Phenolics: Nonclassical Routes to Solid and Liquid Binders

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ABSTRACT

A nonconventional route for the manufacture of liquid or solid, one-step phenolic resins is discussed in this paper. Base-catalyzed condensation occurs in dispersed particles suspended in water as the continuous phase. Protective colloid type and concentration are major factors in determining particle size and, therefore, the ability to obtain either nonsettling dispersions or particulate solids that can be recovered and handled as powders. The technology is applicable to a variety of phenolic and aldehydic starting materials. In contrast to conventional manufacturing procedures, the current technology affords efficient process control and great latitude in selection of molecular weight, molecular weight distribution, and functionality.

INTRODUCTION

The Second U.S.-Romanian Conference on Polymer Science coincides with the 75th anniversary of Leo Baekeland's discovery of phenolformaldehyde resins. This paper summarizes two areas of development aimed at upgrading certain conventional phenolic resin technologies; namely, one-step resins through phenolic dispersions and phenolic thermospheres (PTS resins) [1, 6]. One-step resins (Fig. 1) are reactive

$$OH + xCH_2O \xrightarrow{\;OH^{\ominus}\;} OH{-}(CH_2OH)_x \quad x = 1\text{-}3$$

$$\downarrow -H_2O$$

$$HOCH_2{-}\left(\!\!\!\begin{array}{c}OH\\ \\R\end{array}\!\!-CH_2\!\!\right)_{\!y}\!\!\left(\!\!\!\begin{array}{c}OH\\ \\R\end{array}\!\!-CH_2OCH_2\!\!\right)_{\!z}\!\!\begin{array}{c}OH\\ \\ \end{array}\!\!-CH_2OH$$

Resole   R = -H, or -CH$_2$OH

$$\downarrow -H_2O$$

Cured Compositions
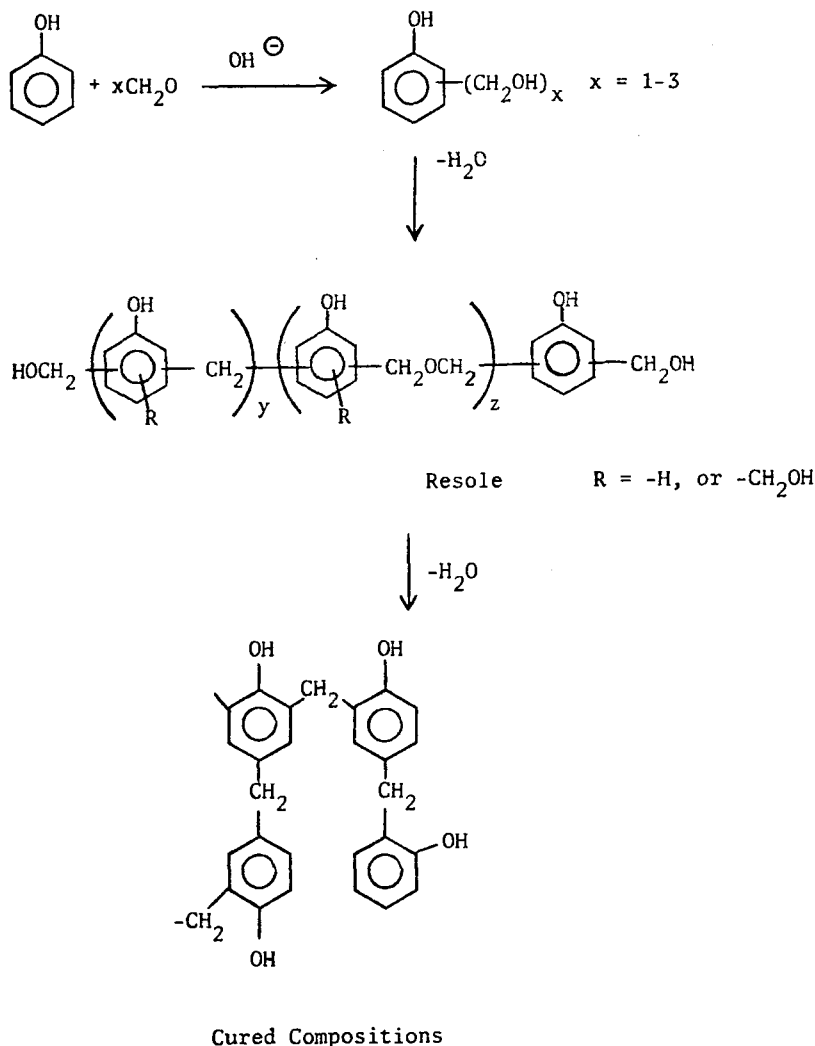
FIG. 1. One-step resins.

