH catalyst gave fairly close agreement that rate constants increase with methylol substitution. In fact, dimethylol-substituted phenols react with formaldehyde two to four times faster than phenol. As a result, unreacted phenol remains high in resole resins (5–15%) even though the formaldehyde/phenol ratio is as high as 3:1.

The rate studies show that k_{264} is by far the fastest reaction (by a factor of 4–6) than k_2 or k_4, with k_{24} the second fastest (by a factor of 2–4) (22,25).

Although monomeric methylolated phenols are used in certain applications, such as in fiber bonding, higher molecular weight resins are usually desirable. Molecular weight is increased by further condensation of the methylol groups, sometimes after the initial pH has been reduced. Dibenzyl ether (**9**) and diphenylmethylene formation are shown in the following. The formation of diphenylmethylene bridges is favored above 150°C and under strongly alkaline conditions; dibenzyl ether formation is favored at lower temperatures and near neutral pH.

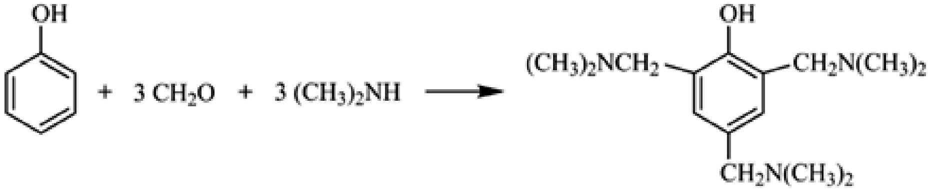


(9)

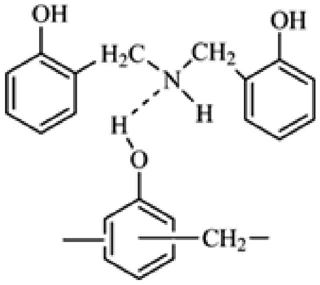


(8) (5)

Special resoles are obtained with amine catalysts, which affect chemical and physical properties because amine is incorporated into the resin. For example, the reaction of phenol, formaldehyde, and dimethylamine is essentially quantitative (29).



In practice, ammonia is most frequently used. With hexa, the initial reaction steps differ, but the final resole resins are identical, provided they contain the same number of nitrogen and CH_2 groups. Most nitrogen from ammonia or hexa is incorporated as dibenzylamine with primary, tertiary, and cyclic amine structures as minor products.



The physical properties of a resole resin prepared with hexa catalyst are shown in Table 5. Compared to the resin catalyzed with NaOH, this resin has higher molecular weight, less free phenol, lower water solubility, and a higher T_g.

This increase in T_g is higher than that expected if only phenol and formaldehyde were used, and is a result of the hydrogen-bonding interaction between the backbone amine units and the phenolic hydroxyls. Taking advantage of this effect, hexa and ammonia have been frequently used to produce solid, grindable, and water-insoluble resoles for molding compounds.

The methylene-isomer distributions of NaOH and hexa-catalyzed resoles are shown in Table 6. The distribution of amine structures is

$$\text{secondary} > \text{primary} \approx \text{tertiary}$$

and most benzylamines are ortho in the phenol ring from early steps in the reaction sequence.

4. Manufacture

The final state of a phenolic resin varies dramatically from thermoplastic to thermoset and from solid to liquid, and includes solutions and dispersions. With a bulk process, resole resins, in neat or concentrated form, must be produced in small batches ($\approx 2-10$ m^3) in order to maintain control of the reaction and obtain a uniform product. On the other hand, if the product contains a large amount of water, such as liquid plywood adhesives, large reactors (20 m^3) can be used. Melt-stable products such as novolaks can be prepared in large batches (20–40 m^3) if the exotherms can be controlled. Some reactors are reportedly as large as 60 m^3 (Ref. 9, p. 83).

Batch processes for most phenolic resins employ the equipment shown in Fig. 2. Liquid reactants are metered into the stirred reaction vessel through weigh tanks, whereas solid reactants such as bisphenol A and $Ba(OH)_2$ present handling problems. Facilities are provided to carry out the reaction under vacuum or an inert gas.

4.1. Materials of Construction. Compatibility of the materials of construction and the process chemicals is extremely important. The reactors are usually made of stainless steel alloys. Copper is avoided because of the possible presence of amines. Glass-lined reactors are occasionally used for nonalkaline resins. Because the use of HCl has been largely discontinued, material requirements are less stringent. The reactor contains a bottom discharge, which for solid heat-reactive resins must be large. Solid resole resins are discharged for rapid cooling in order to quench the thermosetting reactions. Resin coolers are made up of vertical plates with internally circulating water. The product can also be discharged to a large cooled surface. Discharges to belt and drum flakers are highly automated; however they can only be used for less-reactive resins.

Novolak resins can be stored molten in heated holding tanks under nitrogen. Because novolaks are used mainly in pulverized form with hexa and additives, a process that includes belt flaking and feeding directly into the blending and pulverizing system is preferred. Liquid and solution resole resins are cooled in the reactor by using jacket cooling and vacuum refluxing. Discharged products are filtered and pumped to refrigerated intermediate holding areas or packaged for shipping. The stability of liquid resole products varies greatly from product to product and depends on the storage temperature. The viscosity of a liquid resole resin increases but the water miscibility decreases as time and temperature increase. Generally, resoles, both liquids and solids, must be refrigerated.

4.2. Novolak Resins. In a conventional novolak process, molten phenol is placed into the reactor, followed by a precise amount of acid catalyst. The formaldehyde solution is added at a temperature near 90°C and a formaldehyde-to-phenol molar ratio of 0.75:1 to 0.85:1. For safety reasons, slow continuous or stepwise addition of formaldehyde is preferred over adding the entire charge at once. Reaction enthalpy has been reported to be above 80 kJ/mol (19 kcal/mol) (30,31). The heat of reaction is removed by refluxing the water combined with the formaldehyde or by using a small amount of a volatile solvent such as toluene. Toluene and xylene are used for azeotropic distillation. Following decantation, the toluene or xylene is returned to the reactor.

The reaction is completed after 6–8 h at 95°C; volatiles, water, and some free phenol are removed by vacuum stripping up to 140–170°C. For resins requiring phenol in only trace amounts, such as epoxy hardeners, steam distillation or steam stripping may be used. Both water and free phenol affect the cure and final resin properties, which are monitored in routine quality control testing by gas chromatography (GC). Oxalic acid (1–2 parts per 100 parts phenol) does not require neutralization because it decomposes to CO, CO_2, and water; furthermore, it produces milder reactions and low color. Sulfuric and sulfonic acids are strong catalysts and require neutralization with lime; 0.1 parts of sulfuric acid per 100 parts of phenol are used. A continuous process for novolak resin production has been described (32,33). An alternative process for making novolaks without acid catalysis has also been reported (34,35), which uses a peroxidase enzyme to polymerize phenols in an aqueous solution. The enzyme can be derived from soybeans or horseradish.

4.3. High Ortho Novolaks. The process for high ortho novolaks is similar to the one used for those catalyzed by strong acid. Zinc acetate is used at concentrations higher than the acids, typically 2% or more. The formaldehyde/phenol ratio is similar (0.75–0.85) but yields are 5–10% lower than those produced with strong acids, and reaction times are longer. Problems with gel particles and bulk gelation occur more frequently because small amounts of reactive dibenzyl ether groups are present. Overall, the process is more expensive because of higher raw material costs, lower yields, and longer cycle times.

Another process employs a pH maintained at 4–7 and a catalyst that combines a divalent metal cation and an acid. Water is removed continuously by azeotropic distillation and xylene is recycled. The low water content increases the reaction rate. The dibenzyl ether groups are decomposed by the acid; the yield of 2,2′-methylene can be as high as 97% (36).

4.4. Resoles. Like the novolak processes, a typical resole process consists of reaction, dehydration, and finishing. Phenol and formaldehyde solution are added all at once to the reactor at a molar ratio of formaldehyde to phenol of 1.2–3.0:1. Catalyst is added and the pH is checked and adjusted if necessary. The catalyst concentration can range from 1 to 5% for NaOH, 3 to 6% for $Ba(OH)_2$, and 6 to 12% for hexa. A reaction temperature of 80–95°C is used with vacuum-reflux control. The high concentration of water and lower enthalpy compared to novolaks allows better exotherm control. In the reaction phase, the temperature is held at 80–90°C and vacuum-refluxing lasts from 1 to 3 h as determined in the development phase. Solid resins and certain liquid resins are dehydrated as quickly as possible to prevent overreacting or gelation. The endpoint is found by monitoring the gel time, which decreases as the reaction progresses. Automation includes on-line viscosity measurement, GC, and gel-permeation chromatography (GPC).

4.5. Phenolic Dispersions. These systems are predominantly resin-in-water systems in which the resin exists as discrete particles. Particle size ranges from 0.1 to 2 μm for stable dispersions and up to 100 μm for dispersions requiring constant agitation. Some of the earliest nonaqueous dispersions were developed for coatings applications. These systems consist of an oil-modified phenolic resin complexed with a metal oxide and a weak solvent.

In the postdispersion process, the solid phenolic resin is added to a mixture of water, cosolvent, and dispersant at high shear mixing, possibly with heating. The cosolvent, frequently an alcohol or glycol ether, and heat soften the resin and permit small particles to form. On cooling, the resin particles, stabilized by dispersant and perhaps thickener, harden and resist settling and agglomeration. Both resole and novolak resins have been made by this process (26).

The *in situ* process is simpler because it requires less material handling (37); however, this process has been used only for resole resins. When phenol is used, the reaction system is initially one-phase; alkylated phenols and bisphenol A present special problems. As the reaction with formaldehyde progresses at 80–100°C, the resin becomes water-insoluble and phase separation takes place. Catalysts such as hexa produce an early phase separation, whereas NaOH-based resins retain water solubility to a higher molecular weight. If the reaction medium contains a protective colloid at phase separation, a resin-in-water dispersion forms. Alternatively, the protective colloid can be added later in the reaction sequence, in which case the reaction mass may temporarily be a water-in-resin dispersion. The protective colloid serves to assist particle formation and stabilizes the final particles against coalescence. Some examples of protective colloids are poly(vinyl alcohol), gum arabic, and hydroxyethylcellulose.

For products intended to remain stable dispersions for an extended period, a particle size of 2 μm or less is desirable. A thickening agent is usually added after the reaction has been completed and the mixture is cooled in order to prevent settling and agglomeration. Examples of thickeners are guar gum, xanthan gum, and hydroxyethylcellulose. The final products are generally between 40 and 50% solids, with a viscosity of 1500–5000 mPa·s (=cP).

Resole dispersions intended for isolation as discrete particles (27) can be used as flatting agents in coatings (28). Particles larger than 1000 μm are used in friction-element compositions. A-stage, thermosetting phenolic particles have been isolated from dispersion (27,38). With a hexa catalyst (6–12 parts) and a formaldehyde/phenol ratio of 1.5:1, the reaction is carried out at 50% solids for ≈90 min at 85°C. Poly(vinyl alcohol) and gum arabic are the preferred protective colloids. The particles (20–80 μm) are isolated from the mixture by filtration and, in the patent examples, by fluid-bed drying. These A-stage products (gel time at 150°C, 50–100 s) are suitable in applications where pulverized phenolic resins are being used, as well as in applications that take advantage of their spherical nature. One patent describes a sinter-resistant product for wood-bonding applications (39). In another patented process, both the production of particulate novolak resins and the aqueous dispersions of these resins are described (40).

4.6. Spray-Dried Resins. Spray drying produces resins in particulate form. Spray-drying a resole solution containing a blowing agent (41) produces phenolic microballoons. Spray drying also produces A-stage resins (42). The resins, prepared with a high NaOH content, are spray dried to give a final particle size of 40–60 μm. The particles are hygroscopic because of the high caustic content, but are sinter-resistant when kept dry. The principal application for this type of product is believed to be wood binding, especially for waferboard applications.

4.7. Cyanate Ester Resins. Cyanate ester resins, sometimes called triazines or cyanurates after the cured structure that they produce, are derived from phenols and phenolic resins. Specifically the starting phenols are reacted with cyanogen chloride, ClCN, and base to give the resins. In the cure step the cyanate groups trimerize to form triazine rings when heated in the range 180–250°C. Performance is generally intermediate between aromatic amine cured epoxides and toughened bismaleimides. Glass-transition temperature T_g is about 250°C and the heat distortion temperature is about 250°C dry and 175°C wet. Electrical properties are excellent due to very low residual chlorine content. Principal applications are printed wiring boards and structural composites (Fig. 3) (43).

4.8. Benzoxazine Resins. Benzoxazine resins are prepared by the reaction of phenol, formaldehyde, and an amine. In one particular example a benzoxazine is prepared from bisphenol A, formaldehyde, and aniline to give 2,2′-bis(3-phenyl-4-dihydro-1,3,2-benzoxazine) propane. When heated to about 200°C the methylene bond to oxygen breaks and reforms onto the available ortho positions of adjacent moieties to give dibenzylamine structures. Resin formulations have been developed and formulated, in some cases with epoxy and phenolic resins to give ternary systems with T_g as high as 170°C (Fig. 4) (43–46).

4.9. Biomass and Biochemical Processes. Phenolic resins have been produced from biomass and using biochemical processes in various ways. In Japan biomass from wood waste or waste from the food industry is treated with phenols and strong acid catalysis and heat to produce phenolic resins (47). Research at the National Renewable Energy Laboratory has shown that ablative fast pyrolysis can be used to convert a wide variety of biomass feedstocks into a liquid oil. The phenolic rich component can be extracted from this oil and used as a low cost replacement for synthetic phenol in phenolic resins (48). In another approach, soybean peroxidase enzymes have been used to prepare resins from phenolic moieties without the use of formaldehyde (49).

5. Cure

A typical resin has an initial molecular weight of 150 to perhaps 1500. For systems of unsubstituted phenols, the final cross-link density is 150–300 amu per cross-link. In other words, 25–75% of the ring-joining reactions occur during the cure phase.

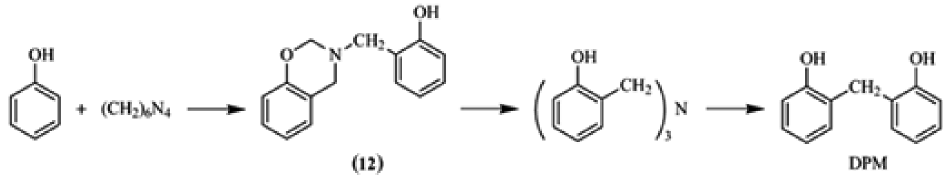
5.1. Resoles. The advancement and cure of resole resins follow reaction steps similar to those used for resin preparation; the pH is 9 or higher and reaction temperature should not exceed 180°C. Methylol groups condense with other methylols to give dibenzyl ethers and react at the ortho and para positions on the phenol to give diphenylmethylenes. In addition, dibenzyl ethers eliminate formaldehyde to give diphenylmethanes.

