

## Phenol-Formaldehyde Wood Adhesive Characterization by Proton Magnetic Resonance Spectroscopy

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### Synopsis

Acetylation of phenol-formaldehyde (PF) wood adhesives afforded derivatives which could be characterized by proton magnetic resonance (PMR) spectroscopy. Through use of the chemical shift and integral parameters, relative comparisons were made for the degree of polymerization of resins prepared with different molar ratios. Additionally, PMR studies of these acetylated derivatives provided a means of determining methylol content and number of aromatic protons remaining, and to some extent gave an estimate of molar formaldehyde-to-phenol ratio. Experiments conducted with  $\text{Ca}(\text{OH})_2$  and  $\text{NaOH}$  as catalysts showed the latter to be the more effective catalyst for PF systems.

### INTRODUCTION

Phenol-formaldehyde (PF) resin is a common plywood and particle-board adhesive which, when properly cured, provides high strength and water resistance in addition to excellent temperature stability. This thermosetting resin is normally applied in a liquid state, usually with water as a solvent, and then polymerized in situ to afford a solid, highly crosslinked system with a durable wood-adhesive interface. Analytical methods, such as x-ray spectroscopy, infrared, thermal analysis, broad-line proton magnetic resonance (PMR) spectroscopy or mechanical strength tests, have been used to study the solid cured state of PF resins with, in many cases, data interpretation reflecting a general physical property rather than a specific assignment of chemical structure. At the other extreme, during the initial polymerization stage, the reaction of phenol with formaldehyde has been examined by numerous methods, especially in terms of reaction kinetics,<sup>1</sup> and rather specific statements can be made concerning reaction mechanisms and chemical structures present. It is the intermediate state, where this resin is polymerized to a molecular weight range of a useful adhesive, that is of interest here. Often an analytical technique which can be successfully applied to monomeric species proves insensitive to macromolecular systems because of the state of the sample,

its limited solution properties, or the poor resolution of a spectroscopic method.

PMR offers a means of characterizing the PF system during its reaction to a degree of polymerization where it becomes a useful adhesive.<sup>2</sup> The four primary PMR parameters of chemical shift, integral, coupling constant, and relaxation time can all provide useful information for structural determination. With increasing molecular weight, the coupling constant parameter becomes difficult to determine because of spectral-line broadening. The relaxation time parameter is not easily determined with commonly available PMR instrumentation.

Previously, Woodbrey and co-workers<sup>3</sup> have published an excellent article discussing the application of PMR to the study of the initial stages of condensation in both acid- and base-catalyzed PF reactions. They demonstrated that protons in a different chemical environment could readily be distinguished by the chemical shift parameter and that one could differentiate between ortho and para reactive positions. In addition, evidence was found of stable benzyl-type hemiformal formation at higher formaldehyde-to-phenol molar ratio (F/P). These structures tended, however, to decompose at higher temperatures associated with resin cure. Freeze drying of the resin followed by acetylation was reported to provide the best material for PMR spectra. This study dealt primarily with resins having a number-average molecular weight range of 250 to 500 on a nonacetylated basis, although the authors indicated that as long as complete resin solubility was present, much higher molecular weight ranges could be studied by PMR. Number-average molecular weights for PF wood adhesives commonly fall in the 2500 to 3500 range.

Recently, Kopf and Wagner<sup>4</sup> have used PMR to study the kinetics of novolac reactions and their cure mechanism with hexamethylenetetramine. Others<sup>5,6</sup> have applied the PMR method to alkylphenolic resins to determine the sequence of methylene and methylene ether bridges in the polymer, while Anderson and co-workers<sup>7</sup> have used Woodbrey's approach to study phenol-resorcinol-formaldehyde resins.

The present report is concerned with the semiquantitative application of PMR chemical shifts and integrals in the analysis of PF wood adhesives. Specifically, this report shows how PMR can be used to determine F/P molar ratio, to monitor the effects of different catalyst types and concentrations, and to give an indication of crosslinking present in the resin.