materials where a postheating operation is used to cure the product. Depending on end use, the one-step resin can be an aqueous or organic solution, a liquid prepolymer, or an advanced solid particulate (after pulverizing). Manufacture of conventional products is still largely based on processes developed decades earlier. Molecular weight control, especially for higher molecular weight products, is a significant problem. Frequently, operations are manpower and energy intensive.

Phenolic dispersions and particulates made from them offer advan-
tages over the historical routes.

Phenolic Dispersions

Stable, nonsettling, aqueous phenolic dispersions can be prepared
from phenol or substituted phenols, plus an aldehyde, in conjunction
with a combination of selected polysaccharide-type colloids [2-5].
Specifically, both a protective colloid and a viscosifier are employed.
Reaction occurs in two stages: 1) condensation of phenol and aldehyde
to a predetermined molecular weight, at or near the cloud point; pro-
tective colloid and viscosifier (for nonsettling compositions) are added
at this point, resulting in inversion to an oil-in-water dispersion; 2)
polymerization to the desired endpoint; this can range from a DP as
low as 3-4 ($z = 1$, 2 in Fig. 1) up to a fully cured, intractable particle.
Gel permeation chromatography shows that at the end of Stage 1,
methylolation is essentially complete, with oligomeric species ranging
up to about five phenolic units. Further polymerization takes place
through condensation of these lower molecular weight compounds. The
catalyst for both phases of the reaction is an alkaline earth or alkali
metal hydroxide.

Of particular importance for dispersion stability is the role of pro-
tective colloid. Carboxyl-modified polysaccharides, such as gum
arabic, are especially useful. It is believed that the carboxyl function-
alities of arabic and ghatti are oriented toward the aqueous phase,
with the more lipophilic portion attached to the phenolic sphere, af-
fording an anionic-type dispersion. As shown in Tables 1 and 2, both
the concentration of protective colloid and the pH of the system affect
particle size. The stabilization of the dispersion arises from the for-
mation of an interfacial film by the protective colloid surrounding the
resin particles. Maximum dispersion stability should be obtained
when the interfacial film is electrically charged (pH dependent) and
completely covers the dispersed particles. At optimum film thickness
and charge density, application of shear should have little or no effect
on particle size distribution. Under less than optimum conditions, ap-
plication of shear should result in particle redistribution, i.e., to an
optimized interfacial film thickness. The interfacial film thicknesses
under various experimental conditions were estimated by assuming:
a) that the particles are spherical and b) that the filming solution for
the case of gum arabic is a 40% aqueous solution. The results, sum-
marized in Table 3, show that an optimum film thickness occurs in
the region of 500-700 Å. The application of shear in this region of
particle coverage, for example, by passing the dispersion through an
intensive shear field provided by an Oakes mixer, had no significant
effect on the particle size, as can be seen by comparing the first three
sets of experiments (1a through 3b). When the film thickness was
greater than this range, shear resulted in the redistribution to a
smaller particle size in which the film thickness again approached

TABLE 1. Effect of Protective Colloid Concentration on Particle Size

Gum arabic, g/100 g phenol	Average diameter, μm
2	13 ± 4
1	27 ± 5
0.5	58 ± 20

TABLE 2. Effect of pH on Particle Size

pH	Average particle diameter, μm	Standard deviation, μm
6.7	10	4
4.1	20	7
3.2	38	20
2.8	75	35 unstable

the optimum region (4a and 4b). Conversely, for systems where the protective film was very thin, applied shear resulted in redistribution to a larger particle size system (compare 5a and 5b).

