

Differential Scanning Calorimetry of Phenol-Formaldehyde Resols

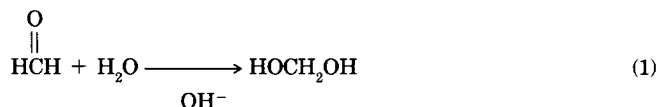
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Synopsis

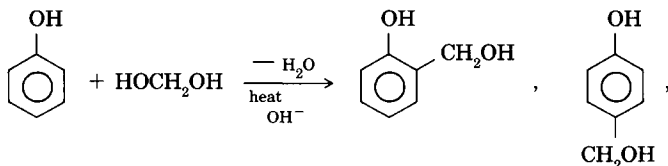
Differential scanning calorimetry was used on a range of synthesized phenol-formaldehyde (PF) resols to discover relationships between formulation parameters or physical properties of resols, and their thermal behavior during cure. The thermograms showed either one or two exothermic reactions. The lower exothermic peak temperature varied between 98 and 129°C with changes in the free formaldehyde content. This exotherm is caused by the addition of free formaldehyde to phenolic rings. The upper exothermic peak temperature varied from 139 to 151°C, with the higher temperatures occurring when the formaldehyde-to-phenol molar ratio was low or the total amount of sodium hydroxide relative to phenol was high. These two factors led to resins which contain a somewhat higher level of unreacted *ortho* or *para* aromatic ring positions and no free formaldehyde. Consequently, condensation is probably not solely by the faster self-condensation through hydroxymethyl groups, but also includes the slower condensation of hydroxymethyl groups with unreacted ring positions. Gel times show trends with changes of formulation parameters somewhat similar to trends of the upper exothermic peak temperatures.

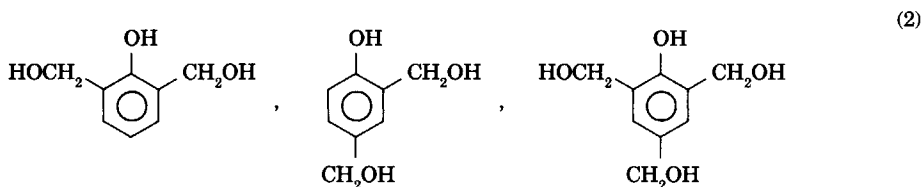
INTRODUCTION

Phenolic resols comprise the adhesives most useful for wood panel products, such as plywood and flakeboard, suitable for exterior use. Resols are manufactured from phenol and formaldehyde under base catalysis to provide polymers with low degrees of polymerization, typically in aqueous solution. In basic aqueous solution formaldehyde exists primarily as methanediol (methylene glycol)

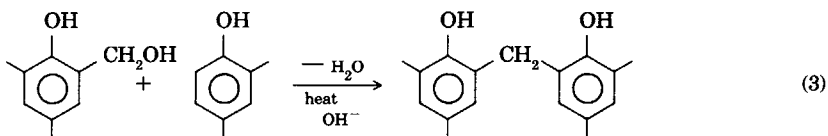


and it is this species which attacks the active *ortho* and *para* positions of a phenol ring

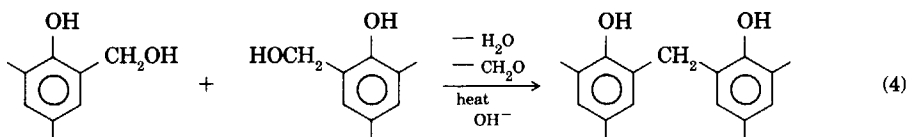




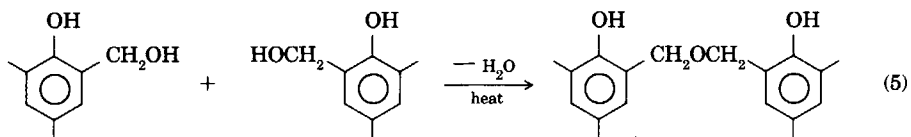
This is called the addition reaction of formaldehyde to phenol. The hydroxymethyl groups on these compounds can condense with unreacted but active positions on other phenolic rings,