## EXPERIMENTAL

### Synthesis of PF Resins of Molar F/P of 0.75-2.6

The following general technique was used to prepare all PF resins. For each molar ratio, the calculated amounts of phenol, formaldehyde, and water to give approximately a 50% solution were placed in a reaction vessel together with one third of the total NaOH required and heated to 60°C. Following the initial exothermic reaction, the mixture was placed

under reflux and the progress of the reaction monitored by viscosity measurements (Gardner-Holt viscosity tubes at 25°C). Upon reaching a viscosity of 1000 to 2500 centipoises (cps), the second third portion of the NaOH solution was slowly added. The solution viscosity correspondingly decreased. The mixture was further reacted under reflux until a viscosity of 1000 to 2000 cps was obtained, whereupon the solution was cooled to 25°C. The last third portion of NaOH was then added. Final resin viscosities fell in the range of 300 to 600 cps, with all resins containing a NaOH-to-phenol molar ratio of 0.9. For resins with molar F/P greater than 1.6, cooling of the reaction mixture was necessary during the initial exotherm and with subsequent NaOH addition to ensure a controlled reaction.

### Comparison of NaOH and Ca(OH)<sub>2</sub> as Reaction Catalysts

Two experiments were performed, each at F/P of 2.0 and catalyst-to-phenol molar ratio of 0.2. The first involved the reaction of 94 g (1 mole) phenol, 129 g (2 moles) 46.5% formaldehyde solution, 65 g water, and 16 g (0.2 mole) 50% NaOH solution as catalyst. The mixture was initially heated to 60°C and then further to 95°C, as the exothermic reaction subsided. Samples (10 g) were removed and immediately stored at 0°C at 15-min intervals until 90 min of reaction time had passed. The second experiment followed an identical procedure except that 0.2 mol Ca(OH)<sub>2</sub> was used as catalyst. In this latter case, the reaction was terminated at 70 min because of solution insolubility.

### Effect of NaOH Content on PF Polymerization

The influence of NaOH content on the degree of PF polymerization was evaluated for a F/P = 1.8 resin through addition of five successive increments of catalyst to bring NaOH-to-phenol molar ratio from 0.2 to 1.0. The mixture was reacted after each stage of catalyst addition until a viscosity of 500 cps was reached, whereupon a 2-g sample was removed and the next increment of NaOH added. Specifically, an initial formulation of 94 g (1 mole) phenol, 117 g (1.8 moles) 46.5% formaldehyde, 70 g water, and 16.0 g (0.2 mole) 50% NaOH solution was heated to 60°C, where an exothermic reaction took place. The mixture was maintained at reflux until the second sample was removed, and then the solution temperature was decreased to 85°C. At reaction times of 65, 75, 90, 150, and 175 min, samples were removed. At reaction times of 68, 78, 93, and 153 min, 0.2-mole increments of NaOH were added.

### PMR characterization

All samples were freeze dried and fully acetylated in the usual manner at 25°C with pyridine-acetic anhydride (1:1 v/v) prior to PMR analysis. Their spectra were recorded on a Varian HA-100 spectrometer using CDCl<sub>3</sub> as solvent and tetramethylsilane as internal standard. Two values of each

integral were recorded and the average taken. All chemical shifts are reported as  $\delta$ -values.

## RESULTS AND DISCUSSION

Typical PMR spectra for acetylated PF resins are shown in Figure 1. The sample at 25 min reaction time represents a low degree of condensation, probably somewhat similar to those resins reported by Woodbrey.<sup>3</sup> The sample at 120 min is more representative of a fully synthesized PF plywood adhesive where the resonance peaks show considerable broadening and some tendency to shift slightly upfield. Major peak assignments are: 6.5 to 7.3 $\delta$  for aromatic protons (Ar), 4.7 to 5.3 $\delta$  for methylene protons (methylol) of acetoxymethyl groups (Mo), 3.5 to 4.2 $\delta$  for methylene protons of diphenylmethane-type bridges (Mb), and 1.5 to 2.5 $\delta$  for methyl protons of acetoxymethyl groups (Ac). For resins with a low degree of condensation, the acetoxy resonances may be further resolved into those associated with the phenoxy groups 2.2 to 2.5 $\delta$  and those derived from the hydroxymethyl groups 1.5 to 2.1 $\delta$ .

