The Chemistry of Fast-Curing Phenolic Adhesives.   I

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Synopsis

Certain low molecular weight, resinous polymers, such as those derived from phenol and formaldehyde, may be chemically modified with aromatic amines to produce other resins of physical properties similar to those of the original resins, but with chemical reactivity which is orders of magnitude faster than that of the unmodified resins. This means that while an ordinary phenolic adhesive cures in minutes at high temperature, a properly modified phenolic can be advanced in seconds at ambient conditions to a cured resin of strength and durability comparable to those of ordinary phenolic adhesives.
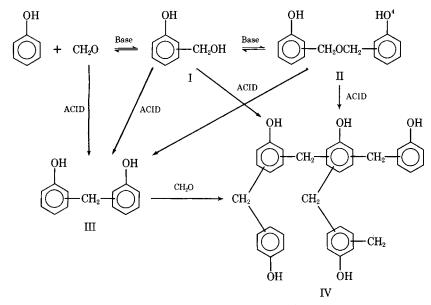
INTRODUCTION

Phenolic resins, made by the acid- or base-catalyzed condensation of phenols with formaldehyde, are well known and have been described at length many times.[1]

Phenolic resins have been used extensively as molding compounds and adhesives and in other applications where low cost and chemical durability are desirable. Most phenolic resins have the disadvantage that they cure rapidly only at considerably elevated temperatures or in the presence of such large concentrations of acid that the cured products are not suitable for common applications such as wood gluing. This paper describes new chemistry of phenolic resins which permits formation of cured resins with physical properties and chemical durability comparable to conventional phenolic resins. However, gel times have been shortened from minutes at elevated temperatures to seconds at ambient conditions, while operating in a pH range compatible with wood.

The reaction products of formaldehyde with phenol probably include the prominant structures shown in the scheme at the top of page 1814.

Mixtures which predominate in methylol (I) or methylene ether (II) phenols are called *resoles*. Resoles advance in molecular weight spontaneously, with acceleration by heat or acid catalysis. Mixtures which predominate in methylene (III) phenols are called novolaks and have little capacity for spontaneous chemical reaction. The introduction of additional formaldehyde is required to advance the average molecular weight of these resins. In either case, the final product is the cured resin IV, which is a highly cross-linked, three-dimensional network of phenol units linked by methylene bridges.
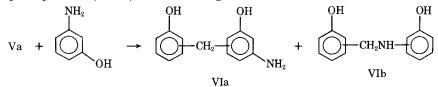
OH + CH₂O $\underset{}{\overset{\text{Base}}{\rightleftharpoons}}$ [I] —CH₂OH $\underset{}{\overset{\text{Base}}{\rightleftharpoons}}$ [II] —CH₂OCH₂—

ACID ... ACID ... ACID ... ACID

III —CH₂— $\xrightarrow{\text{CH}_2\text{O}}$ CH₂ ... CH₂ ... IV

Resoles may be considered mixtures of certain kinds of benzylic phenols, predominantly Va and Vb.

OH —CH₂X

V

Va: X = OH
Vb: X = OR
Vc: X = NR₂
Vd: X = halide

However, other benzylic species such as Vc and Vd also exhibit considerable chemical reactivity. The general reactivity of many benzylic compounds under appropriate conditions permits conversion of typical resoles V into stable, modified species analogous to novolaks. The incorporation of nitrile groups into phenolic resins has been accomplished by modification of the phenolic with aminonitriles.[2] If the fragment X of structure V is properly chosen, the modified novolak can be cured to an infusible resin orders of magnitude more rapidly than either conventional novolak III or resoles Va or Vb.

