Phenol–Formaldehyde Resin Curing and Bonding in Steam-Injection Pressing. I. Resin Synthesis, Characterization, and Cure Behavior

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SYNOPSIS

Two different phenol–formaldehyde (PF) resole resins are serving as models in a study aimed at establishing the effects of moisture, temperature, pressure, and time on resin cure and bonding during the pressing of wood flakeboard. This phase of the program had two goals: first, to characterize the two resins in terms of their structure and chemistry during synthesis, aging, and cure—using viscosity measurement, gel permeation chromatography (GPC), nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and dynamic mechanical analysis (DMA); second, to make a preliminary evaluation of the utility of DSC, FTIR, and DMA for measuring the degree of resin cure. The two resins differed significantly in relative amounts of hydroxymethyl groups and methylene linkages (NMR), in molecular weight and its distribution (GPC), and in reaction rate (as measured by viscosity, DSC, FTIR, or DMA). The degree of cure developed during constant heating rate DSC scans was calculated for a series of maximum DSC temperatures from both the loss in hydroxymethyl groups (FTIR) and the decrease in available exothermic heat (DSC). Agreement between the two methods was quite good, considering the inherent difficulties in quantifying infrared data. For comparison, the degree of cure developed during constant heating rate DMA scans was calculated for a series of maximum DMA temperatures from both the increase in storage modulus (DMA) and the decrease in exothermic heat (DSC after rewetting). Samples that apparently achieved complete cure in the DMA still exhibited significant residual cure potential in the DSC. We attribute the lower apparent cure in the DMA to loss of moisture from samples during the DMA scan, with consequent loss in plasticization and molecular mobility.

INTRODUCTION

Steam-injection pressing is a recent development for manufacturing reconstituted wood panel products. Compared with conventional panel pressing, steam-injection pressing permits more rapid cure of thicker panels and yields more uniform density cross sections.[1] However, the very different time–temperature–moisture regime during steam injection may cause profound differences in the chemistry and physics of resin cure and resin–wood bonding. Unfortunately, the present understanding of the chemistry and physics of resin cure and bonding is limited, even for conventional pressing of reconstituted wood products. As a result, the industry optimizes adhesives and the bonding process primarily on an empirical basis.

An investigation is underway at the Forest Products Laboratory in cooperation with the University of Wisconsin-Madison to establish how the cure and wood bonding of different phenol–formaldehyde

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Journal of Applied Polymer Science, Vol. 43, 237–250 (1991)

Published by John Wiley & Sons, Inc. CCC 0021-8995/91/020237-14$04.00

Table I Resin Compositions

Ingredient	Formula 1		Formula 2	
	Weight (Percent of Total Weight)	Moles per Mole Phenol	Weight (Percent of Total Weight)	Moles per Mole Phenol
Phenol (100%)	23.21	1.00	32.40	1.00
Formaldehyde (50% aqueous solution)	32.59	2.20	45.50	2.20
Water (additional)	30.20		14.10	
Sodium hydroxide (50% aqueous solution)	14.00	0.709	8.00	0.290

(PF) resins are influenced by the variables in pressing phenol–formaldehyde-bonded flakeboard.[2] The investigation involves several phases: (a) synthesis and characterization of selected resins, (b) development and employment of techniques to measure resin cure under a range of temperatures and humidities, (c) development and employment of techniques to measure degree of bonding over the same range of conditions, (d) comparison of these data with actual flakeboard properties, and (e) correlation of the data and derivation of guidelines for optimum resin composition and properties.

We chose two PF resins (formulas 1 and 2, Table I) for our initial investigations, primarily on the basis of the significant differences between their compositions and molecular weight distributions. Formula 2 is a conventional alkaline resole PF flakeboard adhesive, whereas formula 1 is a more alkaline resole of higher molecular weight.

To rationalize the different responses of these two formulas to pressing variables, it was important to characterize their initial differences in composition, structure, and cure behavior, and to minimize changes during storage prior to use. This paper therefore deals with phase (a) and reports the results of resin characterizations during synthesis, aging, and cure, using techniques such as viscosity measurement, gel permeation chromatography (GPC), ^{13}C nuclear magnetic resonance (NMR), differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FTIR), and dynamic mechanical analysis (DMA).