Traditionally, the increase in polymer size during PF resin synthesis is followed by viscosity, specific gravity, cloud point, or molecular weight measurements.<sup>8</sup> Integration of the peak areas of resonances in the PMR spectrum provides a means of additionally monitoring parameters such as methylol content, amount of methylene bridges formed, and the number of aromatic protons remaining, all of which reflect the degree of resin polymerization in a semiquantitative manner. The following relationships hold:

$$\begin{aligned} \% \text{ methylol} &= \frac{\text{total methylol protons}}{\text{total methylol and methylene bridge protons}} = \frac{\text{Mo}}{\text{Mo} + \text{Mb}} \cdot 100 \\ \text{degree of polymerization} &= \frac{\text{total methylene bridge units}}{\text{total phenol units}} = \frac{\text{Mb}/2}{\frac{\text{Ac} - \text{Mo} \left( \frac{3}{2} \right)}{3}} \\ \text{molar ratio} = \text{F/P} &= \frac{\text{total methylol and methylene bridge units}}{\text{total phenol units}} = \frac{\frac{\text{Mo} + \text{Mb}}{2}}{\frac{\text{Ac} - \text{Mo} \left( \frac{3}{2} \right)}{3}} \\ \text{number of aromatic protons per phenolic unit} &= \frac{\text{total aromatic protons}}{\text{total phenol units}} \\ &= \frac{\text{Ar}}{\frac{\text{Ac} - \text{Mo} \left( \frac{3}{2} \right)}{3}} \end{aligned}$$

The degree of polymerization value provides an indication of increasing molecular size, since it reflects the conversion of methylol groups to meth-