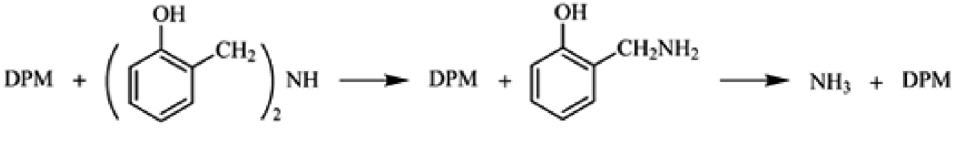
In some resole applications, such as foam and foundry binders, a rapid cure of a liquid resin is obtained at room temperature (RT) with strong acid. The reactions proceed in the same manner as those of novolak resin formation. Methylol groups react at ortho and para phenolic hydrogen to give diphenylmethane units (50).

At pH 4–6, the cure is slower than it is at pH 8 and higher, and much slower than at pH 1–3. Reactions at pH 4–6 resemble those on the more alkaline side, but with a substantial increase in side products. This is partly the result of the low rates of the main reactions and partly the result of stable intermediates at this pH range.

Some resoles contain latent acid catalysts, which on heating generate moderately strong acids. Examples include aryl phosphites such as diphenyl hydrogen phosphite and ammonium sulfate (51,52). The use of latent acid catalysis broadens the range of applications of phenolic resins to include areas such as liquid composite molding and pultrusion. Also resoles, which can contain so-called free formaldehyde, can be formulated with formaldehyde scavengers in form of amines such as melamine.

5.2. Novolaks. Novolak resins are typically cured with 5–15% hexa as the cross-linking agent. The reaction mechanism and reactive intermediates have been studied by classical chemical techniques (3,4) and the results showed that as much as 75% of nitrogen is chemically bound. More recent studies of resin cure (53–56) have made use of TGA, DTA, GC, IR, and NMR (16). They confirm that the cure begins with the formation of benzoxazine (**12**), progresses through a benzyl amine intermediate, and finally forms (hydroxy)diphenylmethanes (DPM).





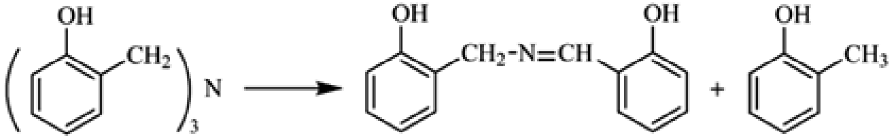
In the reaction of phenol and bisphenol F with hexa, NMR spectra show the transient appearance of benzoxazine intermediates; after 2 h at 103°C, all the benzoxazine decomposed to the diphenylmethylene and benzylamine intermediates (16).

The cure of novolaks with hexa has been studied with differential scanning calorimetry (DSC) and torsional braid analysis (TBA) (57); both a high ortho novolak and a conventional acid catalyzed system were included. The DSC showed an exothermic peak indicating a novolak–hexa reaction ≈20°C higher than the gelation peak observed in TBA. Activation energies were also calculated.

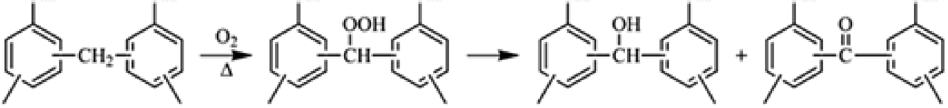
The resin rich in 2,2′-methylene exhibited the lowest activation energy, gel temperature, and DSC exotherm. The high concentration of the slightly acidic 2,2′-diphenylmethane end groups may account for the higher reactivity. These end groups should react with hexa to form benzoxazine intermediates first, which then decompose to react with vacant positions throughout the novolak molecule.

An isothermal method for studying the cure of phenolics employs dynamic mechanical analysis (DMA) (Table 7). The problems associated with programmed heating rates are avoided and mathematical treatment of the results is simplified. Although a more complex treatment is possible, a simple first-order dependence of modulus with time and an Arrhenius-type temperature dependence are sufficient. The rate studies of Table 7 indicate that doubling the amount of hexa doubles the rate at which the modulus approaches its long-term value. The novolak – 12% hexa cures substantially slower than the resole. In addition, they differ in temperature dependence of cure rates; the resole has an activation energy approximately four times greater than that of the novolak – 12% hexa (58).

5.3. Decomposition of Cured Resoles and Novolaks. Above 250°C, cured phenolic resins begin to decompose. For example, dibenzyl ethers such as (**9**) disproportionate to aldehydes (salicylaldehyde) and cresols (*o*-cresol). The aldehyde group is rapidly oxidized to the corresponding carboxylic acid. In an analogous reaction in hexa-cured novolaks, tribenzylamines decompose into cresols and azomethines, which cause yellowing.



Substantial decomposition of phenolic resins begins above 300°C. In the presence of oxygen, the methylene bridging group is converted to a hydroperoxide, which, in turn, yields alcohols and ketones on decomposition.



The ketone is especially susceptible to random chain scission. Decomposition continues up to ≈600°C; the by-products are mostly water, CO, CO_2, and phenols. The first stage of decomposition produces a porous structure having minimal shrinkage. The second stage begins near 600°C and is accompanied by shrinkage and substantial evolution of CO_2, H_2O, methane, and aromatics. The resulting polyaromatic chars represent ≈60% of the original resin when the atmosphere is inert, but this may be substantially less in the presence of air. The char ignites in air above 900°C.

The controlled decomposition of phenolic resins, in an inert atmosphere, is a method used to make carbon–carbon composites. In this case the resin is combined with other forms of carbon, such as carbon fibers, coke, and synthetic graphite, and cured under heat and pressure. Further heating to about 900°C converts the resin to a glassy form of carbon that can serve as a binder for the other carbon forms. The carbon yield from the phenolic resins can be in the range of 60–70% of the initial weight (see under Carbon–Carbon Composites).

6. Economic Aspects

In 2000, worldwide consumption of phenolic resins exceeded 4×10^6 t; slightly less than half of the total volume was produced in the United States (59). The largest-volume application is in plywood adhesives, an area that accounts for ≈49% of U.S. consumption (Table 8). All wood bonding applications account for about two-third of phenolic resin use. During the early 1980s, the volume of this application more than doubled as mills converted from urea–formaldehyde (UF) to phenol–formaldehyde adhesives because of the release of formaldehyde from UF products.

As a mature industry, U.S. production and application of phenolic resins have paralleled the growth in the GNP and the housing industry. The consumption of phenolic resins for coatings and molding powders has continued its decrease. The driving force behind coatings has been the need to reduce the volatile organics content (VOC) and the growth in alternative coatings such as waterborne, powder, and radiation-cured coatings. In the area of molding powders, numerous new engineering thermoplastics and alloys having superior properties have been introduced since the 1970s; however, phenolic molding powders continue to be used extensively in electrical, electronic, and machinery and underhood parts applications.

U.S. phenolic resin manufacturers include Ashland, Borden Chemical, Cytec Fiberite, Durez, FiberCote Industries, H.B. Fuller, P.D. George, Georgia-Pacific, International Paper, Lockport Thermosets, Maruzen America, Plastics Engineering, Resinoid, Sumitomo America, TriQuest, and Vantico (60).

Prices of phenolic resins vary substantially depending on the application. In 2001, the price of general-purpose and semisolids was \$1.50–1.80/kg, whereas epoxy-hardener grades can exceed \$2.20/kg. Because raw materials of phenolic resins are derived from crude oil and natural gas, the prices of phenolic resins depend on the prices of these resources.

7. Analytical Methods

The principal techniques for determining the microstructure of phenolic resins include mass spectroscopy (ms), proton and ^{13}C nmr spectroscopy, as well as gc, lc, and gpc. The softening and curing processes of phenolic resins are effectively studied by using thermal and mechanical techniques, such as tga, dsc, and dma. Infrared (ir) and electron spectroscopy are also employed. Recently matrix-assisted laser desorption-ionization mass spectrometry (MALDI-MS) has been used for the determination of molecular weight and end-group analysis (see MASS SPECTROMETRY). MALDI-MS is a soft ionization technique that has been applied to the determination of mass of large biomolecules and synthetics resins. The approach is useful for molecular weight determination and end-group analysis. Both novolaks and resoles have been studied and individual fragments with m/z up to about 2000 specifically identified. For resoles the technique is even able to resolve the various hemiformal structures that can occur. (Ref. 9, p. 92; 61–63).

7.1. Spectroscopy.

Infrared spectroscopy (64) permits structural definition, eg, it resolves the 2,2′- from the 2,4′-methylene units in novolak resins. However, the broad bands and severely overlapping peaks present problems. For uncured resins, nmr rather than ir spectroscopy has become the technique of choice for microstructural information. However, Fourier transform infrared (ftir) gives useful information on curing phenolics (65). Nevertheless, ir spectroscopy continues to be used as one of the detectors in the analysis of phenolics by gpc (see VIBRATIONAL SPECTROSCOPY).

A great wealth of microstructural information is provided by Fourier transform ^{13}C nmr. Using the much greater chemical-shift range of this technique, detailed structural information is provided for both the aliphatic and the aromatic carbons (Table 9). Current techniques provide highly reliable quantitative data and relative peak areas (19,66–70) and make possible a quantitative measure of the numbers of branch points and end groups. Branching can cause early gelation in a novolak resin, and end groups usually have greater reactivity in the thermosetting reaction than do the backbone units. Another important advantage of ^{13}C nmr is the parametric predictability of the chemical-shift values. As a result, unknown peaks can be assigned to a hypothetical structure with reasonable certainty. At the same time, the process can be reversed and a computer can provide detailed structural analysis. ^{13}C nmr has been applied to cured phenolic resins (71).

7.2. Chromatography.

Gel-permeation chromatography (GPC) is an invaluable technique for determining the molecular size distribution of polymers. Phenolic resins, which have molecular weight components ranging from 100 to rarely more than 5000, require special column arrangements to optimize resolution. By using proper instrument calibration, it is possible to obtain number-average (M_n) and weight-average (M_w) molecular weight as well as quantitative information on free monomer and certain other low molecular weight species (71–73) (see CHROMATOGRAPHY, SIZE EXCLUSION).

Many resole resins exist as phenolate salts in solution. Because these ionic species are sparingly soluble in carrier solvents such as tetrahydrofuran, careful neutralization and filtration are required. Although GPC is an excellent technique for examining medium and high molecular weight fractions, GC and high performance LC are more effective for analyzing low molecular weight species.

Gas chromatography (GC) has been used extensively to analyze phenolic resins for unreacted phenol monomer as well as certain two- and three-ring constituents in both novolak and resole resins (74). It is also used in monitoring the production processes of the monomers, eg, when phenol is alkylated with isobutylene to produce butylphenol. Usually, the phenolic hydroxyl must be derivatized before analysis to provide a more volatile compound. The GC analysis of complex systems, such as resoles, provides distinct resolution of over 20 one- and two-ring compounds having various degrees of methylolation. In some cases, hemiformals may be detected if they have been properly capped (66).

The combined techniques of GC/MS are highly effective in identifying the composition of various GC peaks. The individual peaks enter a mass spectrometer in which they are analyzed for parent ion and fragmentation patterns, and the individual components of certain resoles are completely resolved.

High performance liquid chromatography (HPLC) is extremely effective in separating individual resin components up to a molecular weight of 1000 according to size and polarity. Dilute-solution conditions and low temperatures preserve the structure of unstable components. The resins are usually not derivatized. Gradient solvent elution gives excellent peak separation (74,75). In one study, resoles catalyzed by sodium and barium hydroxide were compared, and the components were separated up to and including methylolated four-ring compounds (66). Resole components resolved by GC and HPLC techniques are shown in Table 10. Like GC, HPLC is most effective when combined with other analytical tools, such as mass and UV spectroscopy. By using preparative-scale HPLC, individual peaks can be analyzed by proton and ^{13}C NMR spectroscopy.

7.3. Thermal Analysis. The main thermal analysis techniques applied to phenolic resins are TGA and DSC. In TGA, the sample weight is monitored microanalytically with time and temperature in air or nitrogen. When applied to resins and molding compounds, the scans indicate cure and decomposition temperatures accompanied by a measurable loss in weight. Resoles and novolaks lose from 5 to 20% of their weight on curing at 100–200°C. Weight loss provides information on shrinkage, void formation, and density change of composites.

Phenolic resins give a high char yield on combustion and TGA provides a measure of the expected yield. Typical values are between 40 and 65% in nitrogen. Decomposition begins at 350°C and continues up to 600°C. Autoignition temperature in air is above 900°C. Thermogravimetric analyses have played an important part in the development of carbon–carbon and carbon–graphite-fiber composites containing phenolic resins. These composites are used in aircraft brake linings and carbon-pipe applications. In DSC and DTA, heat flow and sample temperature are compared to a reference material. Glass-transition temperature T_g is determined by DSC. The T_g of liquid resoles is below RT, that of friable novolaks is in the range of 50–75°C, and that of lightly cross-linked phenolics is between 150 and 225°C.

Cure kinetics of thermosets are usually determined by DSC (76,77). However, for phenolic resins, the information is limited to the early stages of the cure because of the volatiles associated with the process. For pressurized DSC cells, the upper limit on temperature is $\approx 170^\circ$C. Differential scanning calorimetry is also used to measure the kinetics and reaction enthalpies of liquid resins in coatings, adhesives, laminations, and foam. Software packages that interpret DSC scans in terms of the cure kinetics are supplied by instrument manufacturers.

7.4. Dynamic Mechanical Analysis. In DMA, a vibrating or oscillating sample is heated at a programmed rate or held isothermally at elevated temperature. The frequency and damping characteristics of the sample are monitored with time. A change such as gelation or passage through the T_g causes abrupt changes in the fundamental oscillation frequency of the sample and the damping ability of the specimen. The oscillation frequency can be related to the storage modulus of the sample, whereas the damping contains information related to the loss modulus.

Softening and cure are examined with the help of a torsional pendulum modified with a braid (78), which supports thermosets such as phenolics and epoxies that change from a liquid to a solid on curing. Another method uses vibrating arms coupled to a scrim-supported sample to measure storage and loss moduli as a function of time and temperature. An isothermal analytical method for phenolic resins provides data regarding rate constants and activation energies and allows prediction of cure characteristics under conditions of commercial use (58).