or hydroxymethyl groups on different phenolic rings can condense together,



In either case a methylene bridge forms between aromatic rings. The condensation of two hydroxymethyl groups to form a dibenzyl ether linkage occurs near neutral or acidic pH values^{1a}:



but dibenzyl ether species are rare in the alkaline environment^{1b,2} used to produce most resols. It is these condensation reactions between phenolic species that build up the molecular weight and lead to branching and cross-linking for these thermosetting resins. To keep the reaction from proceeding directly to a solid, thermoset resin the condensation reaction usually is stopped by lowering the temperature. This intermediate stage, called a resol, contains species still at low degrees of polymerization, so that they remain soluble in alkaline solution. The normally branched polymer chains of a phenolic resol have a substantial proportion of hydroxymethyl groups attached. To cure the resol, it need only be heated sufficiently to continue the condensation reactions of eqs. (3) and (4).

Although many researchers have looked at parts of the process from synthesis to application, the present work is part of a series of papers³⁻⁵ addressing the relationships between phenolic resin synthesis parameters, the resulting resol molecular structure and physical properties, and the performance of the cured resin adhesives in wood joints. This paper concerns

the effects of synthesis formulation parameters on the thermal reactions of resols as they are being cured.

Few articles have reported the effect of formulation parameters such as formaldehyde-to-phenol molar ratio (F/P) on the thermal reactions during cure of phenolic resins.

Early workers used thermal analysis equipment that allowed volatile components to escape from the samples' immediate surroundings. This is an important point because the curing reaction is an exothermic process,^{6,7} whereas the volatilization is an endothermic process. With substantial quantities of solvent water to be driven off during the cure of liquid resols, much of the curing exotherm can be completely obscured^{8,9} when the heat of reaction is measured.

Katović¹⁰ investigated resols of three F/P ratios, but because the resols were neutralized before cure, the curing reactions are not those of typical alkaline resols.

Eventually researchers used pressurized DSC systems to suppress volatilization. Šebenik et al.⁶ used pressure-resistant DSC capsules to study the reactions of equimolar (F/P = 1) amounts of monomeric phenol and paraformaldehyde in the presence of different levels of sodium hydroxide, from zero to 1 wt % (0–0.031 mol NaOH/mol phenol). It appears these were nonaqueous mixtures, and the molar proportions of catalyst to phenol were substantially below those used in synthesizing commercial resols for wood bonding. The calorimeter scanned the mixtures through both the addition [eq. (2)] and condensation [eqs. (3), (4)] reactions, up to 200°C. Both the addition and condensation reactions were exothermic, and were shifted to lower temperatures by increasing NaOH levels.

It is conceivable that resol samples in sealed capsules may undergo a different reaction process than samples freely allowed to lose water, as in a heated wood bondline. However, the condensation reactions of eqs. (3) and (4) are essentially irreversible, as evidenced by the resistance of cured phenolic resins to even boiling water environments.

Thus, previous work relating thermal curing characteristics of phenolic resols to their formulations has either not been done on resols representative of commercial use with wood, or researchers used instruments that allowed confusion of the exothermic curing reaction with volatilization of water. We are reporting sealed-capsule DSC curing measurements on aqueous phenol-formaldehyde resols representative of a wide range of commercially manufactured formulations. This knowledge should help manufacturers design phenolic resols that have lower curing temperatures for wood bonding.

EXPERIMENTAL

Resin Synthesis

Resins were prepared^{11,12} at Oregon State University according to the following general procedure: Water solutions of 90% phenol, 50% formaldehyde, and the initial portion of 50% sodium hydroxide were measured into a resin kettle to provide a target solids content of 47.7%. The tem-

perature was raised at 2.8°C/min to reflux, except for several syntheses held temporarily at 60°C to promote hydroxymethylation (formaldehyde levels decreased below 2%). After 17 min at reflux the temperature was decreased to 85°C and held until the 25°C viscosity reached 32–48 Pa s. Then a second portion of NaOH was added, and the temperature was decreased to 79.4°C. When the viscosity increased again to 12–16 Pa s, any final portion of NaOH was added and the temperature was lowered to 25°C.