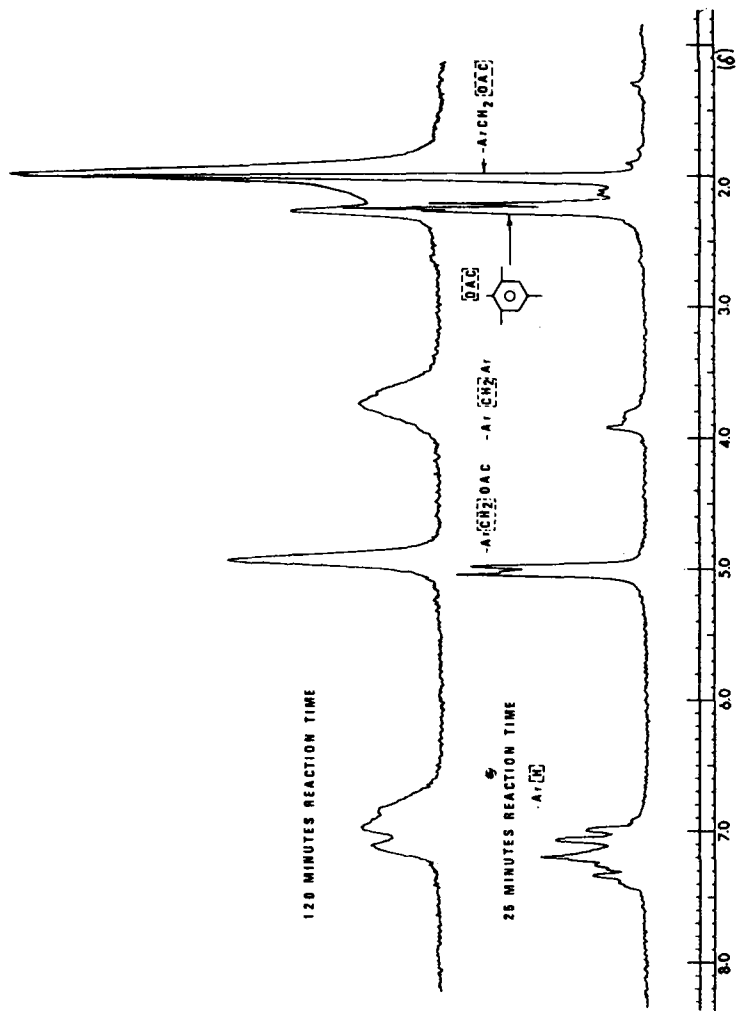


Fig. 1. PMR spectra of NaOH-catalyzed phenol-formaldehyde resin (molar F/P of 2.0) at a low and high degree of condensation.

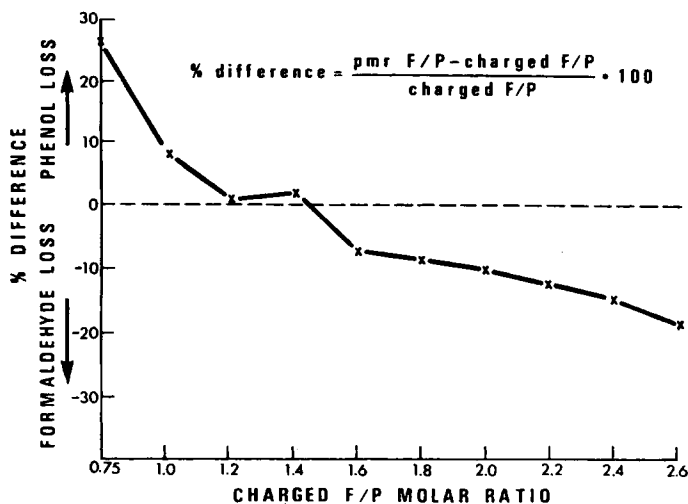


Fig. 2. Comparison of charged molar F/P with calculated molar F/P for phenol-formaldehyde wood adhesives.

ylene bridge linkages relative to the number of phenol units. Because of the peak overlap of the acetoxy resonance from phenoxy and hydroxy-methyl groups in a fully cooked resin, a value for the total phenolic units present is arrived at indirectly by assuming that the methylol groups are fully acetylated and can be subtracted from the total acetoxy resonance. Thus, the methylol integral (Mo) is multiplied by  $\frac{3}{2}$  to account for the difference in protons between a methyl and a methylene unit and the resulting value subtracted from the total acetoxy methyl integral (Ac). This difference represents the amount of phenoxy acetate protons present, and dividing by 3 gives the number of phenol units.

An important consideration in both quality control and general resin characterization of PF systems is the F/P molar ratio. To evaluate the effectiveness of the PMR method in determining molar ratio, a series of different PF resins were prepared, all having a NaOH-to-phenol molar ratio of 0.9, solids content in the range of 41% to 45%, and viscosity in the range of 300 to 500 cps. Figure 2 shows the differences between the charged molar F/P and that calculated from the PMR spectra of the final cooked resin. The percentage difference value was calculated using the following relationship:

$$\% \text{ difference} = \frac{\text{PMR F/P} - \text{charged F/P}}{\text{charged F/P}} \cdot 100$$

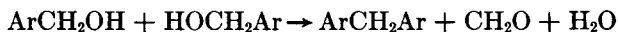
The positive difference between molar ratios of 0.75 and 1.4 arises from the loss of phenol, while the negative differences between 1.6 and 2.6 can be attributed to the loss of formaldehyde. These losses likely occur from volatilization of either free phenol or free formaldehyde during the cooking process or at the freeze-drying stage of sample treatment. Interestingly,

near  $F/P = 1.5$ , the 0% difference line is intersected; and this value corresponds to the theoretically optimum molar ratio for complete cross-linking in PF resins.<sup>9</sup> A two-sample replication of both 1.8 and 2.0 molar ratios showed a  $\pm 3\%$  variation in the difference value. When samples of the same molar ratio, but from different cooks, were compared, the differences in PMR-calculated  $F/P$  could vary up to  $\pm 10\%$ . This variation will depend upon the degree of resin polymerization, since in the early stages of reaction many volatile monomeric species are still present which can be lost during the freeze-drying process.