DSC and DMA scans of a novolac cure are shown in Figures 5a and 5b (79). The sample is a glassy solid initially and the DMA shows the distinctive T_g at 65°C followed by the appearance of a liquid state. From 110 to 125°C, the resin is a liquid and the chemical curing reactions begin, and it is followed by gelation at 140°C. Further reaction continues until 200°C, when a highly cross-linked, infusible solid is obtained. As the sample is cooled to RT, a slight increase in storage modulus is observed. The peak in the damping curve indicates the T_g of the cross-linked system at about 185°C.

Dynamic mechanical analysis provides a useful technique to study the cure kinetics and high temperature mechanical properties of phenolic resins. The volatile components of the resin do not affect the scan or limit the temperature range of the experiment. However, uncured samples must be supported by a braid, a scrim, or paper. This does not influence the kinetic results and can be corrected in the calculations of dynamic mechanical properties. Recent DMA work on phenolic resins has been used to optimize the performance of structural adhesives for engineered wood products and determine the effect of moisture in wood product on cure behavior and bond strength (80–82).

7.5. Control Tests. Numerous chemical and physical tests are used in the manufacture of phenolic resins to ensure correct properties of the finished resins, including the following: refractive index is used to estimate the dehydration during manufacture and is proportional to the solids content; viscosity is used to determine molecular weight and solids content; nonvolatiles content is roughly proportional to polymer content; miscibility with water depends on the extent of reaction in resoles; specific gravity is measured for liquid resins and varnishes; melting point of novolaks and solid resoles affects application performance; gel times determine the reactivity of the resins; resin flow is a measure of melt viscosity and molecular weight; particle size affects performance and efficiency; and flash point and autoignition temperature provide flammability-characteristic measurements required by government agencies regulating safety and shipping. ASTM D4706-93 (1998) describes the standard test method for qualitative determination of methylol group in phenolic resins.

8. Health and Safety Factors

The factors contributing to the health and safety of phenolic resin manufacturing and use are those primarily related to phenol (qv) and formaldehyde (qv). Unreacted phenol in a resin can range from $\sim$5% for liquid resoles used in impregnation processes to well below 1% for novolaks intended for use as epoxy hardeners. Free formaldehyde can be $<$1% in liquid adhesives. Novolaks are usually free of formaldehyde. The toxicity of the resins is significantly lower than that of the phenol and formaldehyde starting materials. No detrimental toxicological effects have been reported for cured phenolic resins, which can be used in direct contact with food as in can coatings.

Uncured resins are skin sensitizers and contact should be avoided, as well as breathing the vapor, mist, or dust. Novolak-based pulverized products generally contain hexamethylenetetramine, which may cause rashes and dermatitis. Phenolic molding compounds and pulverized phenolic adhesives must be controlled as potentially explosive dusts. In addition, they contain irritating or toxic additives. ASTM test method D4639-86 (1996) describes the method for volative content in phenolic resins.

8.1. Phenol. Phenol is highly irritating to the skin, eyes, and mucous membranes in humans after acute inhalation or dermal exposures. Phenol is considered to be quite toxic to humans via oral exposure, with blood changes, liver and kidney damage, and cardiac toxicity reported. Chronic inhalation exposure to phenol in humans has been associated with gastrointestinal irritation, liver injury, and muscular effects. No data are available on the developmental or reproductive effects of phenol on humans. EPA has classified phenol as a Group D, not classifiable as to human carcinogenicity. The NIOSH threshold limit value (TLV) and Occupational Safety and Health Administration (OSHA) permissible exposure limit for phenol is 19 mg/m^3 (83). The health and environmental risks of phenol and alkylated phenols, such as cresols and butylphenols, have been reviewed (84).

8.2. Formaldehyde. Acute and chronic inhalation exposure to formaldehyde in humans can result in eye, nose, and throat irritation and respiratory symptoms. Reproductive effects have been reported in women workers exposed to formaldehyde. Limited human studies have reported an association between formaldehyde exposure and lung and nasopharyngeal cancer. The EPA has classified formaldehyde as a Group B1, probable human carcinogen of medium carcinogenic hazard. The OSHA has set its permissible exposure limit (PEL) at 4.5 mg/m^3 and the American Conference of Governmental and Industrial Hygienists have set the TLV at 1.5 mg/m^3 (85).

8.3. Wastewater. Phenol is a toxic pollutant to the waterways and has an acute toxicity ($\sim$5 mg/L) to fish. Chlorination of water gives chlorophenols, which impart objectionable odor and taste at 0.01 mg/L. Biochemical degradation is most frequently used to treat wastewater containing phenol. Primary activated sludge, along with secondary biological treatment, reduces phenol content to below 0.1 mg/L (86). ASTM D1783-01 describes the standard test methods for phenolic compounds in water.

8.4. Flammability. Phenolics have inherently low flammability and relatively low smoke generation. For this reason they are widely used in mass transit, tunnel building, and mining. Fiber-glass reinforced phenolic composites are capable of attaining the 1990 U.S. Federal Aviation Administration (FAA) regulations for total heat release and peak heat release for aircraft interior facings (1,87). They are also used as “fire restricting material” on cruise ships, high speed ferries, and commercial submarines. The self-ignition temperature is about 600°C and limiting oxygen index (LOI) is in the range 40–49% (88).

9. Recycling

Thermosets are inherently more difficult to recycle than thermoplastics, and thermosetting phenolics are no exception. However, research in this area has been reported, and molded parts have been pulverized and incorporated at 10–15% in new molding powders. Both German and Japanese groups had instituted this type of practice in 1992 (89,90).

A number of alternatives will have to be developed in order to effectively utilize cured phenolic material (91). One approach is the “thermoset recycling pyramid,” a preferred order of execution that includes

1. Tier 1: Reintroduction of the used material into the original material at relatively low levels (~10%) in the raw material mix (this approach is used widely to recycle SMC and BMC thermoset polyesters)
2. Tier 2: Reuse of the material in a lower performance thermoset product at relatively high levels (40–50%)
3. Tier 3: Reuse of the product in alternative materials such as asphalt, roofing materials, concrete, and other construction products
4. Tier 4: Pyrolysis of the material to generate raw material feed stocks and incineration for energy recovery. Phenolic molding compounds can yield a caloric value of 14,000–23,000 kJ/kg, depending on the type of filler.

Plenco and other companies have been working with the SPI’s Phenolic Division to produce a “Recycling Blueprint” shown in Figure 6 below (92).

10. Applications

10.1. Coatings. For coatings applications, phenolic resins are grouped into four classes, depending on heat reactivity and the type of phenol. Substituted phenols are more compatible with oil and hydrocarbons, whereas heat-reactive resins require polar solvents. Depending on its nature, the resin can be used alone or as a modifying resin that acts as an adhesion promoter, a chemical cross-linker, or a hardening agent. In these cases the primary resin may be an alkyd, polyester, or epoxy (93).

Unsubstituted heat-reactive resins are designed for baked-on coatings and are usually not oil-soluble. They require strong solvents and although most are not water-miscible, their low molecular weight, high formaldehyde content promotes water miscibility. These resins are available as solids, viscous liquids, and solutions. Resins prepared with an alkaline catalyst and a slight excess of formaldehyde over phenol are heat-reactive, but not as much as resole resins designed for fiber bonding and paper impregnation. Recommended cure conditions are 30 min and 150°C.

Heat-reactive resins are more compatible than oil-soluble resins with other polar-coating resins, such as amino, epoxy, and poly(vinyl butyral). They are used in interior-can and drum linings, metal primers, and pipe coatings. The coatings have excellent resistance to solvents, acids, and salts. They can be used over a wide range of temperatures, up to 370°C for short periods of dry heat, and continuously at 150°C. Strong alkalies should be avoided.

The maximum recommended film thickness is 25 μm. At greater thicknesses, volatiles from the curing reaction, mainly water and some formaldehyde and phenol, can cause defects. These coatings have excellent electrical insulation properties, ie, up to 20 V/μm, because of low moisture absorption and low conductance. The coatings are hard with low flexibility, depending on curing conditions and film thickness.

Phenolic baking coatings can be used for metal, ceramic, and plastic surfaces. Applications include equipment for heating and air conditioning, chemical processing, petroleum refining, and water treatment. Some types are used in oil-well pipes and marine environments (94). Certain coatings can be used in food and beverage processing, subject to regulations.

The largest use of novolak resins in coatings is as a hardener for epoxy resins. The epoxy is frequently based on bisphenol A or epoxidized novolaks. Basic catalysts such as benzyldimethylamine are required for moderate baking conditions, such as 2 h at 180°C. The phenolic/epoxy ratio is adjusted to be stoichiometrically equivalent in order to give a highly cross-linked coating that has moderate flexibility and excellent resistance to chemicals, heat, and moisture. Powder coating of pipes continues to be a growing application, especially when corrosion resistance is required. In solution form, the epoxy–phenolic systems are used as metal primers and in pipe coating.

Substituted heat-reactive resins are most widely used in contact-adhesive applications and, to a lesser extent, in coatings (95,96); *p*-butylphenol, cresol, and nonylphenol are most frequently used. The alkyl group increases compatibility with oleoresinous varnishes and alkyds. In combination with these resins, phenolics reduce water sensitivity. Common applications include baked-on and electrical insulation varnishes, and as modifiers for baking alkyds, rosin, and ester gum systems. Substituted heat-reactive resins are not used for air-dry coatings because of their soft, tacky nature in the uncured state; substituted nonheat-reactive phenolics are the modifying resin of choice in this case.

Substituted nonheat-reactive resins do not form a film and are not reactive by themselves, but are excellent modifier resins for oleoresinous varnishes and alkyds. Their high T_g and molecular weight provide initial hardness and reduce tack; oxygen-initiated cross-linking reactions take place with the unsaturated oils.

Early phenolic resin drying-oil varnishes were cooked in order to incorporate the phenolic resin into the formula. These resins have been replaced by cold-cut resins that reduce atmospheric emission by permitting direct incorporation of the phenolic after the oleoresinous varnish has been prepared. High solids systems enable coatings to meet the VOC standards required by regulatory agencies. Newer phenolic varnishes, developed in the 1980s, may contain as high as 80% nonvolatile solids (97).

Oleoresinous phenolic varnishes are excellent coatings that dry in 2–4 h and show exterior durability, corrosion resistance (especially when aluminum-modified), compatibility, solubility, and good package stability. Recoatability and intercoat adhesion are also excellent. The films are sensitive, however, to strong solvents and concentrated acids and alkalies. Unlike systems containing cross-linking phenolics, films containing these resins remain flexible.

Phenolics that are not heat-reactive may be incorporated into both air-dried and baked oleoresinous coatings. Applications vary widely and include clear and pigmented exterior varnishes, aluminum-maintenance paints, zinc-rich primers, can coatings, insulation varnishes, and concrete paints. As modifiers in a great variety of applications, they enhance the performance of oleoresinous and alkyd coatings.

10.2. Dispersions.

In phenolic resin dispersions, the continuous phase is water or a nonpolar hydrocarbon solvent. The resin exists as droplets that have particle sizes of 1–20 μm and are dispersed in the continuous phase. Aqueous dispersions are prepared either *in situ* during the preparation of the resin itself or by high shear mixing (26,37).

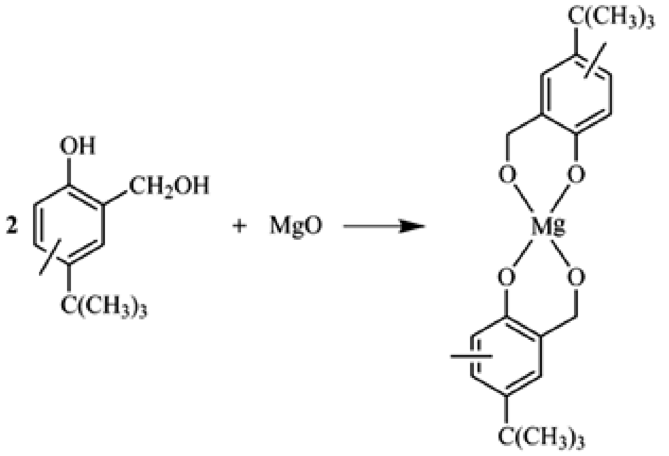
Aqueous dispersions are alternatives to solutions of liquid and solid resins. They are usually offered in 50% solids and may contain thickeners and cosolvents as stabilizers and to promote coalescence. Both heat-reactive (resole) and nonheat-reactive (novolak) systems exist that contain unsubstituted or substituted phenols or mixtures. A related technology produces large, stable particles that can be isolated as discrete particles (55). In aqueous dispersion, the resin structure is designed to produce a hydrophobic polymer, which is stabilized in water by an interfacial agent.

Aqueous dispersions are used in fiber bonding, paper coating, friction and abrasive applications, and laminates and wood bonding. Phenolic dispersions improve the strength of latex-contact adhesive applications. Epoxy-modified phenolic dispersions are prepared by dispersion of the phenolic epoxy resin. The systems are used for baked primer applications and bonding requirements. Minimum baking conditions are 20 min at 150°C (26).

10.3. Adhesives.

Contact adhesives are blends of rubber, phenolic resin, and additives supplied in solvent or aqueous dispersion form; they are typically applied to both surfaces to be joined (98). Evaporation of the solvent leaves an adhesive film that forms a strong, peel-resistant bond. Contact adhesives are used widely in the furniture and construction industries and also in the automotive and footwear industries. The phenolic resins promote adhesion and act as tackifiers, usually at a concentration of 20–40%. In solvent-based contact adhesives, neoprene is preferred, whereas nitrile is used in specialty applications. The type and grade of phenolic resin selected control tack time, bond strength, and durability.

Neoprene–phenolic contact adhesives, known for their high green strength and peel values, contain a resole-type resin prepared from 4-*t*-butylphenol. The alkyl group increases compatibility and reduces cross-linking. This resin reacts or complexes with the metal oxide, eg, MgO, contained in the formulation, and increases the cohesive strength of the adhesive. In fact, the reactivity with MgO is frequently measured to determine the effectiveness of heat-reactive phenolics in the formulation.



Phenolic resins substantially increase open time and peel strength of the formulation (98). For example, higher methylol and methylene ether contents of the resin improves peel strength and elevated temperature resistance. Adhesive properties are also influenced by the molecular weight distribution of the phenolic; low molecular weight reduces adhesion (99).

Waterborne contact adhesives contain an elastomer in latex form, usually an acrylic or neoprene-based latex, and a heat-reactive, cross-linkable phenolic resin in the form of an aqueous dispersion. The phenolic resin improves metal adhesion, green strength, and peel strength at elevated temperature. A typical formulation contains three parts latex and one part phenolic dispersion (dry weight bases). Although metal oxides may be added, reaction of the oxide with the phenolic resin does not occur readily.

Bonding properties of water-based contact adhesives are similar to those of solvent-based systems, but are free of flammability hazards. However, drying times are longer and the bond is sensitive to moisture.