This paper also describes some initial efforts under phase (b), in which we conducted a preliminary evaluation of several techniques (DSC, FTIR, DMA) for their utility in measuring the relative degree of cure achieved by the PF resins as pressing variables changed.

EXPERIMENTAL

Resin Synthesis and Characterization

Table I gives the compositions of the two PF resin formulas. Several batches were synthesized for each formula, as the volume needed for analyses exceeded the volume of one batch. The batches will be referred to by formula number and batch designation; for example, in resin 1-A, the number denotes formula 1 and the letter denotes the particular batch.

The phenol and sodium hydroxide were reagent grade. The nominal 50% formaldehyde solution was prepared by refluxing Aldrich* paraformaldehyde in distilled water for 2.5 days and subsequently storing it at 65–80°C; its actual concentration was determined by the sodium sulfite method.[3]

Resins were synthesized in standard 2- or 3-L resin kettles equipped with thermometer, stirrer, and cooling coil. Two infrared lamps provided heat, and both the lamps and the cooling coil were controlled by a Thermowatch regulator whose capacitance sensor was mounted on the thermometer; temperature variation was less than ±1°C. Table II summarizes the synthesis procedures followed in two of the batches whose detailed characterizations are being reported in this paper.

We define "initial" resins as those existing after synthesis and standing for 40 h at ambient temperature. Several standard properties were determined for all batches of initial resins. Viscosity was measured at 25°C with either a conventional Brookfield 2.5XLVT viscometer or a Wells–Brookfield LVTDCP cone and plate viscometer (shear rate ap-

* The use of trade or firm names in this publication is for reader information and does not imply endorsement by the U.S. Department of Agriculture of any product or service.

Table II Resin Synthesis Procedures

Resin Type[a] and Elapsed Time (min)	Stage	Temperature (°C)	Resin Viscosity[b]
	Resin 2-B		
0	Place phenol in HCHO solution	40	
0	Extract analysis sample *a*[c]		
0–60	Add base slowly in 4 aliquots	40–70	
60	Extract analysis sample *b*	70	
64–70	Heat	70–80	
150	Extract analysis sample *c*	80	B(60)
225	Extract analysis sample *d*	80	I(225)
225–230	Cool	80–75	
257	Extract analysis sample *e*	75	P(400)
	Cool	75–45	
285		45	Q(435)
	Cool	45–22	
40 h	"Ripen"; extract analysis sample i	22	
	Store	−20	
	Resin 1-A		
0	Place phenol in HCHO solution	30	
0–60	Add base slowly in 4 aliquots	30–68	
70	Extract analysis sample b	68	
70–130	Heat	68–95	A(50)
175	Extract analysis sample c	95	B(60)
	Cool	95–85	
235	Extract analysis sample d	85	D(100)
335	Extract analysis sample e	85	L(290)
365	Extract analysis sample f	85	T(550)
	Cool	85–22	
40 h	"Ripen"; extract analysis sample i	22	
	Store	−20	

[a] Number refers to formula; letter identifies batch.
[b] Letters refer to Gardner tube measurements at 25°C. Parenthetic values are those quoted in centipoise in the Gardner literature.
[c] For each stage when samples were extracted for analysis, 3-mL samples were frozen until use.

proximately 25 s^{-1}). Resin solids were determined by heating a 1-g sample at 125°C for 1.75 h.[4] Resins were analyzed for percentage of total alkalinity and free formaldehyde by titration with HCl and a hydroxylamine hydrochloride procedure,[3] respectively, using methanol to enhance solubility.

To obtain molecular weight distributions by GPC, we followed a procedure suggested by Georgia Pacific.[5] A 1% solution of sample in dimethylformamide containing 2% acetic acid was eluted from the columns with the same solvent at a flow rate of 1.00 mL/min. The columns were 10^4 and 500 Å Styragel in series, and the detector used ultraviolet (UV) light at 280 nm. All solutions were spiked with toluene as an internal standard (21.5 min), and retention times were corrected for any shifts in the toluene retention time.