The system of greatest interest at present is an amine-modified novolak, because it is then possible to take advantage in the curing reaction of the great reactivity of amine groups toward formaldehyde. Resoles and *m*-hydroxyaniline (MHA) are reacted together:

Va + (NH₂, OH) → (OH —CH₂— OH, NH₂) VIa + (OH —CH₂NH— OH) VIb

On treatment with a formaldehyde curing agent, the modified novolak VI advances rapidly at ambient conditions to a three-dimensional network analogous to IV, in which some phenol units are replaced by m-hydroxy-aniline (MHA) units. Chemical stability and physical properties of the cured product are comparable to those of the typical cured phenolic.

The ability to make highly reactive novolak analogues is not limited to phenol–formaldehyde condensation resins. Almost any formaldehyde condensation resin which possesses resole-type reactivity can be accelerated by amine modification. Typical examples are the formaldehyde condensation products of urea and of acetone.

Further, the ability to modify resole-like condensation resins to highly reactive novolaks is not limited to amines. Other formaldehyde-reactive materials such as acyl hydrazides or resorcinol also serve as modifying agents. The only apparent limitations on these systems are that the condensation resin have resole-like reactivity and that the modifying agent be at least difunctional and have a rapid rate of reaction with formaldehyde or whatever final curing agent is selected.

EXPERIMENTAL

Resole Preparation

A mixture of 42.06 parts of 100% phenol, 11.35 parts of 91.05 para-formaldehyde flake, 4.51 parts of water, and 0.46 parts of calcium acetate was prepared at 25°C. The mixture was brought to reflux (109°C) in 60 min at a uniform rate, held at reflux for 120 min, cooled, and stored. This material will usually be referred to as "phenolic prepolymer A."

Although the mole ratio of formaldehyde to phenol (0.77) used in preparation suggested that prepolymer A should be a novolak, prepolymer A was actually a mixture of resole which possessed the hydroxymethyl absorption at 10.0 microns typical of resoles[3] and some unreacted phenol.

Preparation of Other Condensation Resins

Urea–formaldehyde, melamine–urea–formaldehyde, and acetone–form-aldehyde condensation resins were purchased from commercial sources. Formaldehyde condensation resins of melamine, thiourea, and nitro-methane were made by adding 50% formalin dropwise to the formaldehyde-reactive compound, with or without catalyst. In those cases where a catalyst seemed necessary, a few drops of 49.7% caustic were used. During addition of the formalin, temperature was maintained below 70–80°C, in order to avoid a runaway reaction. After the addition of formalin was completed, the mixture was usually heated at reflux for 0–2 hr until titration by the hydroxylamine hydrochloride method[4] indicated that more than 90% of the formaldehyde was consumed. The mixture was then reacted with the modifying agent. In all cases, the condensation resin was stirred into the modifier in order to avoid any excess of resin in the presence of unreacted modifier. The mixture was then heated at reflux for 0.5–2.5 hr, cooled, and stored.

Preparation of Amine-Modified Novolaks for Gel Time and Adhesion Screening

A mixture of 100 g prepolymer A (or other condensation resin) and 0.305 mole amine (or other modifying agent) was refluxed for 2.25 hr and cooled, and 26.3 g methanol was stirred in to prevent phase separation.

Gel Time (Pot Life of the Resin)

A 10-g aliquot of the amine-modified novolak was weighed out, the nominal pH (as measured by a glass electrode) was adjusted with concentrated HCl or 50% NaOH, and 25 ml of 55% methyl formcel (55% formaldehyde, 35% methanol, and 10% water) was then added. In some cases, the methyl formcel was thickened with asbestos powder. The mixture was stirred rapidly until gelled, and the time was recorded.

In the case of some nonphenolic, modified resins, solubility problems were overcome by addition of N,N-dimethylformamide. For example, with urea–formaldehyde and melamine–urea–formaldehyde resins, the selected amine (1 part by weight) was dissolved in 1–3 parts by weight N,-N-dimethylformamide, and 3 parts Amres 255 (Pacific Resins and Chemicals, Seattle, Wash.) or Melurac 400 (American Cyanamid) were stirred in with gentle warming. The pH was adjusted by addition of concentrated HCl. To this mixture was added 1 part 55% methyl formcel. The mixture was stirred and the gel time recorded.