10.4. Carbonless Copy Paper. In carbonless copy paper, also referred to as pressure-sensitive record sheet, an acid-sensitive dye precursor, such as crystal violet lactone or *N*-benzoylleucomethylene blue, is microencapsulated with a high boiling solvent or oil within a cross-linked gelatin (94,100,101) or in synthetic mononuclear microcapsules. Microcapsules that have a starch binder are coated onto the back of the top sheet. This is referred to as a coated-back (CB) sheet. The sheet intended to receive the image is treated on the front (coated-front (CF)) with an acid. When the top sheet is mechanically impacted, the dye capsules rupture and the dye solution is transferred to the receiving sheet where the acid developer activates the dye.

The original acid–clay developers have been largely replaced by phenolic compounds, such as para-substituted phenolic novolaks. The alkyl group on the phenolic ring is typically butyl, octyl, nonyl, or phenyl. The acidity is higher than that of a typical unsubstituted novolak because of the high concentration of 2,2′-methylene bridges.

Color intensity and permanence are improved by metal carboxylate salts, especially zinc salts (100), which catalyze the dye development and stabilize the dye in its colored form. The substituted novolak resin, along with extender and binder, can be applied to the receiving sheet as a solution or aqueous dispersion. Aqueous dispersions are probably the most widely used; they are manufactured by the resin supplier or the user from the base resin.

A typical coating composition for the CF component is shown in Table 11. It is dried in a high velocity air oven at 93°C.

10.5. Molding Compounds. Molding compounds were among the earliest applications for solid phenolic resins. Molding neat phenolic resin was almost impossible and the strength, especially on impact, was poor without reinforcement. Combining the resin, usually a novolak, with hexa, wood-flour, or asbestos reinforcement, as well as pigments and additives, gave a moldable thermoset. The molded articles exhibit high temperature, flame, and chemical resistance, retention of modulus at elevated temperature, and hardness. Systems that have good electrical properties can be formulated at low cost. Resins can be compounded with a choice of fillers for a variety of applications.

ASTM D4617-96 is the specification that covers phenolic molding compounds. The general-purpose compounds, having good strength and electrical properties, are used in electrical appliances, automotive ignitions, and handles. Impact-resistant grades contain longer glass and textile fibers and rubber modifiers. Applications include pump housing and switches. Heat resistance is improved by incorporating mineral and glass fillers. Electrical-grade compounds contain mica and fiber glass fillers, and are used in specialty switches and cases. Graphite filler reduces the coefficient of thermal expansion. Although phenolic molding compounds compete with a wide variety of thermoset and thermoplastic compounds, they continue to be the preferred material in numerous applications, such as reinforced phenolic pistons in automotive disk brakes and transmission torque converters. Table 12 lists several applications for molded phenolic parts.

Phenolic molding materials are prepared by first blending the pulverized raw materials. In a compounding operation, the blend is passed through heated rolls to form a sheet as the resin melts. The compounded mixture remains on heated rolls until the desired flow and viscosity are reached. At this point, it is discharged as a thin sheet and allowed to cool. The product is then granulated and packaged. Alternatively, a Banbury-type mixer can be used for the initial mixing; the mix is then fed to a roll mill for finishing and sheeting. Compounding extruders are also used and through a continuous process provide a pelletized product (see Mixing and Blending).

Phenolic resins used in molding materials are predominantly novolaks with hexa as the curing agent. Oxalic acid catalyzed novolaks and high ortho resins are used. Resole resins may be used in place of hexa as the curing agent in certain electrical applications in which the NH_3 generated from the hexa can adversely affect metals such as copper and silver. Typically, the compound contains 40–50 wt% resin binder, 40–45% filler, and 5–10% pigment and additive. Fillers and reinforcements include wood flour, nutshell flour, cellulose fiber, mica (qv), wollastonite, mineral wool, mineral flour, glass fiber, organic fiber, carbon fiber, clay, and talc (qv). Additives and pigments are magnesium oxide, graphite, molybdenum sulfide, stearates, calcium carbonate, carbon black, nigrosine, lime, fluoropolymers, and salicylic acid.

Molding materials are fabricated into articles by compression, transfer, and injection molding processes. For compression molding, the powder is poured into the mold cavity or a preform heated prior to molding. Temperature ranges from 140 to 190°C and pressures from 13.8 to 55.5 MPa (2000–8000 psi). Because the material is more fluid in the mold, transfer molding is suitable for molding around inserts or for intricate shapes. In injection molding, cross-linking in the barrel and sprues must be avoided.

10.6. Abrasives. Abrasive materials are either bonded or coated. Bonded phenolic abrasives have superior strength and shock resistance compared to sintered ceramic compositions. The higher stability permits higher rotational speeds for resin-binder wheels; however, temperatures are lower than with ceramic wheels.

Synthetic aluminum oxide and silicon carbide are the principal inorganic abrasive materials. They are used in grit sizes from 44 or finer to 1680 μm (12–325 mesh). The coarser grit sizes are used for rough work when wheels are as large as 60 cm in diameter and 7.5-cm thick. These wheels are mounted in swinging-frame grinders and used to remove surface imperfections from stainless steel billets. Finer grit (250 μm (60 mesh)) may be used in 45-cm-dia cutoff wheels mounted in automatic grinders. These wheels can slice through a solid 2.5-cm steel bar in 4 s, leaving a clean, shiny cut surface.

In the usual method of manufacture, the grit is first wetted with a low viscosity liquid resole phenolic resin or furfural, using 1–3 wt% of the grit. A dry mixture of phenolic resin and fillers is added and the combination of wet grit and powder is tumbled until each grit particle is coated. The mix is temporarily dry and free-flowing. The powdered phenolic resin varies from 6 to 10% of the weight of the grit. The quantity and type of filler (alumina, cryolite, iron oxide, silicate) depend on the intended use of the wheel, whose grinding characteristics are affected by the filler. The free-flowing grit resin mix is placed into the mold and pressed at RT for 1–2 min at 13.8–34.5 MPa (2000–5000 psi). The dense form is removed and cured for 12–24 h; temperatures are increased gradually to 185°C for 8–12 h. Pressing temperatures may be increased for high density structures.

Heat resistance is an important characteristic of the bond. The strength of typical abrasive structures is tested at RT and at 300°C. Flexural strengths are between 24.1 and 34.4 MPa (3500–5000 psi). An unmodified phenolic resin bond loses about one-third of its RT strength at 298°C. Novolak phenolic resins are used almost exclusively because these offer heat resistance and because the moisture given off during the cure of resole resins results in undesirable porosity.

Some novolaks modified with epoxy or poly(vinyl butyral) resin are used for softer grinding action.

Coated abrasives, such as sheets, disks, and drums, are used for polishing and finishing. Here, too, the abrasives, such as aluminum oxide and silicon carbide, have replaced the flint and garnet of common sandpaper. These industrial coated abrasives are manufactured from cloth or tough paper base. First, a coat of medium viscosity liquid resole resin is laid down on a continuous web of the backing. The web passes wet-side-down over a pan of grit, which adheres to it electrostatically and remains embedded in the resin layer. Altering the strength of the applied electrostatic field and the speed of the web can control the amount of grit deposited, which varies from an open to a closed dense mass of abrasive. The uncured coated sheet is partially dried in a low temperature oven at 60°C, and a second, thinner coating of lower viscosity liquid resole resin is applied as a top to anchor the grit thoroughly. The coated web is taken off in rolls to be cured at 107–120°C for 3–4 h.

The resins should dry quickly and cure well at low temperatures. They usually are made at a high pH with high ratios of formaldehyde to phenol and held to fairly low molecular weight. Typical viscosities are 15,000 mPa·s (=cP) at 75% solids content for a first coat and 1000 mPa·s (=cP) at 50% solids for the top resin. For dense backing materials, such as fiber disks, a typical resin has a viscosity of 50,000 mPa·s (=cP) at 80% solids and is cured at 148°C. New opportunities are arising for coated abrasive belts in high pressure grinding. High strength backing has been developed and zirconia media are available for grinding.

10.7. Friction Materials. Phenolic friction materials are made from molding compounds developed to meet the extraordinary demands required by friction elements in the transportation industries. Friction materials are used for brake linings, clutch facings, and transmission bands. A moderately high coefficient of friction, which is temperature-independent, is needed. In addition, the material must be high in strength, low in wear and abrasion, and resistant to moisture and hydraulic fluids.

In the 1980s, significant changes occurred in automotive brake elements. Reformation of friction elements eliminated asbestos and increased employment of disk brakes. These developments required binder resins that have higher temperature performance without affecting the coefficient of friction and wear. Alternatives to asbestos include mineral, carbon, aramid, and metal fibers, especially iron. Semimetallic linings contain as much as 70% iron fibers. Other inorganic fillers include barites, alumina, lime, magnesia, and clay. Graphite and molybdenum disulfide are used to reduce scoring.

The resins can be a novolak–hexa or a resole–novolak blend. In some applications liquid resoles are used. Addition of alkylated phenol, oil, or cashew nutshell liquid (CNSL) reduces hardness and increases abrasion resistance. Modification by rubber improves the coefficient of friction and reduces brake fading.

Many friction material formulations contain 5–15 wt% of friction particles, the granulated cross-linked products of the reaction of CNSL, a phenol substituted at the meta position with a C_{15}, unsaturated side chain, and formaldehyde.

Friction particles range in size from 50 to 500 μm. They reduce frictional wear and increase pedal softness (103).

Manufacture of friction elements includes the impregnation of fabrics and subsequent lamination, the wet-dough process, and the dry-mix process. Elements from the last two are prepared by compression-molding the formulation for up to an hour at 150–175°C. Thick brake elements require a carefully controlled heating-and-cooling cycle to minimize stresses created by expansion and contraction.

10.8. Foundry Resins. In the foundry industry, phenolic resins are used as the binder for sand in the manufacture of shell molds and cores. The two mating halves are joined by clamps or a bonding agent to form a shell mold into which the molten metal is poured for castings. The shell is formed by depositing a resin–sand mix on a hot metal pattern plate. After a certain period the pattern is inverted and the excess resin–sand is removed. The sand particles are bonded by an oven cure, and the shell is ejected from the pattern plate.

Iron is the preferred metal for casting; steel and nonferrous metals are used in smaller amounts. Most castings are made in green sand molds, ie, uncured molds of sand, clay, and water. However, the use of shell moldings is growing, because such moldings permit reproducibility of castings with close dimensional accuracy. In addition, the simplicity of equipment procedures reduces costs.

The shell-molding process, introduced in the United States in 1948, is an important market for phenolic resins. In the original process, dry sand and powdered resin (6–8%) are blended. However, because of the high binder content and the difficulty in obtaining a uniform mix, precoating methods were developed.

Both cold- and warm-coating processes employ solutions of phenolic resins. The principal process used for foundry resins is the hot-coating process. It is the fastest, least expensive, and safest process, and it requires no volatile removal. The sand is heated to 135–170°C in a muller, and solid novolak resin in flake form is added, which melts quickly and coats the sand. A lubricant may be added at this point. After 1 min of mulling, the batch is cooled by adding water, which evaporates rapidly.

Hexa, which is not supplied with the resin, is usually added either with the water as a solution or just before or immediately after the water addition. By quenching the mix with water, the resin-coated sand is cooled to a point where there is no significant reaction with the curing agent. Any reaction between the resin and the hexa in the muller affects the bonding properties of the coated sand. As the batch cools and begins to break up, more lubricant may be added, which remains on the outside of the coated grains where it is most effective.

The total cycle time for most production batches is 2.5–3.5 min, considerably shorter than the cold- or warm-coating processes. Although a few available units have large capacity per batch, high production rates are possible because of the short cycle. While one batch is being mulled, sand for the next batch can be heated. The typical flake phenolic is an intermediate melting-point novolak containing 4% lubricant.

10.9. Laminates. Laminate manufacture involves the impregnation of a web with a liquid phenolic resin in a dip-coating operation. Solvent type, resin concentration, and viscosity determine the degree of fiber penetration. The treated web is dried in an oven and the resin cures, sometimes to the B-stage (semicured). Final resin content is between 30 and 70%. The dry sheet is cut and stacked, ready for lamination. In the curing step, multilayers of laminate are stacked or laid up in a press and cured at 150–175°C for several hours. The resins are generally low molecular weight resoles, which have been neutralized with the salt removed. Common carrier solvents for the varnish include acetone, alcohol, and toluene. Alkylated phenols such as cresols improve flexibility and moisture resistance in the fused products.

Industrial laminates are composed of two or more webs in sheet form that have been impregnated with a thermosetting resin and molded under heat and pressure. The web is usually made of cellulose paper, cotton fabric, glass cloth, glass mat, asbestos paper, wood veneer, and similar materials. Laminates are manufactured in sheets, rods, tubes, and special shapes, which can be machined by common methods to produce parts for a wide range of uses. An important example is in printed-circuit applications, which require varnishes that impart electrical properties, punchability, machinability, and hot-solder and solvent resistance to the laminate. General-purpose laminates are used in gears, spacers, cams, ball-bearing retainer rings, and other structural parts requiring machinability as well as moisture, oil, and impact resistance.

A decorative laminate is composed of layers of resin-impregnated paper, which have been molded together under heat and pressure to form a solid homogeneous sheet. The component parts are composed of corestock impregnated with phenolic, print, and overlay. The corestock confers body and strength. The print sheet provides the design characteristic; it is impregnated with melamine resin, as is the overlay sheet that imparts abrasion protection to the print sheet. Approximately seven sheets of phenolic-impregnated corestock are covered with one print sheet, which, in turn, is covered with one overlay sheet. This combination is molded against polished steel plates to obtain the desired finish, usually satin or gloss.

The type of varnish used in the process depends on the kraft paper manufacturer and basis weight of the papers; the machine, temperature, and control (scraper bars, squeeze rolls) used; the method of cutting the paper to size; the laminate being produced (post-forming or regular); and the press-cure cycle (see Laminated Materials, Plastic).

10.10. Air and Oil Filters.

Liquid resole resins are used to coat and penetrate the cellulose fibers of filters and separators in order to increase strength and stiffness and protect against attack by the environment. The type of phenolic to be used depends on both the final property requirements and the papermaking process.

Air and oil filters are made by a dry-web process in which the filter paper is dried over heated metal drums. The paper is saturated with the phenolic resin solution, either off- or on-line, and dried in an oven advancing the resin to the B-stage (semicured). The sheet, containing 20–30% resin, is rolled and shipped to the filter-unit manufacturer, where the sheet is convoluted and the filter assembled and cured to the C-stage (fully cured).