For several reasons, calibration of a GPC system to permit accurate calculations of molecular weights is not straightforward.[6] With PF resins, the situation is further complicated by a lack of characterized PF fractions of varying molecular weights, by the multiplicity of PF species with similar hydrodynamic volumes, and by the uncertainty about possible changes in UV absorptivity with molecular species. Therefore, we have not reported any calculated molecular weights.

The ^{13}C-NMR spectra were obtained with a

Bruker WM250 spectrometer (62.89 MHz) using deuterated methanol as solvent (approximately 2 volumes methanol per volume of aqueous resin solution) at 37°C. Instrument parameters for quantitative spectra were 30 kHz sweep width, 7.8-μs (45°) pulse width, 10-s pulse delay, inverse gating, and approximately 500 scans. All absorbances are expressed as moles per mole of carbons at C-1 of the phenol ring 1-position (C-1). To enhance quantitation, that is, to ensure complete relaxation of the C-1 absorption between pulses, 20 g/mL of diethylenetriaminepentaacetic acid, iron (III) disodium salt dihydrate were added to the methanol solutions of resin 2.[7] The 10-s pulse delay was then sufficient for quantitation with monomer or resin solutions above pH 10 but not with monomer at or near neutral pH.

Resin Aging Procedures

One batch of formula 1 and two batches of formula 2 were aged at different conditions until their viscosities exceeded 550 mPa s for formula 1 and 650 mPa s for formula 2. These limiting viscosity values were based on industry practice.[8] Aging conditions were chosen to approximate possible storage and use scenarios. In all cases, the container head space was purged with nitrogen to minimize oxidation.

Samples containing approximately 150 g of resin were sealed in plastic bottles. In the first series, the bottles were taken from storage at selected intervals, allowed to warm to ambient temperature, and mixed by shaking. After aliquots were removed from the bottles, the bottles were purged, resealed, and returned to storage. The bottles were aged at 5 and 24°C. In the second series, separate bottles of resin 2-B were aged in sufficient numbers so that each bottle was sampled only once; aging conditions were −20, 5°C, and Cycle FT (−20°C, except three times per week when the bottles were exposed to 30°C for 1 h and to 24°C for 2 h).

Resin Cure

Dynamic mechanical analysis (DMA) was performed with a DuPont DMA 983 instrument, scanning from ambient temperature at a rate of 5°C/min. Samples were tested at 1 Hz using an amplitude setting of 0.1 mm for an interclamp distance of about 9 mm. Specimens were prepared by soaking a strip (0.2 × 12 × 150 mm) of Whatman GF/C glass microfiber filter cloth in resin solution for 25 min, laying the resin-loaded cloth on a glass plate, and removing excess resin with a rubber roller. Some resins required two such treatments to achieve the desired loading (3–3.5-g dry resin per meter length of glass cloth strip). After impregnation, the samples were dried overnight over phosphorous pentoxide at room temperature. Next, the samples were removed from the desiccator and heated for 2 min in an air oven at 105°C to establish a low level of cure and rigidity. They were then equilibrated overnight at 91% relative humidity over saturated aqueous $BaCl_2$ solution. After these exposures, the samples were mounted in the DMA instrument and scanned to different temperatures selected to yield various states of cure; for example, the temperature of incipient modulus increase, the temperature at approximately half the final modulus value, and the temperature at the final modulus value. The complete sequence of steps can be summarized as

resin impregnation of substrate →

16 h over P_2O_5 → 2 min 105°C →

16 h at 91% RH → DMA scan

Further details of the DMA method are reported elsewhere.[2]

The DSC scans were carried out with a Perkin Elmer DSC-2, using sealed stainless steel large-volume capsules. Indium was used as both a temperature and heat flow reference. In tests on the effects of storage on reactivity, samples of about 10-mg resin solution were sealed in the capsule. To obtain peak temperatures, capsules were heated at 10°C/min. To obtain reaction heats, capsules were heated at the same rate to 140°C and held at that temperature for 30 min. This temperature was chosen as representative of internal mat temperatures during steam-injection pressing of flakeboards.