Three values of each of three formulation parameters were used in an experimental design for the resin synthesis reactions. Molar ratios of formaldehyde to phenol (F/P) were 1.9, 2.2, and 2.5; molar ratios of the first charge of NaOH to phenol (abbreviated *i*NaOH) were 0.15, 0.25, and 0.35; and molar ratios of the total charge of NaOH to phenol (abbreviated *t*NaOH) were 0.45, 0.60, and 0.75. These were combined in 15 ways to form an experimental design. The design is illustrated in Figure 1 as a 3-dimensional representation with the three parameters as the three axes and each circle representing a different type of formulation. As an example, the open circle at the bottom of the front face of the cube represents a synthesis in which F/P was 2.2, *i*NaOH was 0.15, and *t*NaOH was 0.45. This type of representation is used later to present quantitative data for various resol properties. In those cases the numerical values will be substituted for the circles of this figure. The authors feel this compact format will allow readers to recognize some overall trends better than 2-dimensional charts or tables. Where two resin syntheses had the same formulation parameters but a temperature hold for better hydroxymethylation was included for one resin, the numerical value for that resin's properties will be followed by the letter M.

DSC Equipment

Thermograms of samples were obtained with a Perkin-Elmer DSC-2 differential scanning calorimeter. To suppress interfering water and formaldehyde vaporization endotherms, Perkin-Elmer large-volume capsules (LVC) were used. These stainless steel capsules sealed with Viton O-rings can withstand vapor pressures of 1.4–2.1 MPa, which allowed routine operation with aqueous solutions to 200°C. Indium was used to establish the temperature calibrations for these capsules.

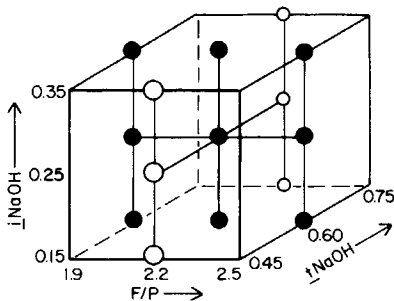


Fig. 1. Experimental plan for resin syntheses.

DSC Samples and Procedures

Two series of resin samples were sent from Oregon State University to the Forest Products Laboratory (FPL) for DSC analysis. The first series was sent as liquids obtained directly from the original syntheses. The second series was provided as powders, which had been obtained by diluting liquid aliquots with water and subsequent freeze drying. Resins of the second series were prepared either to investigate the hydroxymethylation step in syntheses or to provide additional resin for extensive gluing studies. Where replicate resins were prepared, the procedure followed the original conditions as closely as possible.

A 7.5–20-mg droplet of liquid resin was sealed in each DSC capsule. For the freeze-dried resins, water was first added to the powder until each went into solution. Capsules were transferred to the DSC sample holder assembly which had been set at 17 or 27°C. Samples were heated at 10°C/min up to 200°C. Because of the capsule's pressure limitation, the phenolic thermograms beyond 200°C were not scanned. The temperatures corresponding to the exotherm peaks were selected as the characteristic reaction temperatures.

Other Measurements

Other properties of the resols were measured by the following methods, for which detailed information is given elsewhere.^{11,12} Free formaldehyde content of the resols was measured by the hydroxylamine hydrochloride method.¹³ Free phenol content was determined by high-pressure liquid chromatography (HPLC) on a neutralized solution of the resin in tetrahydrofuran and water.

Gel time was determined with a Tecam gelation timer with the resin sample in a jar partly immersed in an 80°C oil bath.

The weight average molecular weight was determined by size exclusion chromatography (SEC) with low-angle laser light scattering (LALLS). LALLS accurately analyzes the molecular weight of all fractions as they are eluted from the column. Neutralized and freeze-dried resin samples were analyzed in a mobile phase of hexafluoroisopropanol and 0.08 wt % sodium trifluoroacetate. Unlike other solvent systems, this combination dissolved all the freeze-dried powder. It also provided the lowest molecular weight values, which indicates that molecular association was lowest in this solution. The SEC column was a Waters μ Bondagel column set consisting of E-linear and E-125 columns in series.