The resins used in air and oil filters are moderate-to-low molecular weight, catalyzed by caustic in one step; 10–20% alcohol is added; solids content is in the range of 50–60%. These resins are designed to penetrate the sheet thoroughly, yet not to affect the porosity of the paper. In the B-stage, the resin must have sufficient flexibility to permit pleating; the C-stage should have stiffness and resistance to hot oil.

10.11. Wood Bonding. This application requires large volumes of phenolic resins (5–25% by weight) for plywood, particle board, waferboard, and fiberboard. Initially, phenolic resins were used mainly for exterior applications, whereas UF was used for interiors. However, the concern over formaldehyde emission has caused the replacement of UF by phenol–formaldehyde adhesives.

Different phenolic resins are used for different types of wood; for example, plywood adhesives contain alkaline-catalyzed liquid resole resins. Extension with a filler reduces cost, minimizes absorption, and increases bond strength. These resins have an alkaline content of 5–7% and are low in free phenol and formaldehyde. Because many resins have a high water content and limited storage stability, they are frequently made at or near the mill producing the plywood product. The plywood veneers are dried, coated with resin, stacked for pressing, and cured at 140–150°C.

Particle board and wood chip products have evolved from efforts to make profitable use of the large volumes of sawdust generated annually. These products are used for floor underlayment and decorative laminates. Most particle board had been produced with UF adhesive for interior use; resin demand per board is high due to the high surface area requiring bonding. Nevertheless, substantial quantities of phenol–formaldehyde-bonded particle board are produced for water-resistant and low formaldehyde applications.

The phenolic resins used for particle board are NaOH-catalyzed resoles of low viscosity and high water miscibility, similar to the liquid resole adhesives used in plywood manufacture. The higher resin and caustic content of the board frequently necessitates the addition of hydrophobic agents such as wax emulsions to increase the barrier properties of the board. The adhesive is applied to the particles in thin streams using high agitation to maximize material usage. Boards are cured in presses for 5–10 min at 150–185°C.

Waferboard, a more recent wood construction product, competes more with plywood than with particle board. Waferboard and strand board are bonded with solid, rather than liquid, phenolic resins. Both pulverized and spray-dried, rapid-curing resins have been successfully applied. Wafers are dried, dusted with powdered resin and wax, and formed on a caul plate. A top caul plate is added and the wafers are bonded in a press at $\approx$180°C for 5–10 min. Physical properties such as flexural strength, modulus, and internal bond are similar to those of a plywood of equivalent thickness.

Fiberboard or hardboard is made of low grade wood and wood waste. In the wet production process, a sheet is produced on a papermaking machine, such as a fourdrinier. A liquid resole is usually added to the beater section and precipitated onto the wood fibers by adjusting the pH. The moderately dry felt is further dried and cured in an off-line press.

10.12. Fiber Bonding. In fiber bonding, the resin is used as a binder in such products as thermal insulation batting, acoustic padding, and cushioning materials. All these materials consist of long fibers (glass or mineral fiber, cotton, polyester) 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.

In the dry-bonded process, fibers are reclaimed from woven textile scraps and powdered resin. Automotive acoustical padding (cotton and synthetic organic fiber) and thermal insulation batting (glass fiber) are made by this process. Inorganic and/or organic fibers are picked open to allow distribution of the phenolic resin among individual fibers. The fiber–resin mixture is formed into a blanket by cross-lapping a series of webs or by being blown into a chamber for deposition. The blanket is oven-cured to fuse the resin. Oven temperatures, dwell times, molding temperatures, and cycle times vary, depending on the type of fiber and curing characteristics of the resin.

The wet-bonded process uses virgin fiber spun from molten glass and liquid water miscible resin. High grade, thermal insulation batting is made by this process. The most common wet-bonded process for manufacturing glass or rock-wool, thermal insulation batting employs steam- or air-blowing. A stream of molten glass falls from the melting furnace into a rapidly spinning platinum cylinder. Centrifugal force causes the glass to be extruded through many small holes in the cylinder wall. At the outside, the fibers are attenuated (drawn) by the action of a jet flame from burners located around the spinning cylinder. Spray nozzles located just below this unit apply liquid binder resin to the fibers, which are sucked onto a moving screen to form a continuous mat. The mat is conveyed through a forced hot-air curing oven similar to that used in the dry-bonded process. Curing is followed by cool-down, trimming, slitting, and roll-up.

Fiber bonding resins are marketed in the form of finely pulverized powders of novolak/hexa mixtures or resoles and water-miscible liquids. Resole resins are the standard for the fiber bonding industry. They have excellent curing properties and low content of solvent extractables after curing. Bond strength to the fiber is high and resin usage is low. Solid resole resins must be stored cool to reduce sintering and aging.

Novolak-based resins are primarily used for organic fibers. They require a cross-linking reagent, usually hexa, for cure. Bond strength is good, producing bonded mats that have high tensile strengths. The storage stability is also good, so that refrigeration is rarely required. A typical binder mix produced by the customer consists of phenolic resin, urea, hydrocarbon oil or wax emulsion, ammonium sulfate, and occasionally a silane adhesion promoter; it is diluted with water to 5–10% solids content. The urea acts as a scavenger for the free formaldehyde (5–8%) invariably present, both as an inexpensive extender and, owing to its high nitrogen content, as an antismoldering agent. The oil or wax emulsion acts as a fiber lubricant and dust suppressant, the ammonium sulfate as a cure accelerator, and the silane as an adhesion promoter. The large volume of water in the binder mix cools the newly spun fibers, thus preventing premature resin cure, ie, before the mat has been formed and compressed to the proper thickness. All water-miscible resins must be stored under refrigeration.

10.13. Composites. There has been substantial progress in improving the processability of phenolics in composite materials (104–106) to the point where a variety of materials are available for pultrusion, filament winding, and resin-transfer molding (see COMPOSITES, FABRICATION). More complicated composite systems are based on aramid and graphite fibers.

Epoxy resins are usually superior to phenolics because of better adhesion, lower shrinkage on curing, and a much lower volatile content. Nevertheless, there are many specific applications for phenolic resins, including formable laminates and sheet-molding compounds having low flammability and smoke generation. These systems are suitable for aircraft interiors. Another area is in binders for carbon–carbon composites for applications such as in ablative coatings of reentry vehicle and aircraft brakes. The high char yield and the strength and porosity of the char are important in these applications. Finally, phenolic novolaks are effective curing agents for epoxies, and epoxidized novolaks are being used in applications requiring high functionality and high cross-link density.

Glass-Reinforced Composites. These composites are prepared from SMC and by liquid injection molding, (LIM). Phenolic resins are usually not amenable to LIM because of the volatiles generated. However, a resin suitable to LIM has been prepared (107). The properties of the 60% glass-mat-reinforced product obtained from this resin were compared to conventional isophthalic polyester and vinyl ester sheet-molding compounds at equivalent glass loading; the mechanical properties are shown in Table 13 (108,109). The phenolic resin systems have slightly lower strength values but measurably higher impact resistance. In addition, the phenolic glass composite has a UL-94 V0 rating, whereas the polyester SMC burns.

A patent describes the glass-reinforced pultrusion of phenolic resin composites (110). In pultrusion, bundles of continuous fiber are wetted with resin and shaped and cured through a series of heated dies. A sulfonic acid accelerates the cure rate, which must be high. The mechanical properties are reported to be equivalent to those obtained from conventional unsaturated polyesters, but the heat-distortion temperature and flammability resistance are superior. An acid-free phenolic pultrusion system has been announced that can produce large panels for buildings, ships, aircraft, and mine ducts. The system involves an injection-type die rather than conventional dip tanks, and up to 70% glass loadings can be attained (111).

Phenolic sheet-molding compound is seeing increased use in interior and exterior applications in mass transit. The trains in service on the English Channel tunnel have several panels made from phenolic SMC, which had to meet the strict European safety standards for fire and smoke generation.

Phenolic resin prepregs on glass fibers are prepared from alcohol solution and occasionally from aqueous solutions. The glass web is dipped in a tank containing resin solution; the resin content in the web is controlled by metering rolls. The wet web is dried in a horizontal or vertical oven arrangement and cured to B-stage of the resin. The dry web is cut, stacked, and stored under refrigeration until used in a laminate. Depending on the application, the prepreg can be rigid, similar to the epoxy-type prepregs used in laminated circuit boards, or soft and flexible, which provides the tack and drape required to conform to a shaped article. Autoclave molding is essential for shaped articles to reduce void formation by trapped air and volatiles. Examples of shaped articles include interior parts of commercial airplanes such as the composite duct assembly, based on wrapped phenolic – fiber glass, being used on the Boeing 737. Although not equal to epoxy-prepreg systems in strength, phenolic resins provide superior flammability resistance and lower smoke toxicity, because antimony and halogens are absent.

Carbon-Fiber Composites. Cured laminates of phenolic resins and carbon-fiber reinforcement provide superior flammability resistance and thermal resistance compared to unsaturated polyester and epoxy. Table 14 shows the dependence of flexural strength and modulus on phenolic–carbon-fiber composites at 30–40% phenolic resin (112). These composites also exhibit long-term elevated temperature stability up to 230°C.

Carbon–Carbon Composites. Above 300°C, even such polymers as phenolics and polyimides are not stable as binders for carbon-fiber composites. Carbon–carbon composites are used at elevated temperatures and are prepared by impregnating the fibers with pitch or synthetic resin, followed by carbonization, further impregnation, and pyrolysis (112).

Carbon–carbon composites are used in high temperature service for aerospace and aircraft applications as well as for corrosion-resistant industrial pipes and housings. Applications include rocket nozzles and cases, aircraft brakes, and satellite structures. Carbonized phenolic resin with graphite fiber functioned effectively as the ablative shield in orbital reentry vehicles for many years (113).

Phenolic and furfuryl alcohol resins have a high char strength and penetrate into the fibrous core of the fiber structure. The phenolic resins are low viscosity resoles; some have been neutralized and have the salt removed. An autoclave is used to apply the vacuum and pressure required for good impregnation and sufficient heat for a resin cure, eg, at 180°C. The slow pyrolysis of the part follows; temperatures of 1000–1800°C are recommended for the best properties. On occasion, temperatures above 1800°C are used and constant weight is possible even up to 2760°C (114). A new process for carbon–carbon composite has been developed for engine components using phenolic resin and PAN fiber to produce near netshape parts (115,116).

10.14. Nanocomposites.

Work conducted at Toyota in nylon-6 nanocomposites (qv) has generated several commercial products and stimulated substantial interest in a variety of polymer/nanoclay systems. The melt intercalation and curing behavior of phenolic resin were investigated using layered silicates such as montmorillonite and alkyl ammonium modified layered silicates. It was found by X-ray diffraction that the uncured phenolic was effectively intercalated. Depending on the surface treatment, the resulting interaction between organic modifier and phenolic resin played an important role in determining the stable nauostructure and the final morphology of the layered silicate composite (117,118).

Figure 7 shows a representation of a nanocomposites, polymer–clay.

10.15. Liquid-Injection Molding.

In LIM, monomers and oligomers are injected into a mold cavity where a rapid polymerization takes place to produce a thermoset article. Advantages of these processes are low cost, low pressure requirement, and flexibility in mold configuration. Conventional systems, such as isocyanate with polyol, release little or no volatiles. The generation of substantial volatiles in the mold is obviously undesirable and has represented a significant obstacle to the development of a phenolic-based LIM system. A phenolic LIM system based on an anhydrous high ortho liquid resole has been reported (119,120). Formaldehyde is present in the form of both methylol and phenolic hemiformals. A formaldehyde/phenol ratio of ≈1.5–1.0 is used at a pH of 4–7. Divalent salts catalyze the reaction at 80–90°C for 5–8 h and the water is removed by an azeotropic solvent. Uncatalyzed resoles have excellent storage stability.

An important aspect of this procedure is the use of latent acid catalysts, such as phenyl hydrogen maleate, phenyl trifluoracetate, and butadiene sulfone. These catalysts reduce the peak exotherm from over 200°C to 130–160°C. The resin catalyst mixture has a working life of up to several days at RT. The elevated temperature of molding these latent catalysts generates the corresponding acids, namely, maleic, trifluoracetic, and phenolsulfonic, which catalyze the resole reaction. Typically, a cycle time of 1–2 min is required for a mold temperature of ~150°C.

The water liberated during the cure has no apparent effect on the composite properties. Glass-filled composites prepared in this manner retain mechanical properties at elevated temperatures as well as solvent and flammability resistance (108,109). Phenolic–graphite-fiber composites that exhibit superior mechanical properties have also been prepared by this process.

10.16. Foam. Phenolic resin foam is a cured system composed of open and closed cells with an overall density of 0.16–0.80 g/cm^3. Principal applications are in the areas of insulation and sponge-like floral foam. The resins are aqueous resoles catalyzed by NaOH at a formaldehyde/phenol ratio of ≈2:1. Free phenol and formaldehyde content should be low, although urea may be used as a formaldehyde scavenger.

The foam is prepared by adjusting the water content of the resin and adding a surfactant (eg, an ethoxylated nonionic), a blowing agent (eg, pentane, methylene chloride, or chlorofluorocarbon), and a catalyst (eg, toluenesulfonic acid or phenolsulfonic acid). The sulfonic acid catalyzes the reaction, while the exotherm causes the blowing agent, emulsified in the resin, to evaporate and expand the foam (121). The surfactant controls the cell size as well as the ratio of open-to-closed cell units. Both batch and continuous processes are employed. In the continuous process, the machinery is similar to that used for continuous polyurethane foam.

The properties of the foam depend mainly on density and the cell character. For insulation, a high content of closed cells, along with an encapsulated fluorocarbon blowing agent, is desired. The foam must have sufficient strength and be able to resist smoldering, ie, a glowing combustion characteristic of early foams. Smoldering is controlled by additives and foam structure. For floral foam, lower density and an open-cell structure having low toughness are desirable. Floral foam usually contains a wetting agent in the formulation to ensure the rapid uptake of water.

An all-phenolic sandwich structure for aircraft interior applications has been developed using syntactic and expandable semisyntactic phenolic foam. The parts have outstanding fire behavior and are moldable to complex sandwich cores (117,118).

When smoldering is eliminated, phenolic foams exhibit excellent flammability resistance. Their LOI is 32–36%, and their smoke density is lower than that of polyisocyanurate foam of similar density. High thermal insulation K values have been obtained on foams of small cell size containing fluorocarbon blowing agents. Phenolic foams are used for building products and warehouse insulation and ASTM C1126-00 is the standard for faced or unfaced rigid cellular phenolic thermal insulation (see FOAMS; TITLE UNAVAILABLE (ARTICLE PST167)).