To correlate mechanical property development with degree of resin chemical cure, DSC scans were performed at 10°C/min on 5-mm-diameter pieces cut from specimens that had been already scanned in the DMA to various temperatures. Dry sample weights were 7–11 mg. A drop of distilled water (15–18 mg) was added to bring the water content to approximately that of uncured liquid resin, and the capsule was quickly sealed. The capsule was stored overnight for the moisture to diffuse through the sample. Each sample was then scanned to 200°C, held there for 10–20 min to achieve complete cure, cooled to below ambient temperature, and rescanned

to establish a baseline. The exotherm areas from these scans yielded the residual heat of cure in the samples previously scanned in the DMA; heats were expressed per unit resin weight by correcting for the glass filter cloth weight as determined by ashing. For this procedure, we assumed that each DMA sample experienced essentially the same conditions at the same temperatures, and that the resin content of impregnated cloth was reasonably uniform along the DMA sample.

Infrared spectra were obtained on a Nicolet Model 6000 Fourier transform infrared spectrometer. To correlate resin chemical cure as measured by DSC and by Fourier transform infrared spectroscopy (FTIR), resin samples that had been heated to chosen temperatures in the DSC were extracted from the DSC capsules. These samples were then dried under vacuum at ambient temperature, ground to a powder, redried, and incorporated into potassium bromide pellets. Similar correlations between DMA and FTIR could not be examined because the DMA glass cloth substrate strongly interfered with the resin FTIR spectra.

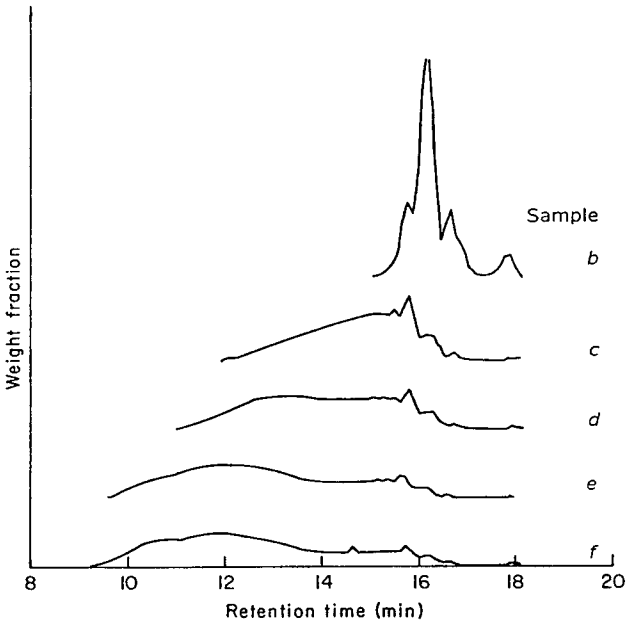

Figure 1 GPC of resin 1-A during synthesis (see Table II for identification of curves and synthesis procedures) (ML89 5861).

RESULTS AND DISCUSSION

Resin Initial Characterization

In addition to the standard tests for characterizing resins, gel permeation chromatography and nuclear magnetic resonance were used for initial resin characterization.

Standard Properties

Table III gives some "initial" (40 h after synthesis) standard properties for the test batches. Note that formula 1 had lower solids and free formaldehyde content than formula 2 and higher pH and alkalinity content.

Gel Permeation Chromatography

Figures 1 and 2 illustrate the changes in GPC chromatograms during synthesis of resins 1-A and 2-B, respectively; the different synthesis stages (a, b, c, . . . , i) are defined in Table II. The increase in molecular weight (lower retention times) and complexity of the distribution in the course of synthesis are evident, particularly during the early stages. Moreover, resin 2-B is clearly much lower in molecular weight and narrower in distribution than resin 1-A. The greater advancement of formula 1 is

Table III Initial Resin Properties

Resin Type	Viscosity (mPa s)	Solids (wt %)[a]	Free Formaldehyde (wt %)[a]	pH	Total Alkalinity (NaOH, wt %)[a]
1-A	430	41.1	0.1	12.4	6.29
1-B	601	42.2	0.2[a]		6.55[b]
2-A	420	51.1	1.0	10.4	3.83
2-B	513	51.0	0.6	11.0	3.88
2-C	396	42.3	1.1	10.4	3.20

[a] Percentage of total resin (solids plus water).
[b] Measured after 1 year at −20°C.