Prior to proton nuclear magnetic resonance (¹H-NMR) measurements, resols were neutralized, freeze-dried, and acetylated. This product was dissolved in deuterated chloroform, with 1% TMS (tetramethylsilane) for the chemical shift reference, and analyzed at 100 MHz.

RESULTS AND DISCUSSION

Examples of thermograms from DSC scans of three phenol-formaldehyde resin formulations are shown in Figure 2. In these cases, the initial sodium hydroxide content and the F/P ratio varied among the syntheses, and the

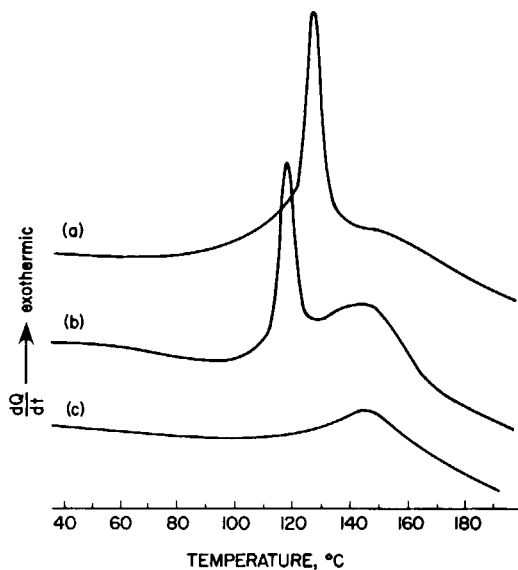


Fig. 2. DSC thermograms ($\beta = 10^\circ\text{C}/\text{min}$) of three phenol-formaldehyde resins with the following formulation parameters, F/P-*t*NaOH-*i*NaOH, and free formaldehyde contents in parentheses: (a) 2.5-0.60-0.25 (3.1%); (b) 2.2-0.60-0.15 (1.2%); (c) 2.2-0.60-0.35 (0.0%).

free formaldehyde content differed in the final resins. The most striking difference between the thermograms is the presence or absence of a sharp exotherm and its location on the temperature scale. Also, a second exotherm at a higher temperature is evident as a broad peak in the last two of the three thermograms in Figure 2. The peak temperatures found for each resin are shown in Table I along with the formulation variables and resulting properties—free formaldehyde content, 80°C gel time, final weight average molecular weight, and free phenol content. In general, the sharp exotherm of the lower temperature peak, $T_p(1)$, appeared in the temperature range 98–129°C. The higher temperature peak was always quite broad and its maximum, $T_p(2)$, was in the range of 139–151°C. We attribute the lower peak to initial addition reactions of free formaldehyde to phenol, and the upper peak to chain-building condensation reactions involving hydroxymethyl groups attached to various phenolic species.

Three forms of evidence support this interpretation. First an industrial procedure for producing phenolic resols¹⁴ uses a lower temperature hydroxymethylation step (near 65°C for several hours), before raising the temperature to reflux to increase molecular weight through condensation reactions. Secondly, Šebenik et al.⁶ showed by paper chromatography that phenol and 2-hydroxybenzyl alcohol are still major components of a phenol-formaldehyde mixture heated only to 87°C, near the mixture's first DSC reaction peak. This showed that condensation was not predominant yet. The third piece of evidence is our DSC analyses (at 10°C/min) on separate alkaline (NaOH/P = 0.6), aqueous solutions of phenol plus formaldehyde (F/P = 1.8), of 2-hydroxybenzyl alcohol, and of 4-hydroxybenzyl alcohol. Phenol reacting with formaldehyde gave two peaks, the lower at 85°C and the upper at 150°C, which correspond with the two exothermic peaks seen

TABLE I
 Formulation Variables and Resulting Properties for the Phenol-Formaldehyde Resins