It would appear that the PMR method provides a reasonable estimate of molar  $F/P$  present in the resin, provided a relatively high level of condensation exists and one applies appropriate corrections, when excess phenol or formaldehyde is present in the formulation. In cases of molar ratios of 2.2–2.6, resonance peaks similar to those reported by Woodbrey<sup>3</sup> for benzyl-type hemiformal (4.9 $\delta$ ) and benzyl ether-type bridges (5.28 $\delta$ ) were observed. The former was included in the integral for Mo species, while the latter was considered an Mb species.

A comparison of methylol content, number of aromatic protons per phenol unit, and degree of polymerization for this series of PF resins is presented in Figure 3. The methylol content steadily increased with increasing  $F/P$  until about a molar ratio of 1.8, when a leveling out occurs. This result, together with the graph showing the number of aromatic protons per phenol unit for these resins, strongly suggests that at this point further reactive sites on the aromatic ring are unavailable for hydroxymethylation. In contrast, the degree of polymerization remains relatively constant throughout the series of resins. A theoretical degree of polymerization curve, calculated on the assumption that the meta positions on the aromatic ring are unreactive, is also shown in the diagram. Comparison of the theoretical and the experimental curves indicates that polymerization is greater than the theoretical value at  $F/P$  of 0.75, while approaching the theoretical curve at 1.0 and somewhat approaching at 1.2. The other molar ratios attain less than 75% of the theoretical polymerization value. The discrepancy in the  $F/P = 0.75$  value likely arises from the loss of unreacted phenol during sample preparation. A parallel study in progress, involving softwood-plywood bonding tests of these resins, has shown that molar ratios less than 1.4 do not provide waterproof bonds of high strength and good wood failure.<sup>10</sup>

Since the theoretical polymerization curve represents the total amount of formaldehyde incorporated into a resin at a specific molar ratio, a summation of PMR-measured methylol units and methylene bridges in the degree of polymerization calculation should give a value approaching that of the theoretical curve. To test this hypothesis, it is best to deal only with molar ratios greater than 1.8, where the condensation mechanism is likely restricted to



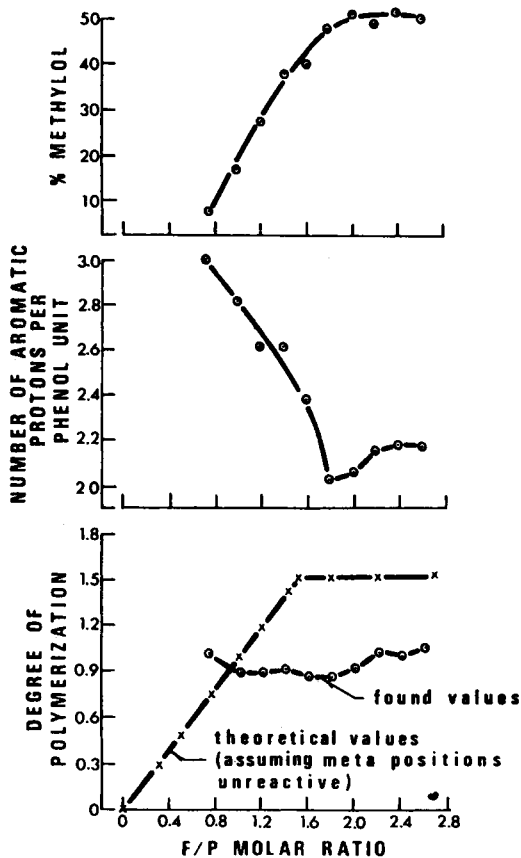


Fig. 3. PMR values for methylol content, number of aromatic protons per phenol unit, and degree of polymerization for phenol-formaldehyde wood adhesives.