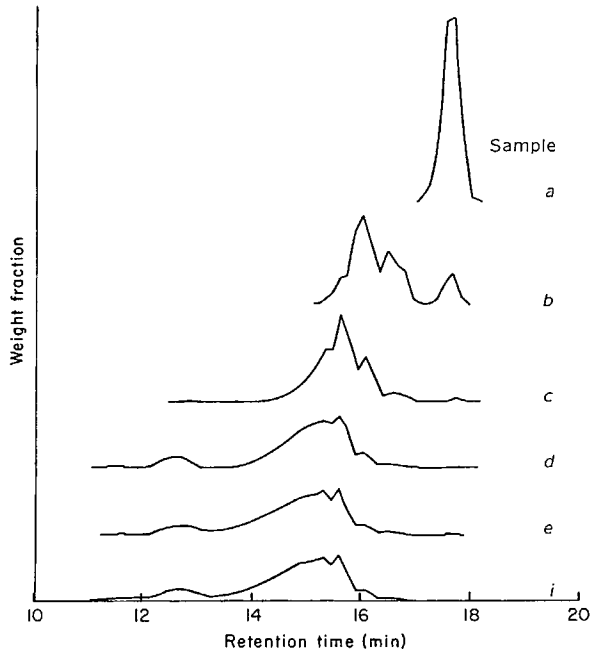

Figure 2 GPC of resin 2-B during synthesis (see Table II for identification of curves and synthesis procedures) (ML89 5862).

consistent with its much lower free-formaldehyde content and higher pH.

Several peaks in the chromatograms of the resins can be assigned by comparing their retention times with those observed for low molecular weight model compounds:

Compound	Retention Time (min)
Phenol	17.7
4-Hydroxymethylphenol	16.5
4,4′-Dihydroxydiphenylmethane	16.5
2,4,6-Trimethylphenol	18.7

The single peak in sample a from resin 2-B (Fig. 2) is phenol, as would be expected from the absence of base at that point in the synthesis (see Table II). A sample a was not taken for resin 1-A, but some unreacted phenol apparently remains in sample b of both resin 1-A and resin 2-B (compare Figs. 1 and 2), and a small amount is still evident in sample c from resin 2-B. As the retention time indicates, the peak at about 16.5 min in the resin chromatograms might be either 4-hydroxymethylphenol or the "dimer" 4,4′-dihydroxydiphenylmethane. This lack of separation between different PF species is typical of PF behavior in conventional GPC.[6,9] This behavior results from the multiplicity of PF species having similar hydrodynamic volumes as well as the possible complications caused by association. More elaborate separation procedures have produced better species resolution, for example, high performance liquid chromatography[10,11] or gas–liquid chromatography and gas chromatography–mass spectrometry on silylated derivatives,[12,13] but we did not employ these methods.

Nuclear Magnetic Resonance

Figure 3 illustrates ^{13}C-NMR spectra for stages during the synthesis of resin 2-B. Structural assignments were derived from the literature (for example, Refs. 14–17) and from model compound spectra. The signals of primary interest (in units of parts per million) and their corresponding assignments are as follows: 35 and 40 ppm for 2,4′- and 4,4′-methylene links, respectively; 61–62 and 65 ppm for 2- and 4-hydroxymethyls, respectively; 83–94 ppm for various forms of formaldehyde; 116–118 and 118–121 ppm for unsubstituted 2- and 4-phenolic ring positions, respectively; 124–134 ppm for unsubstituted