Formulation parameters F/P- <i>t</i> NaOH- <i>i</i> NaOH ^a	DSC peak temperatures (°C)		Free formaldehyde (%)	80°C gel time (min)	Final $\bar{M}_w \times 10^{-3}$ (daltons)	Free phenol (%)
	Lower	Upper				
2.5-0.60-0.15 M ^b	128 (129) ^c	* ^d (140)	3.2	47	44.6	0.1
2.5-0.60-0.15	NA ^e	NA	3.1	30	126.0	0.5
2.5-0.60-0.25	126 (123)	* (139)	3.1	30	185.2	0.8
2.5-0.60-0.35	—	143	0.0	73	203.3	0.3
2.2-0.75-0.15	109	148	1.1	184	33.3	0.1
2.2-0.75-0.25	— (98)	147 (150)	0.3	197	75.6	0.1
2.2-0.75-0.35	—	148	0.0	195	161.2	0.1
2.2-0.60-0.15 M	117 (112)	144 (145)	1.2	89	27.4	0.0
2.2-0.60-0.15	115 (112)	145 (147)	1.2	89	36.4	0.1
2.2-0.60-0.25	—	144 (147)	0.0	159	52.4	0.1
2.2-0.60-0.35	—	145 (146)	0.0	107	148.0	0.0
2.2-0.60-0.35 M	(—)	(147)	NA	86	191.3	NA
2.2-0.45-0.15	122	141	1.2	75	42.4	0.1
2.2-0.45-0.25	115 (110)	143 (145)	1.1	59	132.8	0.1
2.2-0.45-0.35	—	141	0.0	102	47.2	0.1
1.9-0.60-0.15	—	147	0.0	169	42.2	0.2
1.9-0.60-0.15 M	—	147	0.0	218	32.6	0.3
1.9-0.60-0.25	—	151 (150)	0.0	208	59.5	0.3
1.9-0.60-0.35	—	150 (142)	0.0	126	186.1	0.4

^a Mole ratios: F/P = formaldehyde to phenol; *t*NaOH = total NaOH to phenol; *i*NaOH = initial NaOH to phenol.

^b M indicates this resin was held in a hydroxymethylation stage.

^c Parentheses indicate second series samples, which were freeze-dried and later had to be dissolved in water before DSC analysis.

^d * indicates that it was not possible to identify the higher-temperature exothermic peak because of its shallowness and the overlap with a lower peak.

^e NA = not available.

in our resins. Self-condensation of each of the two hydroxybenzyl alcohols produced a peak temperature of 144°C for 4-hydroxybenzyl alcohol and 165°C for 2-hydroxybenzyl alcohol. Thus it seems the addition reactions are associated with the earlier of the two reaction peaks and condensation reactions to the later peak.

The DSC peaks were compared against various resin characteristics (Table I) to bring out any correlations. The DSC values for the first series of samples are given prominence. The values for the second series are given in parentheses for two reasons: (1) they had all undergone freeze-drying and later dissolution before DSC analysis, and (2) many were second batches with the same formulation and reaction procedures but the resin properties of all were not checked in detail. Those of the second batch that were checked exhibited properties that agreed well with the first batch.

There is an obvious correlation between the occurrence of a lower temperature exothermic peak and the presence of free formaldehyde (Table I

and Fig. 3). The intensity of the lower temperature peak increases with free formaldehyde content, though less than proportionately. The increase of peak size is understandable, as more reaction can occur when more formaldehyde is present. The $T_p(1)$ values also generally increase with higher free formaldehyde contents. The delay of reaction with increased formaldehyde may result from either (1) less reactivity or less accessibility of the reactive phenolic ring positions that are left or (2) lowered availability of the formaldehyde possibly caused by its conversion to more polymeric species in the resol as its concentration increases.

Since the range of the $T_p(2)$ values is small compared to their absolute magnitude, we have emphasized the trends by using temperature differences. These difference quantities are taken relative to the central point of the experimental design, i.e., $T_p(2) - 144^\circ\text{C}$. Some of these temperature differences are the same magnitude as the accuracy of estimating temperatures from charts ($\pm 0.5^\circ\text{C}$) and of temperature reproducibility ($\pm 1^\circ\text{C}$) for a particular sample's peak maximum.