10.17. Honeycombs. Honeycomb structures usually involve resin-treated papers and fiberglass, sometimes with a core filler and surface skins bonded to the honeycomb. Uses can be in aircraft interior panels as well as more demanding parts. Phenolic resin-impregnated aramid paper honeycomb cores have been developed for fighter aircraft applications. These new honeycomb structures provide greater structural strength than other honecomb products currently available. One particular part application is the inlet cowl, which incorporates a complex structure, core machining, and core forming (122).

10.18. Spheres. Hollow spherical fillers have become extremely useful for the plastics industry and others. A wide range of hollow spherical fillers are currently available, including inorganic hollow spheres made from glass, carbon, fly ash, alumina, and zirconia; and organic hollow spheres made from epoxy, polystyrene, UF, and phenol–formaldehyde. Although phenol–formaldehyde hollow spheres are not the largest volume product, they serve in some important applications and show potential for future use.

In an early process by Sohio, a variety of compositions were produced by dissolving a film-forming polymer in a solvent (or water), adding a blowing agent, and spray drying the resulting solution under carefully controlled conditions. The use of spray drying to produce discrete, uniform hollow spheres, organic or inorganic, requires high skills in formulation, process control, and engineering. Some of the organic materials described include phenolic resins, poly(vinyl alcohol), polystyrene, methylcellulose, and protein. In the case of the phenolic resins, water-miscible resoles were used; water was the solvent and ammonium carbonate – ammonium nitrate or dinitrosopentamethylenetetramine was the blowing agent. Hollow phenolic spheres in sizes of 5–50-μm dia were obtained. The principal intended use was as a floating cap on petroleum naphtha and crude oil to retard evaporation.

Emerson & Cumming, Inc., eventually bought the rights to the Sohio process and produced a variety of microspheres. Union Carbide was licensed to produce the phenolic microspheres offered under the name Phenolic Microballoons (Table 15). When Phenolic Microballoons are introduced into a crude-oil storage tank, they form a fluid seal that rises and falls with the level of the oil. A continuous vapor-barrier seal is formed, which reduces evaporational losses up to 90%. Tests have been conducted under various mechanical and weather conditions and with crude oils of varying vapor pressure.

Phenolic Microballoons applications in plastics take advantage of low density, porosity, and surface-to-volume ratio to produce lightweight parts. Probably the most notable example is the syntactic foam.

While a conventional foam uses a blowing agent to form a cellular structure as the resin sets, syntactic foams are made by incorporating hollow spheres into liquid resins, especially epoxy resins in the case of Phenolic Microballoons, although urethanes and polyesters are also used. Having a continuous polymer phase and taking advantage of the high compressive strength of the spheres, syntactic foams can be made much stronger than conventional foams. In addition, they are being formed in place. As a result, syntactic foams have become widely used as a modeling, styling, and structural core material in automotive, marine, and aerospace applications.

A mixture of Phenolic Microballoons and resin binder has a putty-like consistency. It can be molded to shape, trowelled onto surfaces, or pressed into a core. Curing gives a high strength, low density (0.144 g/cm^3) foam free of voids and dense areas, and without a brittle skin. Syntactic foams are used in widely diverse applications, including boat flotation aids; structural parts in aircraft, submarines, and missiles; structural cores for wall panels; and ablative heat shields for reentry vehicles and rocket test engines.

Microballoons have been used for gap filling, where the spheres dampen sound or vibration in the structure. In the medical area, microballoons have been evaluated as a skin replacement for burn victims and phantom tissue for radiation studies. An important application is in nitroglycerin-based explosives, in which microballoons permit a controlled sequential detonation not possible with glass spheres.

In the 1990s, carbon microbeads have been produced by a proprietary process using phenolic resin. Potential applications are lubricants, adhesives, and conductive fillers for plastics, rubbers, and coatings (123).

10.19. Fibers. The principal type of phenolic fiber is the novoloid fiber (124). The term novoloid designates a content of at least 85 wt% of a cross-linked novolak. Novoloid fibers are sold under the trademark Kynol, and Nippon Kynol and American Kynol are exclusive licensees. Novoloid fibers are made by acid-catalyzed cross-linking of melt-spun novolak resin to form a fully cross-linked amorphous network. The fibers are infusible and insoluble, and possess physical and chemical properties that distinguish them from other fibers. Applications include a variety of flame- and chemical-resistant textiles and papers as well as composites, gaskets, and friction materials. In addition, they are precursors for carbon fibers.

The fibers are prepared from a high molecular weight novolak resin. Uncured fibers are prepared by melt-spinning the novolak. These fibers are then immersed in aqueous formaldehyde solution containing an acidic catalyst. As heat is applied, curing commences and the novolak resin is transformed into a cross-linked network through the formation of methylene and dibenzyl ether linkages. The final cross-linked structure is free of molecular orientation, and the density of cross-linking is low. The fiber contains ≈ 5 wt% unreacted methylol groups, which can be utilized in the formation of novoloid-fiber composites, or be reduced by heating the cured fiber to 180°C.

Optimum mechanical properties of the fibers are developed provided the precursor novolak filaments are less than 25 μm in diameter to ensure sufficient diffusion of the formaldehyde and catalyst into the fiber. The individual fibers are generally elliptical in cross section. Diameters range from 14 to 33 μm (0.2–1.0 tex or 2–10 den) and fiber lengths are 1–100 mm. Tensile strength is 0.11–0.15 N/tex (1.3–1.8 g/den) and elongation is in the 30–60% range. Elastic recovery is as high as 96%.

The LOI of novoloid materials varies with the particular structure (fiber, felt, fabric) being evaluated; it is generally in the 30–34% range. By comparison, aramid fiber has a LOI of 28–31 and wool of 24. When exposed to flame, novoloid materials do not melt but gradually char until completely carbonized. The high strength of the phenolic char results in the fiber retaining its original fiber structure, and the char effectively absorbs heat from the materials. When novoloid products are exposed to flame, the products of combustion are principally H_2O, CO_2, and carbon char. Smoke emission is minimal, less than that of any other organic fiber.

Applications for novoloid fibers include a variety of flame-resistant protective clothing, safety accessories, and flame barriers for upholstered furniture. As an asbestos replacement, novoloid fibers have been used in gasketing, packings, brake linings, and clutch facings. In electrical applications, novoloid fibers and papers can be used as flameproof coatings and as wrapping tapes in wire and cable applications.

The novoloid molecular structure includes methylol groups, which are available for cross-linking with reactive sites in the matrix material. The ability of the fibers to react with matrix resins yields synergistic improvements in the properties of the composite. Novoloid fibers have been incorporated into composites with thermoplastic resins such as polypropylene, PVC, and polyamide polyesters. Thermosetting resins include phenolics, epoxies, and melamines. In certain elastomers, the methylol reactivity can be used to upgrade the high temperature performance, for example, in chlorinated polyethylene. A process has been announced that produces carbonized Kynol fiber having extremely high surface area (125).

BIBLIOGRAPHY

"Phenolic Resins and Plastics" in *ECT* 1st ed., Vol. 10, pp. 335–370, by K. C. Frisch, General Electric Co.; "Phenolic Resins" in *ECT* 2nd ed., Vol. 15, pp. 176–208, by W. A. Keutgen, Union Carbide Corp.; in *ECT* 3rd ed., Vol. 17, pp. 384–416, by G. L. Brode, Union Carbide Corp.; in *ECT* 4th ed., Vol. 18, pp. 603–644, by Peter W. Kopf, Arthur D. Little, Inc.; "Phenolic Resins" in *ECT* (online), posting date: December 4, 2000, by Peter W. Kopf, Arthur D. Little, Inc.

1. *SPI Phenolic Molding Division Technical Conference*, Cincinnati, Ohio, June 1987.
2. S. R. Sandler and W. Caro, *Phenol Aldehyde Condensation*, Vol. 1, Academic Press, Inc., New York, 1977, Chapt. "2".
3. R. W. Martin, *The Chemistry of Phenolic Resins*, John Wiley & Sons, Inc., New York, 1956.
4. N. J. L. Megson, *Phenolic Resin Chemistry*, Butterworth & Co. Ltd., Kent, U.K., 1958.
5. J. F. Walker, *Formaldehyde*, Van Nostrand Reinhold Co., Inc., New York, 1974.
6. T. S. Carswell, *Phenoplasts*, Interscience Publishers, New York, 1947.
7. A. Knop and W. Scheilb, *Chemistry and Applications of Phenolic Resins*, Springer, Berlin, 1979.
8. A. Knop and L. Pilato, *Phenolic Resins*, Springer, Berlin, 1985.
9. A. Gardziella, L. A. Pilato, and A. Knop, *Phenolic Resins*, Springer, Berlin, 1999.
10. *ACS Symposium on Phenolic Resins*, Washington, D.C., Aug. 1983.
11. U.S. Pat. 643,012 (Feb. 6, 1900), A. Smith.
12. U.S. Pats. 939,966 (Nov. 15, 1909) and 942,852 (Dec. 12, 1909), L. H. Baekeland.

13. J. B. Flemming, *Hydrocarbon Process* **55**(1), 185 (Jan. 1976).
14. K. Kamide and Y. Miyakawa, *Makromol. Chem.* **179**, 359 (1978).
15. *Hydrocarbon Process.* 90 (Mar. 1976); 216 (Nov. 1965); 183 (Nov. 1969); 150 (Nov. 1975); 135 (Nov. 1973).
16. P. Kopf and E. Wagner, *J. Polym. Sci., Polym. Chem. Ed.* **11**, 939 (1973).
17. Y. Ihashi, K. Sawa, and S. Morita, *Kogyo Kagaku Zasshi* **68**, 1427 (1965).
18. U.S. Pats.4,433,119 and 4,433,129 (Feb. 21, 1984), S. W. Chow and G. L. Brode (to Union Carbide Corp.).
19. S. Sojka, *Macromolecules* **12**, 767 (1979).
20. S. Ishida, Y. Tsutsumi, and K. Katsumasa, *J. Polym. Sci., Polym. Chem. Ed.* **19**, 1609 (1981).
21. H. Bender, *Ind. Eng. Chem.* **44**, 1619 (1952).
22. A. Zsavitsas and A. Beaulieu, *Am. Chem. Soc., Div. Org. Coat. Plast. Chem.* **27**, 100 (1967).
23. H. Peer, *Rec. Trat. Chim.* **78**, 851 (1959). *Rec. Trat. Chim.* **79**, 825 (1960).
24. J. H. Freemann and C. Lewis, *J. Am. Chem. Soc.* **76**, 2080 (1954).
25. K. Eapen and L. Yeddanapalli, *Makromol. Chem.* **4**, 119 (1968).
26. U.S. Pat. 4,124,554 (Nov. 7, 1978), J. Fry (to Union Carbide Corp.).
27. U.S. Pat. 4,206,095 (June 3, 1980), J. Wynsta and S. Schultz (to Union Carbide Corp.).
28. U.S. Pat. 3,943,080 (Mar. 9, 1976), M. Wismer (to PPG Industries).
29. H. A. Bruson and C. W. MacMullen, *J. Am. Chem. Soc.* **63**, 270 (1941).
30. T. T. Jones, *J. Soc. Chem. Ind. London* **65**, 264 (1946).
31. O. Vlk, *Plaste Kautsch.* **4**, 127 (1957).
32. U.S. Pat. 3,687,896 (Aug. 29, 1972), S. Vargia and U. Nistri (to Societa Italiana Resine SpA).
33. *Mod. Plast. Int. Ed.* **58**(4), 45 (Apr. 1981).
34. *Chem. Eng.* **99**(6), 19 (June 1992).
35. U.S. Pat. 4,900,671 (1990), A. Pokora (to Mead Corp.); U.S. Pat. 5,153,298 (1992), A. Pokora (to Mead Corp.).
36. U.S. Pat. 4,113,700 (1978), W. Aubertson (to Monsanto Co.).
37. U.S. Pat. 3,823,103 (July 9, 1979), J. Harding (to Union Carbide Corp.).
38. G. Brode, T. Jones, and S. Chow, *Chem. Technol.* **13**, 676 (1983).
39. U.S. Pat. 4,366,303 (Dec. 28, 1982), P. W. Kopf (to Union Carbide Corp.).
40. U.S. Pat. 4,788,236 (Nov. 29, 1988), P. W. Kopf (to Union Carbide Corp.).
41. U.S. Pat. 2,797,201 (July 11, 1957), F. Veatch (to Sohio).
42. U.S. Pat. 4,098,770 (July 4, 1978), A. Berchem, K. Sudan, and E. Gres (to Reichhold Chemicals, Ltd.).
43. R. B. Graver, in S. Lee, ed., *International Encyclopedia of Composites*, 2nd ed., SAMPE Publisher 2000, p. 176.
44. H. Ishida and Y. Rodriquez, *Polymer* **36**, 3151 (1995).
45. H. Ishida and Y. Rodriquez, *J. Appl. Polym. Sci.* **58**, 1751 (1995).
46. U.S. Pat. 6,207,786 (Mar. 27, 2001), H. Ishida and S. Rimdusit (to Edison Polymer Innovation Corp.).
47. *Chem. Eng. News* 21 (Jan. 22, 2001).
48. S. Kelley, M. Myers, D. Johnson, X.-M. Wang, and M. Davis, *Production of Chemicals and Materials from Renewable Resources*, (ACS Symposium Series), American Chemical Society, Washington D.C., 2001, p. 784.
49. U.S. Pat. 5,367,043, J. Butter and R. Brandon (to Enzymol, Inc.).
50. K. Hultzsch, *Kunstostoffe* **37**, 205 (1947).
51. U.S. Pat. 5,334,675 (Aug. 2, 1994), A. Gerber (to Borden, Inc.).