TABLE I
Selected Resole-Modifying Agents

Modifying compound	Approx. pH	Gel time, sec	Tensile break, psi
1,8-Diaminooctane	9–11	100	—
Diethylenetriamine	11	9	115
1,6-Dihydrazinohexane	7	63	—
Hydrazine	8	20	115
Adipic dihydrazide	3–7	80	130
p-Aminobenzoic hydrazide	8	50	115
Carbohydrazide	8	65	210
Isophthalic dihydrazide	8	75	132
Succinic dihydrazide	4–8	100	—
2,6-Diaminopyridine	8	25	195
3,3'-Dimethoxy-4,4'-bis-(4-semicarbazido)biphenyl	3	15	90
1,6-Bis(ureido)hexane	2	20	150
1-Amino-5-naphthol	4	99	221
2,4-Diaminoacetanilide	8	16	282
m-Hydroxyaniline	7	30	405
4,4'-Methylenedianiline	7	15	120
4,4'-Oxydianiline	7	20	85
m-Phenylenediamine	8	25	70
1,3,5-Triaminobenzene	8	240	130

Adhesive Properties of Amine-Modified Novolaks

Adhesion screening tests were performed by an extension of the gel time test procedure. After addition of the methyl formcel, but before the resin set, the mixture was spread on a wood block (Douglas fir). Another block was placed on top of the resin to make a contact area of 1 sq in. and pressed at 40 psi for 12 min, followed by measurement of the tensile force per unit area necessary to separate the blocks. Results appear in Tables I to III.

TABLE II
Nonphenolic Modified Prepolymers

Formaldehyde Condensation prepolymer	Modifying agent	Moles modifier per 100 g prepolymer	Approx. pH	Gel time, sec	Tensile break, psi
Acetone	m-hydroxyaniline	0.3	3	30	235
Melamine–urea	4,4'-methylene-dianiline	0.3	4	60	140
Nitromethane	m-hydroxyaniline	0.3	7	6	—
Nitromethane	resorcinol	0.2	1	10	—
Thiourea	m-hydroxyaniline	0.6	4	25	—
Urea	carbohydrazide	0.3	3	80	305
Urea	2,4-diaminoacetanilide	0.3	7	120	230
Urea	glutaric dihydrazide	0.3	3	80	375
Urea	hydrazine	0.3	9	10	215
Urea	m-hydroxyaniline	0.3	7	25	110

TABLE III
Strength Increase in MHA-Modified Prepolymer A as a Function of Time [a]

Time before tensile break, min	Tensile break, psi	
	A	B
1	—	85
2	70	290
4	275	405
6	355	—
8	430	—
10	400	—
15	485	—

[a] A, Sample had 53 sec gel time; B, sample had 30 sec gel time.

RESULTS AND DISCUSSION

Table I lists the gel time and adhesive performance of resoles modified with a wide range of formaldehyde-reactive compounds. In the tensile break test, wood failure becomes predominant at about 150 psi. The unmodified phenolic would not cure and produced no adhesive bond strength under the conditions used to cure the modified prepolymers.

The modification process is not restricted to phenolic resoles.   Many prepolymers with resole-like reactivity (hydroxymethyl groups or their equivalents) produced modified "novolak analogues" which cured rapidly at ambient conditions on addition of formaldehyde donors.   Table II illustrates the point.

Table III shows the rate of strength built up in m-hydroxyaniline-modified phenolic prepolymer A on mixing with formaldehyde donor at ambient conditions.   Within 2 min, the strength of the bond exceeded the nominal wood failure limit.

References

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3. P. J. Secrest, *Off. Dig. Fed. Paint Technol.*, **37** (481), 187 (1965).

4. J. F. Walker, *Formaldehyde*, 2nd ed., Reinhold, New York, 1953.