We have found correlations between the formulation parameters and the $T_p(2)$ values. Larger positive temperature differences, i.e., increases of $T_p(2)$, correlate with lower F/P values [Fig. 4(a)] and with larger $t\text{NaOH}$ values [Fig. 4(b)]. These charts are essentially vertical slices through a 3-dimensional display of temperature differences ($T_p - 144^\circ\text{C}$) shown fully in Figure 5(a). There seems to be no correlation between $T_p(2)$ and $i\text{NaOH}$ (values stacked vertically). It is important for understanding the following arguments to realize that reactions which occur earlier than others during an

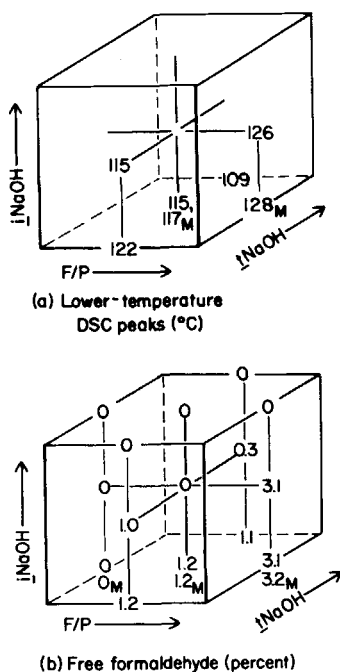


Fig. 3. Triaxial displays relative to formulation parameters (a) the lower-temperature DSC peaks ($^\circ\text{C}$) for the first series of resins and (b) free formaldehyde contents (%) of these resins. An "M" indicates the resin synthesis included a hydroxymethylation step.

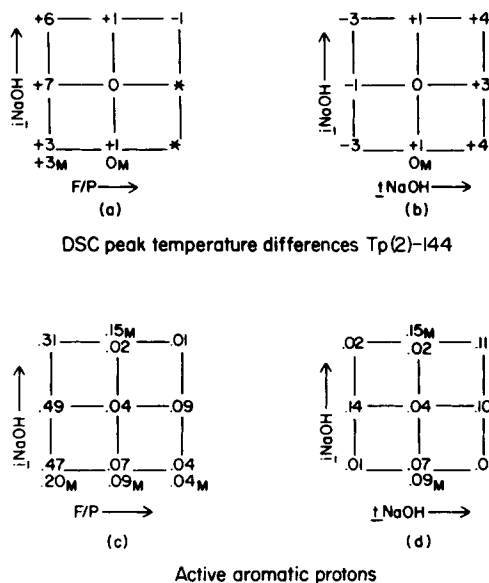


Fig. 4. Biaxial display relative to formulation parameters of (a) and (b) DSC peak temperature differences, $T_p(2)-144^\circ\text{C}$ and (c) and (d) average number of reacted *ortho* and *para* sites per phenol unit by $^1\text{H-NMR}$ analysis. "M" indicates a hydroxymethylation step.

isothermal procedure will also occur earlier, i.e., at lower temperatures, during heating scans in a DSC or DTA experiment.*

Gollob's $^1\text{H-NMR}$ data¹² show that the highest proportion of unreacted *ortho* and *para* sites on phenolic rings is associated with the lowest F/P values [Fig. 4(c)], and the next highest proportion of unreacted sites is for the largest $t\text{NaOH}$ values [Fig. 4(d)]. In both these situations there is also little or no free formaldehyde available in the resin. Consequently, during the DSC scans those unreacted sites must condense directly with a hydroxymethyl (methylol) group, if they are to condense at all. Yeddapanalli and Francis¹⁵ and Francis and Yeddapanalli¹⁶ have shown that condensation of a phenolic hydroxymethyl group with an unreacted site on phenol itself is much slower than self-condensation of two phenolic hydroxymethyl groups. For the resins studied here it seems likely that the unreacted phenolic ring sites and lack of formaldehyde which could add to them during the DSC scans cause those resins with low F/P or high $t\text{NaOH}$ to have higher condensation exotherm temperatures, $T_p(2)$.