52. U.S. Pat. 5,952,440 (Sept. 14, 1999), W. Walisser and C. Johnson (to Borden, Chemical).
53. E. Orrell and R. Burns, *Plast. Polym.* **68**, 469 (Oct. 1968).
54. V. Pshenitsyna and M. Kotrelev, *Polym. Sci. U.S.S.R.* **11**, 829 (1969).
55. V. Kurachenkov and L. Igonin, *J. Polym. Sci., Part A: Polym. Chem.* **1**, 2283 (1971).
56. M. Yamao, N. Yoshimi, and S. Tanaka, *Kogyo Kagaku Zasshi* **74**, 1938 (1971).
57. J. Gillham, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **22**(2), 131 (1981).
58. R. Young, P. Kopf, and O. Salgado, *Tappi* **64**(4), 127 (1981).
59. American Plastics Council, 2000 Sales and Production Data, Arlington, Va.
60. *Plastics Technology Online Supplier Directory for Phenolic Resins*, Oct. 2001.
61. M. Karas and F. Hillenkamp, *Anal. Chem.* **60**, 2299 (1988).
62. H. Paschy, K. Rode, R. Ghahary, and D. Braun, *Die Angew. Makromol. Chemie* **241**, 95 (1996).
63. H. Mandal and A. Hay, *Polymer* **38**, 6267 (1997).
64. H. L. Bender, *Mod. Plast.* **30**, 136 (1953).
65. D. Boeschel, M. Fedtke , and W. Geyet, *Polymer* **38**, 1291 (1997).
66. B. Mechin, D. Hanton, V. Le Geoff, and J. Tanneur, *Eur. Polym. J.* **20**, 333 (1984).
67. J. Shaefer, *J. Am. Chem. Soc.* **98**, 1031 (1976).
68. R. Bryson, G. Hatfield, T. Early, A. Palmer, and G. Maciel, *Macromolecules* **16**, 1669 (1983).
69. C. Fyfe, *Macromolecules* **16**, 1216 (1983).
70. G. Maciel, I. Chuang, and L. Gollob, *Macromolecules* **17**, 1081 (1984).
71. E. Wagner and R. Greff, *J. Polym. Sci., Part A: Polym. Chem.* **1**, 2193 (1971).
72. D. Braun and J. Arnelt, *Angew. Makromol. Chem.* **73**, 133 (1978).
73. A. Rudin, C. Fyfe, and S. Vines, *J. Appl. Polym. Sci.* **28**, 2611 (1983).
74. E. Tesarova and V. Pacakova, *Chromatographia* **17**, 269 (1983).
75. W. Werner and O. Barber, *Chromatographia* **15**, 101 (1982).
76. L. Taylor, *Anal. Chem.* **42**, 297 (1970).
77. M. Kamal and S. Sourour, *Polym. Eng.* **13**, 59 (1973).
78. J. Enns and J. Gillham, *J. Appl. Polym. Sci.* **28**, 2567 (1983).
79. W. Stark, J. Döring, V. Bovtun, and C. Kürten, *NDT. net* **3**(11), 141 (Nov. 1998).
80. L. Lorenz, and A. Christiansen, *Ind. Eng. Chem. Res.* **34**, 4520 (1995).
81. X.-M. Wan, B. Riedl, R. Geimer, and A. Christiansen, *Wood Sci. Technol.* **30**, 423 (1996).
82. R. Geimer and A. Christiansen, *For. Prod. J.* **46**, 67 (1996).
83. U.S. Environmental Protection Agency, Technology Transfer Network, www.epa.gov, see phenol (108-95-2), May 17, 2001.
84. H. Babich and D. Davies, *Reg. Tox. Pharm.* **1**(1), 90 (1981).
85. U.S. Environmental Protection Agency, Technology Transfer Network, www.epa.gov, see formaldehyde (50-00-0), May 17, 2001.
86. A. Housden, *Water Pollut. Control* **80**, 490 (1981).
87. Reinforced Plast. **35**(7/8), 17 (1992).
88. *Rogers Corp., Molding Material Division, Manchester, Conn. Product Literature*, 2001.
89. *Plast. Week* 2 (Mar. 23, 1992).
90. *Plast. Environ.* 5 (July 10, 1992).
91. B. Olson and H. De Keyser, *Recycling Cured Phenolic Material*, Rogers Corp. Molding Materials Division, Manchester, Conn. Copyright 2001 and SAE International Congress and Exposition, 1992, 2001.
92. *Recycling Special Report, Phenolic Division of The Society of the Plastics Industry*, 2001.
93. G. Bosshard, *Prog. Org. Coat.* **10**, 205 (1982).

94. U.S. Pats. 3,723,156 (Mar. 27, 1973) and 3,732,120 (May 8, 1973), B. Brockett; 3,737,410 (June 5, 1973), H. Mueller; 3,936,573 (Feb. 3, 1976), B. Brockett; and 4,165,102 (Aug. 21, 1979), J. Bodmer (to National Cash Register).
95. W. A. Boyd, C. Merriam, and J. Fry, in R. Tess and G. Behlein, eds., *Applied Polymer Science*, (ACS Symposium Series), 2nd ed., American Chemical Society, Washington, D.C., 1985, pp. 1141–1158.
96. D. M. Berger, *Met. Finish.* **74**(9), 52 (1976).
97. J. Fry, C. Merriam, and G. Misko, *Am. Chem. Soc., Div. Org. Coat. Plast. Chem.* **47**, 540 (1982).
98. B. Barth, in E. Skeist, ed., *Handbook of Adhesive*, Van Nostrand Reinhold Co., Inc., New York, 1977, Chapt. “23”, p. 382.
99. H. Kollek, H. Brockmann, and H. Mueller, *Int. J. Adhesion Adhes.* **6**(1), 37 (1986).
100. U.S. Pat. 4,025,490 (May 24, 1977), F. Weaver (to Mead Corp.).
101. J. Perry, *Pulp Pap.* **46**, 93 (Aug. 1973); *Pulp Pap.* **46**, 116 (Oct. 1973).
102. G. Elbe, *Plastics Design Forum*, 66 (Nov./Dec. 1993).
103. U.S. Pats. 4,316,827 (Feb. 23, 1982) and 4,420,571 (Dec. 13, 1983), L. Pacala and J. Blickensderfer (both to Union Carbide Corp.).
104. J. Taylor, *44th International SAMPE Symposium*, Long Beach, Clif., 1999, p. 1123.
105. S. Qureshi, *51st Annual Conference, Composites Institute, SPI*, 1996.
106. K. Yoshioka and J. Seferis, *46th International SAMPE Symposium*, Long Beach, Clif. 2001.
107. U.S. Pat. 4,403,066 (Sept. 6, 1983), G. L. Brode, S. Chow, and W. Hale (to Union Carbide Corp.).
108. *ACS National Meeting*, Washington, D.C., Aug. 1983.
109. G. L. Brode, *Polym. Prepr.* **24**(2), 194 (1983).
110. U.S. Pat. 4,419,400 (Dec. 6, 1983), R. Hindersinn (to Occidental Petroleum).
111. Plast. World **47**(6), 42 (1989).
112. J. Delmonte, *Technology of Carbon and Graphite Fiber Composites*, Van Nostrand Reinhold Co., Inc., New York, 1981.
113. E. F’itzer and W. Schafer, *Carbon* **8**, 353 (1970).
114. S. Siebold, *SAMPE Symp.* **20**, 327 (Apr. 1975).
115. W. Kowbel, J. Webb and J. Withers, *44th International SAMPE Symposium*, Long Beach, Clif., 1999, p. 1878.
116. U.S. Pat. 6,051,167 (Apr. 18, 2000), J. Withers, R. Loutfy, W. Kowbel, C. Bruce, and R. Vaidyanathan.
117. M. Chio, I. Chung, and J. Lee, *Chem. Mater.* **12**, 2977 (2000).
118. I. Kleba and E. Haberstroh, *46th International SAMPE Symposium*, Long Beach, Clif., 2001.
119. U.S. Pat. 4,395,521 (July 26, 1983), S. W. Chow (to Union Carbide Corp.).
120. G. L. Brode, S. W. Chow, and M. Michno, *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **24**(2), 192 (Aug. 1983).
121. U.S. Pats. 4,423,163 (Dec. 27, 1983), H. Doerge; 4,165,413 (Aug. 21, 1979), R. Sefton; and 444,912 (Apr. 24, 1984), J. Carlson (to Koppers Co., Inc.).
122. S. Linder and B. Brailsford, Phenolic Resin-Impregnated Aramid Paper Honeycomb Core Program, Navy Mantech Program, Office of Naval Research, FY96-98, 1998.
123. K. Esumi, S. Eshima, Y. Murakami, H. Honda, K. Esumi, and H. Oda, *Colloids Surf.* **108**, 113 (1996).
124. U.S. Pats. 3,650,102 (Mar. 21, 1972) and 3,723,588 (Mar. 27, 1973), J. Economy and R. Clark (to Carborundum Co.).
125. *J. Chem. Week*, 5 (Aug. 10, 1989).

GENERAL REFERENCES

E. Dradi and G. Casiraghi, *Macromolecules* **11**, 1295 (1978).
T. Liu and S. Rhee, *Wear* **76**, 213 (1978).
J. Woodbrey, H. Higginbottom, and H. Culbertson, *J. Polym. Sci., Part A: Polym. Chem.* **3**, 1079 (1965).
R. Hirst and co-workers, *J. Polym. Sci., Part A: Polym. Chem.* **3**, 2091 (1965).
T. Yoshikawa and J. Kumanotani, *Makromol. Chem.* **131**, 273 (1970).
T. Sterling and J. Weinkam, *J. Occup. Med.* **30**, 895–901 (Nov. 1988).
U.S. Pat. 3,595,821 (July 27, 1971), S. Spector (to PPG Industries).

Peter W. Kopf
TIAX, LLC

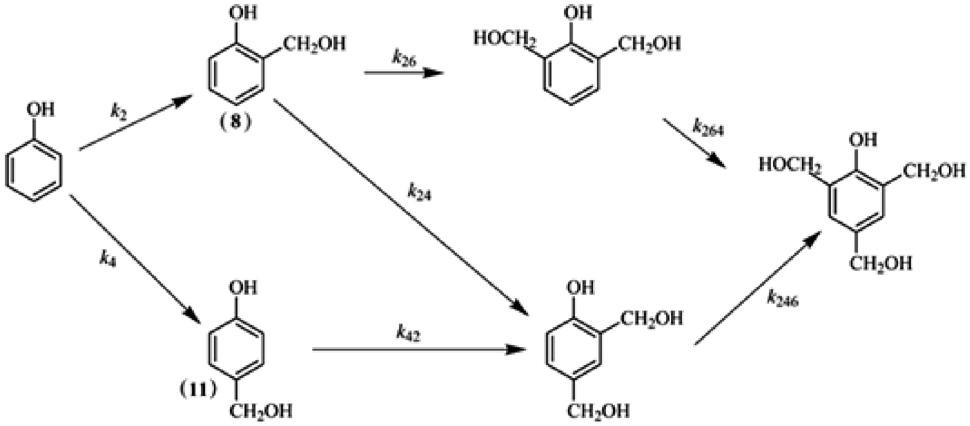


Fig. 1. Possible pathways and rate constants for the methylolation of phenol.

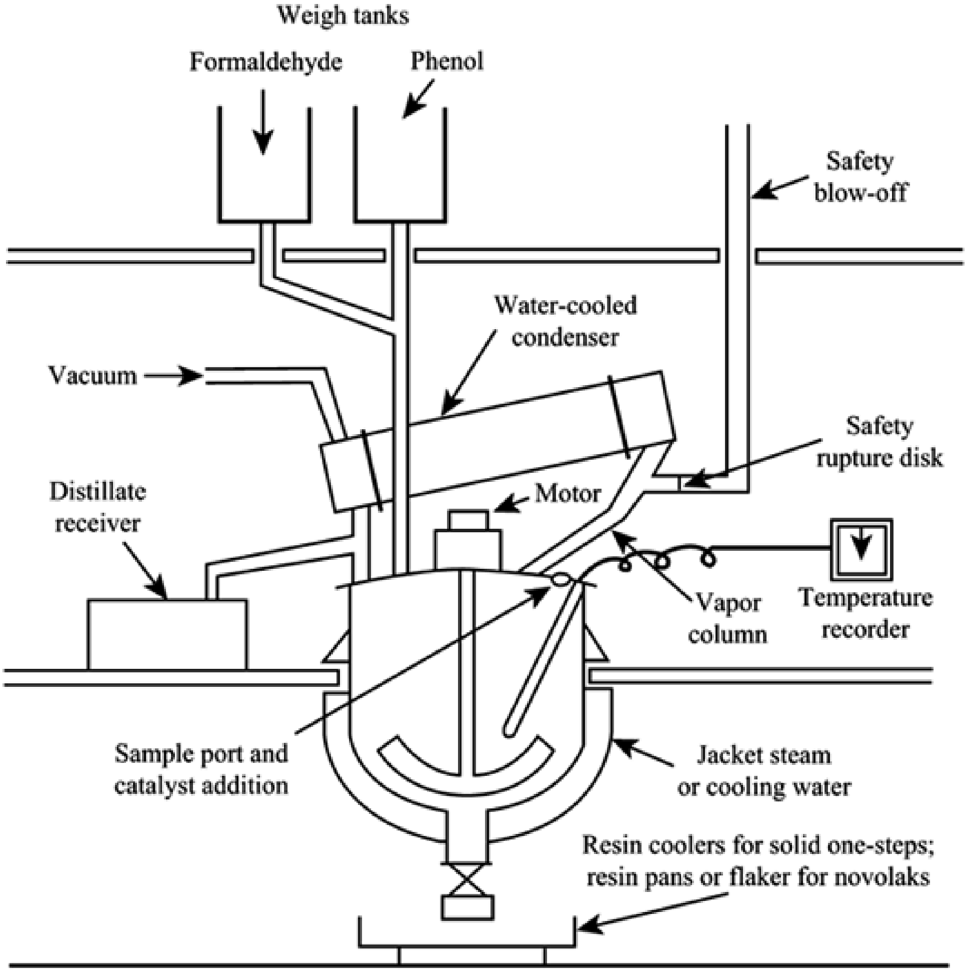


Fig. 2. Typical phenolic resin production unit.

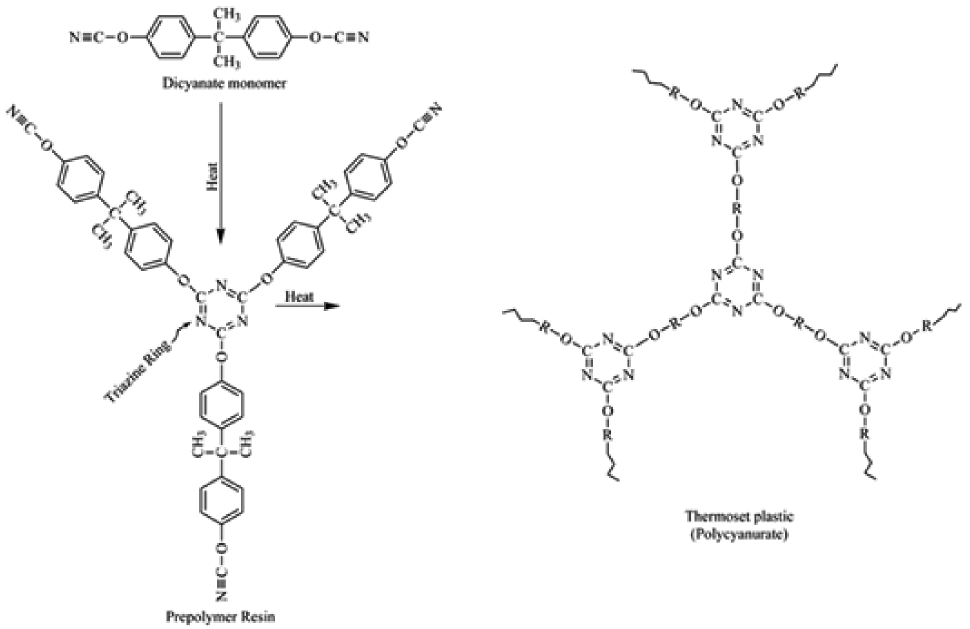


Fig. 3. Curing via cyclotrimerization; R = bisphenol unit. From Ref. 43.