At lower molar ratios, other condensations mechanisms come into play which complicate the calculation. Thus, by adding to the numerator in the degree-of-polymerization equation, half the number of methylol units present (because of formaldehyde loss) in F/P of 2.0, 2.2, 2.4, and 2.6, one obtains values of 1.38, 1.46, 1.50, and 1.56, respectively, for the degree of polymerization. The similarity of these values to the theoretical one of 1.5 further supports the use of this PMR approach to characterize PF resins.

A further point of interest in PF synthesis is the influence of catalysts on reactivity. Figure 4 shows a comparison of methylol content, number of aromatic protons remaining, and degree of polymerization for molar F/P = 2.0 resins prepared under identical conditions, except that either NaOH or Ca(OH)<sub>2</sub> was used as catalyst. In both cases, molar ratio of catalyst to phenol was 0.2. The data show that the reactivity of the Ca(OH)<sub>2</sub>-catalyzed resin is slower than its NaOH counterpart, although both catalysts follow the same pattern of change in the PMR spectrum. The Ca(OH)<sub>2</sub>-catalyzed reaction was terminated after 70 min of reaction



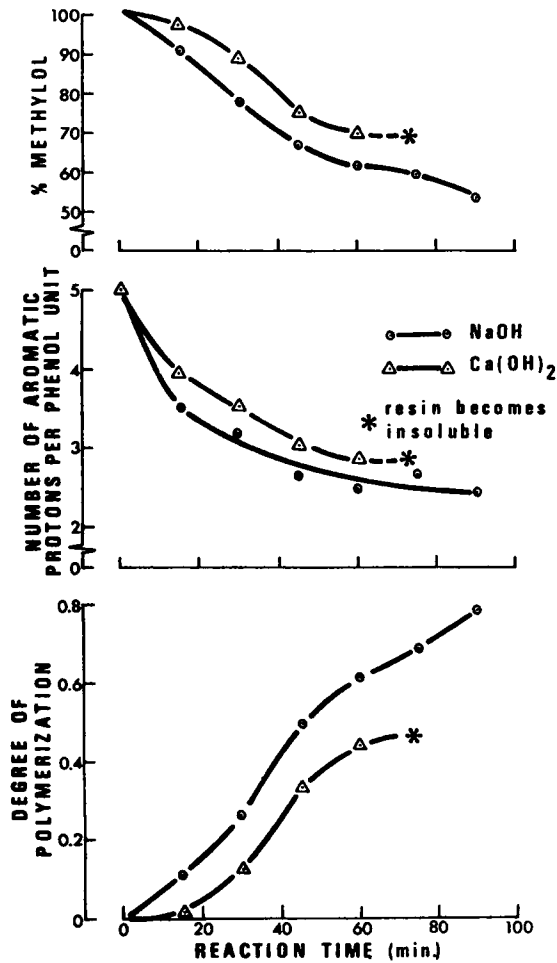


Fig. 4. Comparison of catalytic effects of NaOH and Ca(OH)<sub>2</sub> at molar catalyst/P of 0.2 and molar F/P of 2.0.

time because of insolubilization, while the NaOH system gelled after 140 min of reaction. Comparison of methylol content and the number of aromatic protons remaining to the degree of polymerization indicates that during the first 25 min of reaction, when the initial exotherm is occurring, primarily addition reactions are taking place. During this period, one observes a large decrease in aromatic protons with only a minor change in polymerization degree. Between 25 and 50 min of reaction time, there is a sudden increase in the degree of polymerization coupled with a steady decrease in both methylol content and the number of aromatic protons. This suggests that condensation polymerization reactions are rapidly taking place here. Following this, the degree of polymerization tends to hold relatively constant until 75 min of reaction time, where another increase occurs.