With increasing levels of $t\text{NaOH}$ one might expect the peak temperature to decrease because of catalytic effects. However, condensation reaction rates are level or decrease with increasing sodium hydroxide contents for resols at $t\text{NaOH}$ values above a few hundredths^{17,18} or pH values above 11.¹⁹ The $t\text{NaOH}$ values here were above 0.45, and measured pH values for these resins were all above 10.9, increasing in step with $t\text{NaOH}$.

Resin gel times, weight average molecular weights, and free phenol contents of the various formulations are also displayed in three-dimensional

* However, if the two reactions are independent and have significantly different activation energies their reaction rate-temperature plots could cross one another.

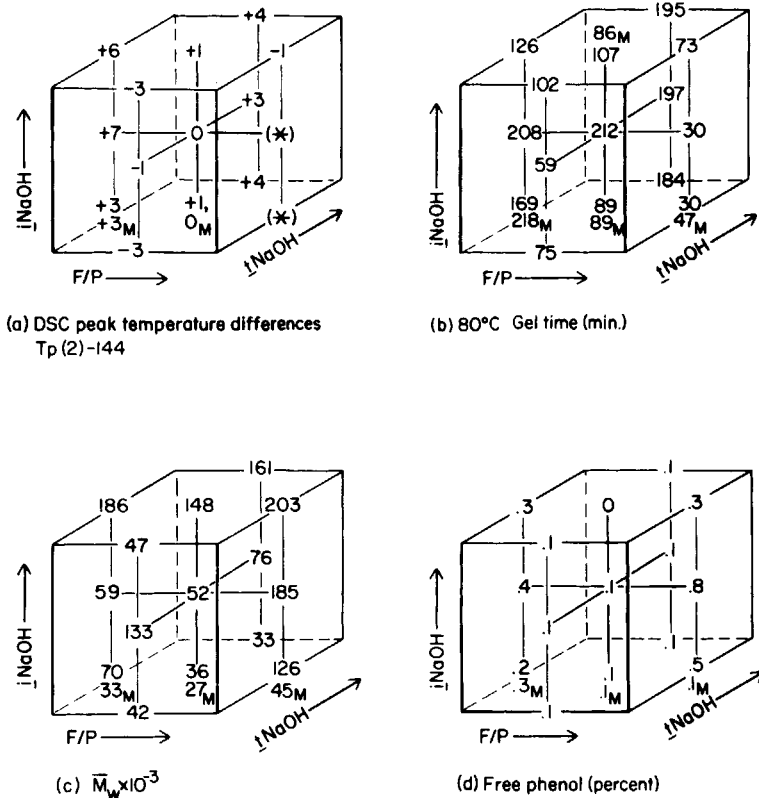


Fig. 5. Triaxial displays relative to formulation parameters of (a) DSC peak temperature differences, $T_p(2)-144^\circ\text{C}$; (b) 80°C gel time (min); (c) weight average molecular weight $\times 10^{-3}$ (daltons); (d) free phenol content (%). "M" indicates a hydroxymethylation step.

formats in Figure 5. Gel times generally increase with lower F/P and with higher $t\text{NaOH}$ (Fig. 6), confirming decreased reactivities for resols made with these formulations. Ranking resins by increasing gel time values (less reactivity) shows several differences when compared with a ranking of resins by increasing $T_p(2)$ values (also less reactivity). No correlation was found for $T_p(2)$ values with either molecular weight or free phenol content.