Phenolic Thermospheres (PTS Resins)

The conventional method [1, 6] for making solid, one-step resins, Fig. 1, (prior to advancement to the crosslinked state) involves base-catalyzed condensation of a phenol with formaldehyde in an aqueous medium, followed by neutralization and distillation to remove the dilution water. This low molecular weight condensate is then further polymerized thermally and in bulk, while the water of reaction is continually removed by distillation. When the desired endpoint is reached, the viscous mass is rapidly cooled to arrest the polymerization. Due to high viscosity of the reaction mixture, both heat transfer and material transfer are inefficient, resulting in marginal endpoint control and product uniformity. Moreover, the solid resoles have poor moisture and sinter resistance. Finely divided powders of this type are difficult to obtain. Therefore, pulverized one-step resins are generally obtained as a mixture of a resole and novolac, so-called "one-step two-step resins."

Phenolic dispersion technology offers an approach to this class of materials which largely obviates the deficiencies of the conventional

TABLE 3. Particle Size as a Function of Interfacial Film Dimension

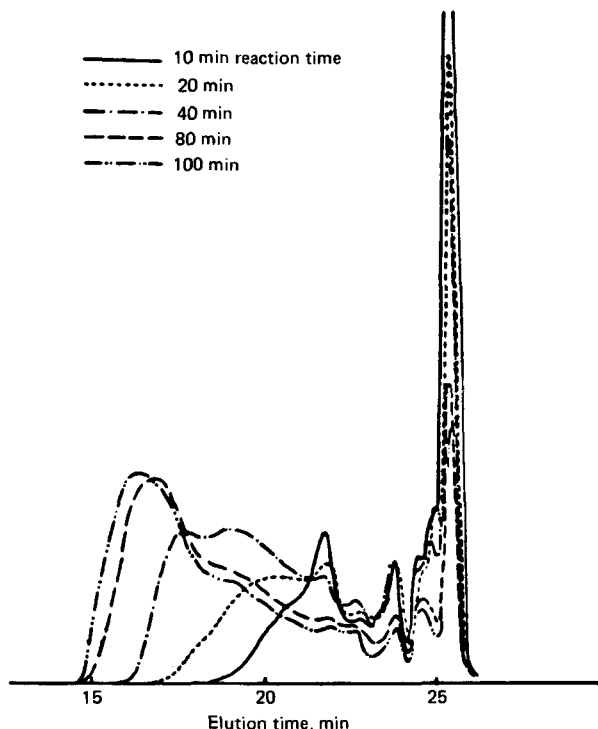| Experiment	Shear ($\checkmark$)	Particle diameter, μm	Gum arabic[a]	Volume fraction disperse phase	Estimated film thickness, Å
1a		12	2	0.5	510
1b	$\checkmark$	13	2	0.5	560
2a		31	1	0.5	650
2b	$\checkmark$	27	1	0.5	580
3a		55	0.5	0.5	620
3b	$\checkmark$	48	0.5	0.5	720
4a		44	1	0.57	940
4b	$\checkmark$	28	1	0.57	600
5a		18	1	0.5	390
5b	$\checkmark$	43	1	0.5	920

[a]Percent of phenol charged.

FIG. 2.   Gel permeation chromatogram of particulate resole.

process.   By omitting the viscosifier and incorporating hydrophobic structural units, a suspension process is feasible which allows isolation of solid product as discrete and finely divided particles without pulverization, i.e., the product is recovered by filtration [7-9].   Dispersion polymerization also allows reaction in a low-viscosity medium, where heat and material transfer are easily controlled.