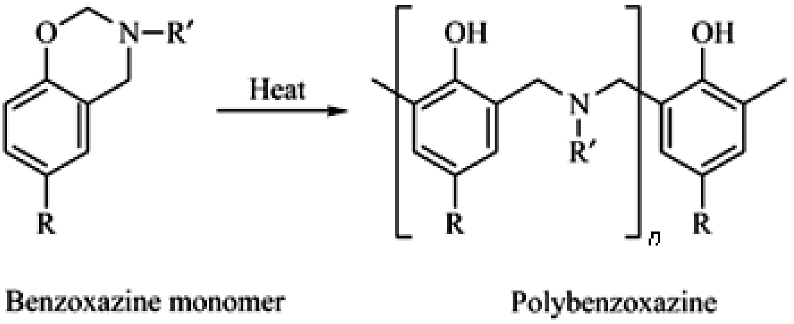
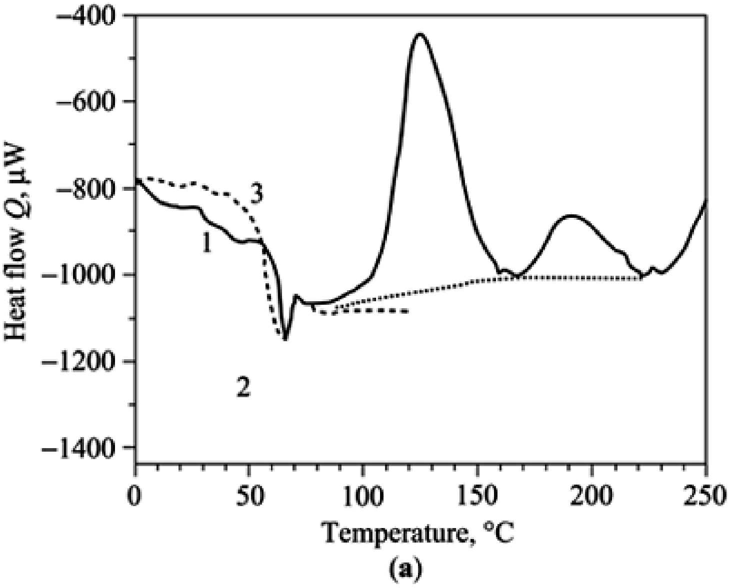


Fig. 4. Polymerization reaction of benzoxazine resins.



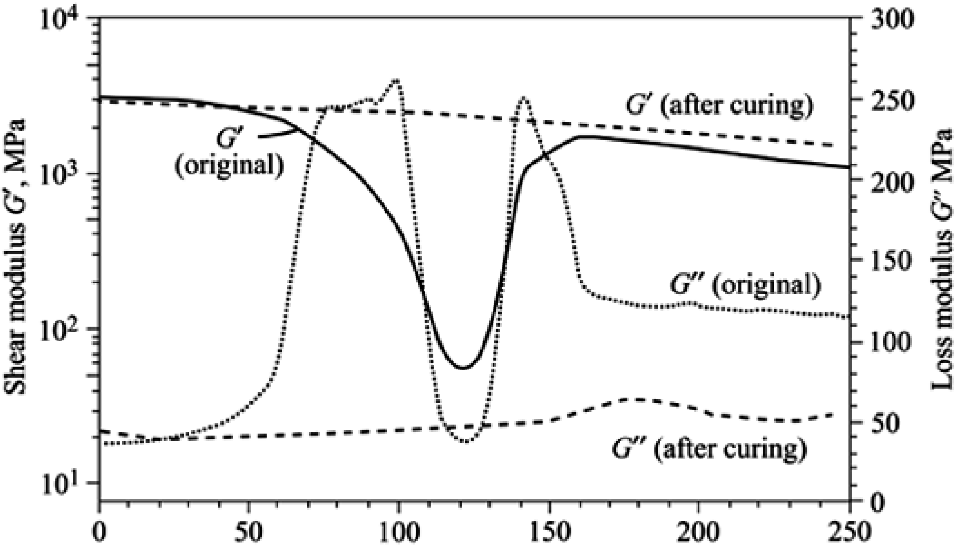


Fig. 5. DSC and DMA of novolac resin. (**a**) DSC Measurement of (1) original PF resin, (2) cured PF resin, and (3) novolac. (**b**) Torsion pendulum measurement of original and cured PF. To convert MPa to psi, multiply by 145. From Ref. 79.

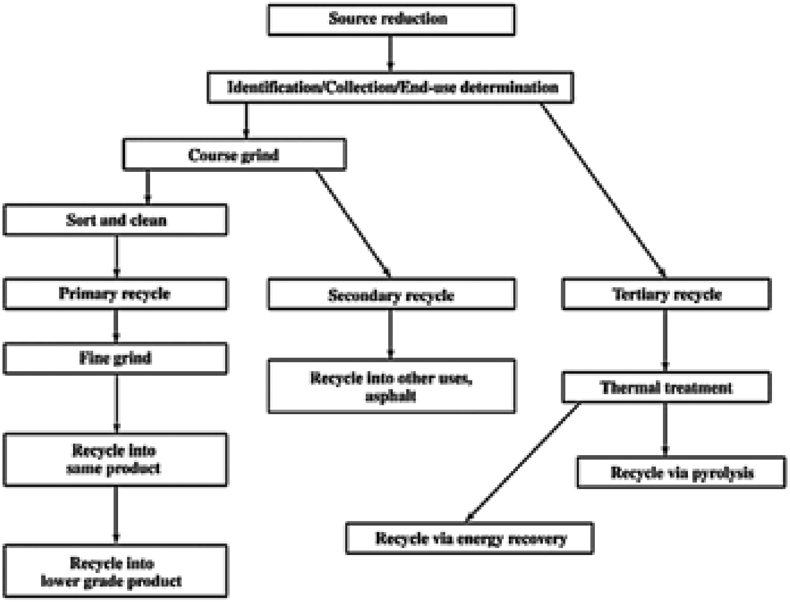


Fig. 6. SPI Blueprint for the reclamation of molded phenolics.

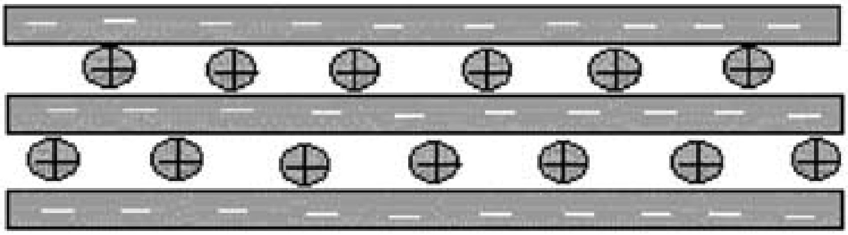


Fig. 7. Nanocomposites, polymer clay.

Table 1. **Properties of Phenol**

Property	Value
mol wt	94.1
mp, °C	40.9
bp, °C	181.8
flash point, °C	79.0
autoignition temperature, °C	605.0
explosive limits, vol%	2–10
vapor pressure at 20°C, Pa[a]	20

[a] To convert Pa to mm Hg, multiply by 7.5×10^{-3}.

Table 2. **Substituted Phenols Used for Phenolic Resins**

Substituted phenol	Resin application
cresol (*o*-, *m*-, *p*-)	coatings, epoxy hardeners
p-*t*-butylphenol	coatings, adhesives
p-octylphenol	carbonless paper, coatings
p-nonylphenol	carbonless paper, coatings
p-phenylphenol	carbonless paper
bisphenol A	low color molding compounds, coatings
resorcinol	adhesives
cashew nutshell liquid	friction particles

Table 3. **Forms of Formaldehyde**

		Resin preparation	
Type	Chemical formula	Advantages	Disadvantages
gaseous	CH_2O		unstable
formalin			
36%	$HO(CH_2O)_nH$[a]	easy handling, moderate, reactivity, stable at RT	high water content
50%	$HO(CH_2O)_nH$[b]	increased capacity	elevated temperature storage, formic acid formation
paraformaldehyde	$HO(CH_2O)_nH$[c]	increased capacity, water-free	dangerously high reactivity, solids handling
trioxane	$(CH_2O)_3$	water-free	catalyst requirements, high cost
hexamethylenetetramine	$(CH_2)_6N_4$	autocatalytic	amine incorporation

[a] $n \approx 2$.
[b] $n \approx 3$.
[c] $n = 20–100$.

Table 4. **Novolak Resin Properties**

	Catalyst	
Property	Acid	Zn acetate[a]
formaldehyde/phenol molar ratio	0.75	0.60
nmr analysis, %		
2,2′	6	45
2,4′	73	45
4,4′	21	10
gpc analysis		
phenol, %	4	7
M_n	900	550
M_w	7300	1800
water, %	1.1	1.9
T_g, °C	65	48
gel time, s	75	25

[a] High ortho.

Table 5. **Properties of Resole Resins**

	Catalyst	
Property	NaOH	Hexa
concentration, pph	3	10
formaldehyde/phenol ratio	2.0	1.5
water solubility, %	100	Swells
gpc analysis		
phenol, %	6	8
M_n	280	900
M_w	500	3000
T_g, °C	35	47
gel time, s	65	110

Table 6. **Methylene Group Distribution, % in Resoles**

	Catalyst	
Methylene group	NaOH	Hexa[a]
2-CH_2OH	30	24
2-CH_2OCH_2OH	24	1
2-CH_2OR	2	4
4-CH_2OH	12	9
4-CH_2OCH_2OH	16	0
4-CH_2OR	2	4
2,2′-CH_2	0	0
2,4′-CH_2	7	12
4,4′-CH_2	7	10
2-CH_2N	0	27
4-CH_2N	0	7
benzoxazine	0	2

[a] 6 pph.

Table 7. **Isothermal DMA Results**

Sample	Rate, $\min^{-1}$ at 150°C	Rate, $\min^{-1}$ at 185°C	Activation energy, kJ/mol[a]
hexa-catalyzed resole	0.22	1.00	71.1
novolak			
6% hexa	0.07	0.09	8.8
12% hexa	0.12	0.19	18.8

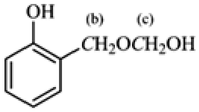
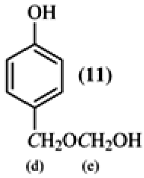
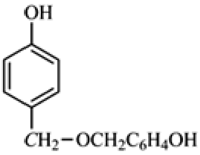
[a] To convert kJ to kcal, divide by 4.184.

Table 8. **Long-Term Use of Phenolic Resins[a], 10^3 t**

End use market	1983	1993	2001
bonding	295	454	645
laminating	67	78	111
plywood	580	687	976
other	173	173	248
Total	*1115*	*1392*	*1980*

[a] Ref. 59.

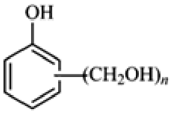
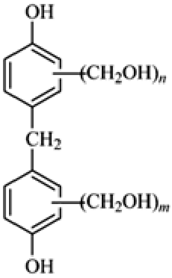
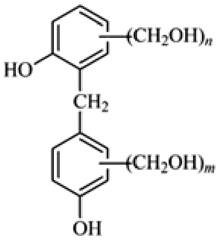
Table 9. **Chemical Shifts of Methylene Carbons in Liquid Resoles**

Structure[a]	Chemical shift,[b] ppm
methylol C in (**8**)	61.3
	65.4 (b) 88.0 (c)
benzyl C in (**9**)	68.9
methylol C in (**11**)	63.8
 **(11)**	68.5 (d) 88.0 (e)
	71.5
methylene C in (**5**)	31.5
methylene C in (**6**)	35.0
methylene C in (**7**)	40.4

[a] Designated carbon is shown in italic or described.

[b] From tetramethylsilane in d_6-acetone solution.

Table 10. **Resole Components Resolved by HPLC and GC**

Resin[a]	Components
	2; 4; 2,4; 2,6; 2,4,6
	2; 2,6; 2,2′; 2,6,2′; 2,6,2′,6′
	2′; 6; 4; 2′,6′; 6,2′; 4,2′; 4,6; 4,2′,6′; 4,6,2′; 4,6,2′,6′

[a] Also, **5**, **6**, and **7**, ie, 2,2′-, 2,4′-, and 4,4′-DPM.

Table 11. **CF Coating Slurry Formulation**

Constituent	Parts
kaolin clay	64
$CaCO_3$	3
colloidal silica	5.4
hydroxyethyl starch	3
styrene–butadiene latex	12
Novolak resin dispersion	12

Table 12. **Applications for Molded Phenolic Parts**[a]

Market	Key features	Examples
appliances	heat, moisture and chemical resistance; thermal and electrical insulation	coffee pot handle and base; steam iron parts
automotive and transportation	heat, moisture, and hydrocarbon resistance; dimensional stability	disc brake caliper pistons, transmission parts; water pump parts, torque converters; oil pump covers
electrical	heat and wear resistance; thermal and electrical insulation	circuit breakers; motor control parts; commutators and alternators
aerospace	heat and chemical resistance; rigidity	interior partitions; ablative surfaces
packaging	dimensional stability; chemical resistance	closures

[a] Ref. 102.

Table 13. **Mechanical Properties of Composites**[a]

Matrix resin	Flexural strength[b], MPa[c]	Elongation, %	Notched Izod, J/m[d]	UL-94
phenolic	228	2	1868	V0
polyester	276	1.75	960	burns
vinyl ester	310	2	1227	burns

[a] Glass content, 60%.

[b] For all three matrix resins, the flexural modulus is 12 GPa (1.7×10^6 psi).

[c] To convert MPa to psi, multiply by 145.

[d] To convert J/m to ft·bf/in., divide by 53.38.

Table 14. **Strength Properties of Phenolic–Carbon-Fiber Composites**

	Resin, %		
	Phenolic		Epoxy novolak
Property	40	35	27
tensile strength, MPa[a]	115	63	64
flexural strength, MPa[a]	183	126	110
flexural modulus, GPa[b]	15.8	6.3	6.4

[a] To convert MPa to psi, multiply by 145.

[b] To convert GPa to psi, multiply by 145,000.

Table 15. **Physical Properties of Phenolic Microballoons**

Property	Value
average particle size, μm	43
typical particle range, μm	20–120
liquid displacement density, g/cm^3	0.15–0.35
bulk density, g/cm^3	0.07–0.15
toluene flotation, %	∼90