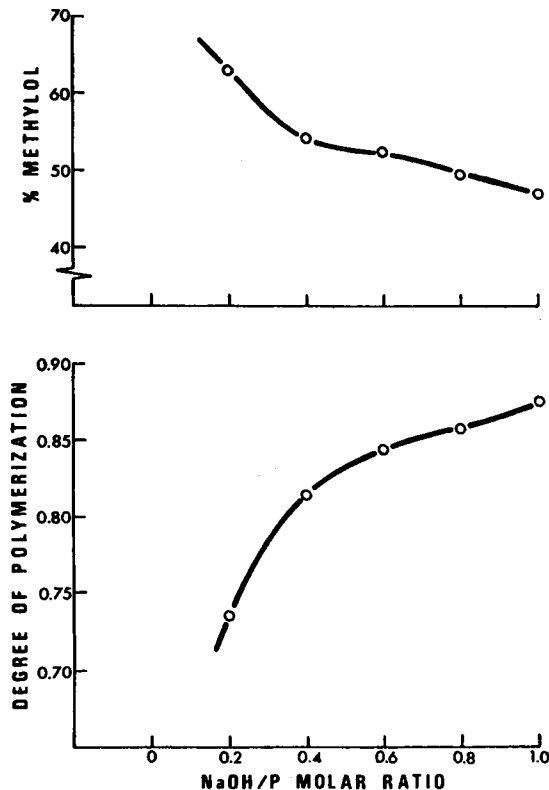


Fig. 5. Effect of NaOH concentration on the extent of polymerization in phenol-formaldehyde resin of molar F/P of 1.8.

Another facet of PF wood adhesive preparation which has aroused some controversy is the ultimate effect of NaOH catalyst on the durability of a glue-wood bond. High NaOH content is needed to provide soluble aqueous resin at the viscosity and molecular weight range required for optimum spreading control and cure time. Such large amounts of catalyst do not increase the reaction rate of the resin.<sup>11</sup> To examine how PMR can be used to quantify the effects of NaOH amount on the chemical structure of a PF resin, an experiment was conducted at F/P = 1.8 involving successive additions of NaOH. After each addition, the mixture was reacted to give a viscosity of 500 cps, and a sample was withdrawn. Each sample thus gave an indication of the resin's reaction state at a specific catalyst level and a constant viscosity. The results shown in Figure 5 demonstrate how the degree of polymerization can be increased by increasing the NaOH content. To have the same degree of polymerization at molar ratio NaOH/P of 0.2 as that at 1.0 would result in the resin already passing to a gel-like state. By increasing the caustic content, one effectively increases the average molecular weight of the resin in solution to provide shorter adhesive cure time in the bonding process.

## SUMMARY

PMR spectroscopy was used to characterize a series of acetylated PF resins. Parameters such as methylol content, F/P molar ratio, degree of resin polymerization, and number of aromatic protons remaining were readily determined from the integrals of appropriate resonance peaks.

Resins cooked to a similar viscosity and having a molar F/P range between 0.75 and 2.6 showed increasing methylol content and decreasing number of aromatic protons with increasing molar ratio until a F/P of 1.8, after which both parameters reach a constant level. Above a molar F/P of 1.4, the degree of resin polymerization was found to be 60–70% of the theoretical value, assuming that meta ring positions are unreactive; while below this molar ratio, the degree of polymerization approaches 90–100% of the theoretical value. This suggests a very limited number of reactive sites available for wood bonding in these low molar ratio resins.

Comparison of NaOH- and Ca(OH)<sub>2</sub>-catalyzed resin systems by PMR indicated that the former was a more effective catalyst and provided better resin solubility at higher degrees of polymerization.

These results show PMR to be useful for quality control work and for monitoring the preparation of new PF resin formulations. Further, the large chemical shift differences between major resonance peaks suggest that only a relatively low-cost instrument (i.e., radio frequency of 30 MHz) of moderate resolution could be used to perform this analysis.

Limitations in this method arise when significant numbers of higher molecular weight species exist in solution. Although condensation reactions between these species may create large changes in average molecular weight and viscosity, PMR proves relatively insensitive since it only detects hydrogen content loss which is minimal in this case.

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