The GPC curves of Figs. 2 and 3 show the number-average molecular weight in the dispersion polymerization advances relatively slowly while the weight-average molecular weight increases rapidly, resulting in polymers of high dispersity.   This is also observed with conventional phenolic resins.   Depending on the length and temperature of polymerization, products of various plasticity and rheology are obtained.   For free-flowing, easily isolable products, hexamethylenetetramine (hexa) incorporation is advantageous.   Hydrolysis of hexa has been shown to yield aminomethylated products.   Hexa, or an equivalent amount of ammonia and formaldehyde, can be used interchangeably.   The microstructure of various PTS resins was determined by ^{13}C-NMR, and the results are summarized in Table 4.   A hexa-catalyzed conventional bulk resole is included for comparison.   The data
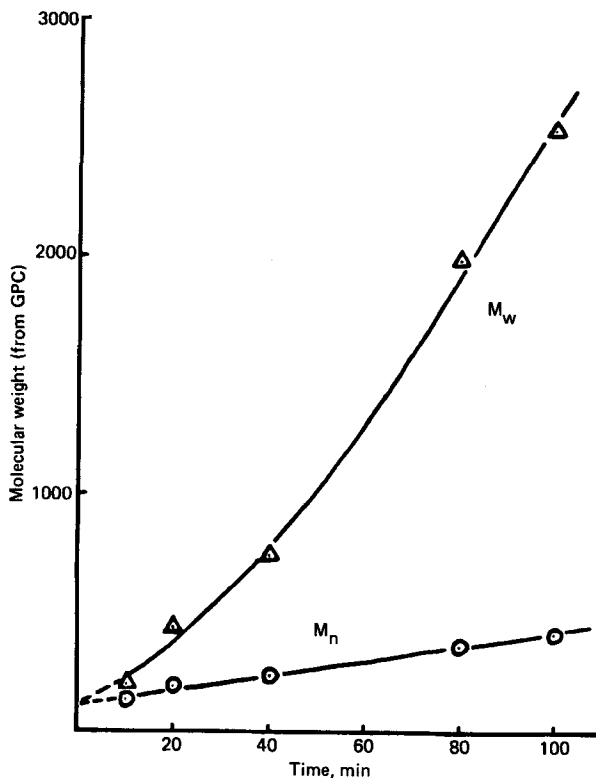
FIG. 3. Molecular weight distribution of particulate resole.

show that the particulate resole contains less methylol structure but increased benzylamine and methylene bridges. The use of hexa for the production of solid resole has been, and is, practiced in phenolic resin manufacture. The formation of benzylamine and azomethine structures in hexa-modified resoles is known, and the characterization of these structures from the reaction of hexa with phenol and novolacs by NMR spectroscopy has been reported [9]. It is believed that these subtle but discernible differences in microstructure account for the lessened tendency to absorb moisture and the increased glass transition temperatures of the particulate resoles. The water absorption data and glass transition temperatures (T_g's) as determined by a dynamic mechanical analyzer (DMA) are summarized in Table 5.

Reactivity of particulate resoles is also an extremely important property. The relative reactivity of a particulate resole at 25-60°C as compared to a bulk resole was evaluated by measuring the inclined plate flow (P.F.) values as a function of time and temperature. The data were treated as first-order kinetics according to

TABLE 4. Microstructures of Solid Resole

Structure	Particulate resole, 9 parts hexa	Particulate resole, 6 parts hexa	Bulk resole, 6 parts hexa
$ArCH_2OCH_2OH$	2	4	0
$ArCH_2OH$	25	22	30
$ArCH_2OCH_2Ar$	6	4	8
$ArCH_2Ar$	26	34	28
$ArCH_2N$	41	33	32

TABLE 5. Glass Transition Temperature and Moisture Absorption of Particulate Resole

Resin	T_g (DMA), °C	Wt% gain, 22°C, 100% RH, 24 h
Particulate resole	48-54	2.5-3.3
Bulk resole	33-43	7.2-8.4
Novolac	58-74	5.7-6.5