CONCLUSIONS

For phenol-formaldehyde resols in the commercial formulation ranges studied here, DSC analysis showed two major exothermic peaks. The first peak, which occurs if the resin contains sufficient free formaldehyde, reaches a maximum between 98 and 129°C. Caused by the addition of formaldehyde to phenolic rings, this peak becomes more intense and moves to higher temperatures as resin free formaldehyde content increases. Curing occurs during the second exothermic peak, caused by condensation reactions involving hydroxymethyl groups. This peak, seen between 139 and 151°C, occurs at the higher temperatures when the resol is made with a low formaldehyde-to-phenol mole ratio or a high total NaOH-to-phenol mole ratio. A resol made under either of these conditions contains unreacted *ortho* and

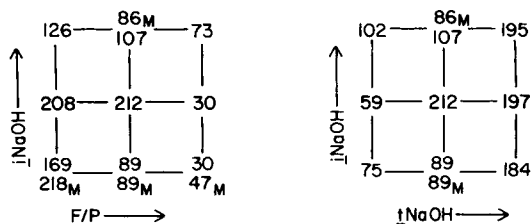


Fig. 6. Biaxial displays relative to formulation parameters of 80°C gel time. "M" indicates a hydroxymethylation step.

para sites on phenolic rings and no free formaldehyde. During adhesive bonding such resols should not cure as quickly, nor at as low temperatures, as resins which are more fully substituted with hydroxymethyl groups or contain sufficient free formaldehyde, regardless of resin molecular weight.

Gel times for these resols generally follow the trends of the higher exotherm's peak temperatures. There are no discernable correlations of DSC peak temperatures with the initial NaOH-to-phenol mole ratio, with molecular weight, or with the small amounts of free phenol in the resols.

The authors wish to acknowledge the help of Robert J. Parker in synthesizing the resins and in the measurement of physical properties. Thanks also go to Wesley L. Rork for preparing samples and making the DSC scans. One of us (Lawrence Gollob) wishes to thank J. D. Wellons for his support, advice, and direction during the course of this work. The use of trade, firm, or corporation names in this publication is for the information and convenience of the reader. Such use does not constitute an official endorsement or approval by the U.S. Department of Agriculture of any product or service to the exclusion of others which may be suitable.

References

1. R. W. Martin, *The Chemistry of Phenolic Resins*, Wiley, New York, 1956, (a) p. 133, (b) p. 265.
2. M. M. Sprung and M. T. Gladstone, *J. Am. Chem. Soc.*, **71**, 2907 (1949).
3. L. Gollob, R. L. Kraemer, J. D. Wellons, and A. W. Christiansen, *Forest Prod. J.*, **35**(3), 42 (1985).
4. S. S. Kelley, L. Gollob, and J. D. Wellons, to appear.
5. G. E. Maciel, I.-S. Chuang, and L. Gollob, *Macromolecules*, **17**, 1081 (1984).
6. A. Šebenik, I. Vizovišek, and S. Lapanje, *Eur. Polym. J.*, **10**, 273 (1974).
7. R. Kay and A. R. Westwood, *Eur. Polym. J.*, **11**, 25 (1975).
8. S. Chow, P. R. Steiner, and G. E. Troughton, *Wood Sci.*, **8**(1), 343 (1975).
9. C.-Y. Hse, *Forest Prod. J.*, **21**(1), 44 (1971).
10. Z. Katović, *J. Appl. Polym. Sci.*, **11**, 85 (1967).
11. J. R. Parker, M.S. thesis, Oregon State University, Corvallis, 1982, 164 pp.
12. L. Gollob, Ph.D. thesis, Oregon State University, Corvallis, 1983, 153 pp.
13. J. F. Walker, *Formaldehyde*, 3rd ed., Krieger, Huntington, NY, 1975, p. 493.
14. A. L. Lambuth, U.S. Pat. 3,342,776 (1967).
15. L. M. Yeddanapalli and D. J. Francis, *Makromol. Chem.*, **55**, 74 (1962).
16. D. J. Francis and L. M. Yeddanapalli, *Makromol. Chem.*, **125**, 119 (1969).
17. D. J. Francis and L. M. Yeddanapalli, *Makromol. Chem.*, **119**, 17 (1968).
18. G. E. Troughton, *Holzforschung*, **26**, 170 (1972).
19. M. F. Drumm and J. R. LeBlanc, in *Step Growth Polymerization*, D. H. Solomon, Ed., Dekker, New York, 1972, p. 245.

Received May 5, 1984

Accepted October 24, 1984