TABLE 6. Relative Reactivity—PTS vs Bulk Resole

Resin	Rate constant, d^{-1}			ln A	E, kcal/mol
	60°C	40°C	25°C		
PTS	0.67	0.029	0.003	44.6	30
Bulk resole	1.50	0.097	0.018	38.1	25.2

$$\ln\left((1/P.F.) - 13\right) = kt \text{ (days)} + C$$

The cure rate constants (k), activation energies, and the frequency factors were calculated from the usual Arrhenius extrapolations and are summarized in Table 6. The results show that the particulate resole cures at about 0.1 times the rate of bulk resole at room temperature. However, this differential reactivity decreases as temperature is increases; at 60°C it is about 0.5 times that of a bulk resole.

Dynamic mechanical analysis thermograms show that both the particulate resole and the bulk resole exhibit the onset of cure at the 130-140°C region. Therefore, the particulate resole achieves improved shelf stability with no significant loss of cure speed at elevated temperatures.

In conclusion, two new processes have been developed for the manufacture of phenolic resins which give broad flexibility in product design. Dispersions are currently being produced commercially. The solid particulate resins have been scaled up in a pilot facility. Field tests with the latter have shown that performance equivalent to conventional products can be obtained [10]. In addition, new products not available from conventional technology have also been prepared.

EXPERIMENTAL SECTION

Phenolic Dispersion

Phenolic dispersion preparation involves charging a reaction flask with, for example, 100 g of phenol, 111 g of 50% formaldehyde, and 2.5 g of barium hydroxide monohydrate and heating to ~50°C (pH ≈8.0). Reaction temperature is then raised progressively to ~105°C. 2.0 g of gum arabic and 0.5 g of Jaguar are added at the cloud point, followed by 0.95 g of sulfuric acid diluted in 3.0 g of water (pH ≈6.0). The product is advanced to the desired molecular weight at 85-100°C. At the desired endpoint, vacuum reflux is used to cool the system rapidly.

PTS Resins

Preparation of particulate resoles can be illustrated by the following example based on phenol: phenol, 100 g; 50% aqueous formaldehyde, 72 g; hexamethylenetetramine, 9 g; gum arabic, 1 g; water, 83 g.

The above were charged into a Morton flask equipped with a mechanical stirrer, thermometer, and reflux condenser, and heated to 85°C. A clear solution was formed initially. After about 5 min the solution became cloudy (cloud point) and turned into a creamy, tan-colored suspension. An exothermic reaction ensued which could be easily maintained at 85°C with a water bath in the laboratory. After the exotherm had subsided, heating was resumed to maintain the reaction at 85°C for 30-100 min. The precise length of reaction time depends on the flow property of the product desired. After the predetermined reaction time had elapsed, the dispersion was cooled to less than 40°C. On large-scale preparations, cooling can be effectively accomplished by vacuum reflux. The reaction was diluted with about 500 mL of water at ambient temperature and subsequently washed by decantation with 500 mL portions of water. The particulate resole was isolated by filtration and dried at ambient conditions for about 10 min and then at

60°C for 20-30 min in a Pfaltz and Bauer fluidized bed drier. The particulate resole was characterized by 150°C hot plate gel time (stroke test) and 126°C inclined plate flow (P. F.) [7].

Gel Permeation Chromatography

Aliquot samples of the dispersion or PTS product were withdrawn from the reaction mixture. The resin and aqueous phase were separated by means of high-speed centrifuge, and the quantities of each were weighed. The unreacted phenol was measured by gel permeation chromatography, while the formaldehyde was determined by the hydroxylamine method. Gel permeation chromatography was performed on a Waters Associates HPLC with a column bank consisting of 1000, 500, 500, 100, and 100 Å μ-Styragel. Tetrahydrofural was used as the solvent.

ACKNOWLEDGMENTS

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