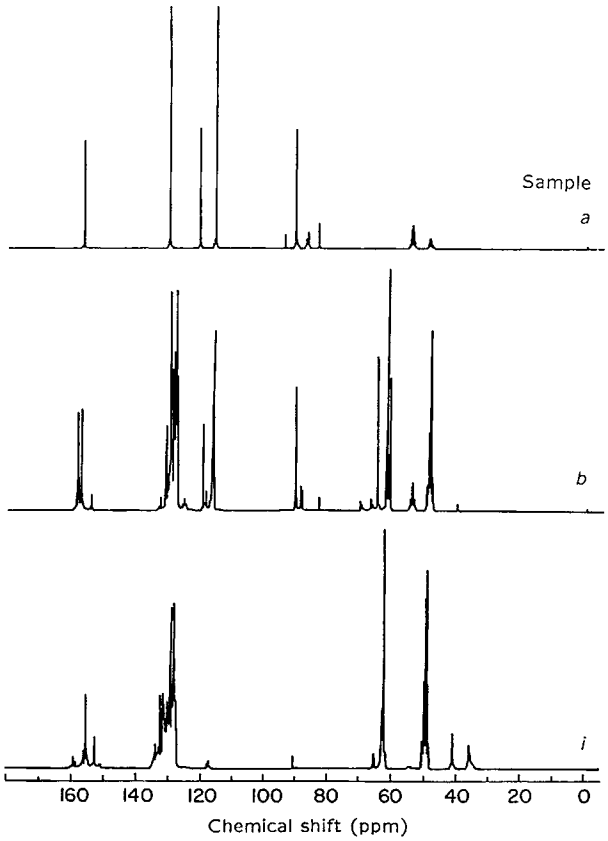

Figure 3 ^{13}C-NMR spectra for resin 2-B (see Table II for identity of samples). Tetramethyl silane was used as the standard for chemical shifts (ML89 5863).

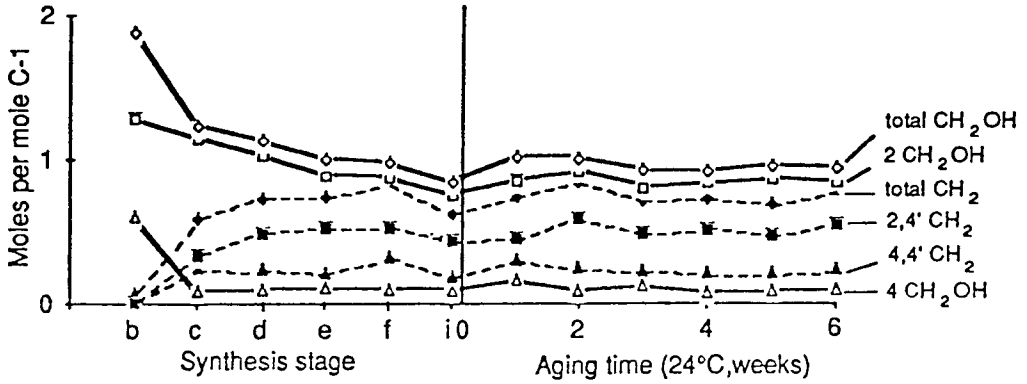

Figure 4 Approximate composition of resin 1-A by NMR during synthesis and aging (solid points, methylene; open points, hydroxymethyl; synthesis stages identified in Table II).

3,5- and substituted 2,4-phenolic ring positions; and 150–165 ppm for C-1 phenolic OH positions.

For spectral quantitation, all peak areas in a given spectrum were divided by the total C-1 area, yielding apparent moles of each species per mole of total phenol present. For 18 synthesis and aging samples from resin 1-A, none of which contained the iron salt relaxation agent, the sum of all apparent non-C-1 ring positions per C-1 gave a mean and standard deviation of 5.2 ± 0.2, in satisfactory agreement with the theoretical 5.0. However, the measured total CH_2 content per phenol varied from 1.7 to 2.1, in contrast to the value of 2.2 from the formulated formaldehyde to phenol ratio. Consequently, the quantitation for resin 1-A must be considered only approximate when comparing aliphatic to aromatic moieties; however, comparisons within the aliphatic or aromatic groups should be more correct. The resin 2-B spectra were all obtained in the presence of the iron salt relaxation agent and yielded good quantitation—with the exception of sample a, which contained no base and possessed low viscosity. For 25 resin 2-B samples (excluding a), for example, the mean number of non-C-1 ring positions per C-1 was 5.0 ± 0.1, and the mean total CH_2 content per C-1 was 2.2 ± 0.1.

Figures 4 and 5 present some quantitative results for resins 1-A and 2-B, respectively, during synthesis and one aging regime. Except for the absence of a sample a for resin 1-A, the patterns are quite similar. The following points are noted:

1. Before base was added (see sample a), no detectable reaction occurred between formaldehyde and phenol.
2. Hydroxymethyl group contents built up rapidly during synthesis and then fell because of subsequent formation of methylene linkages. After normalizing for the twofold greater number of C-2's per ring, it is clear that the 4-position of phenol was attacked more rap-

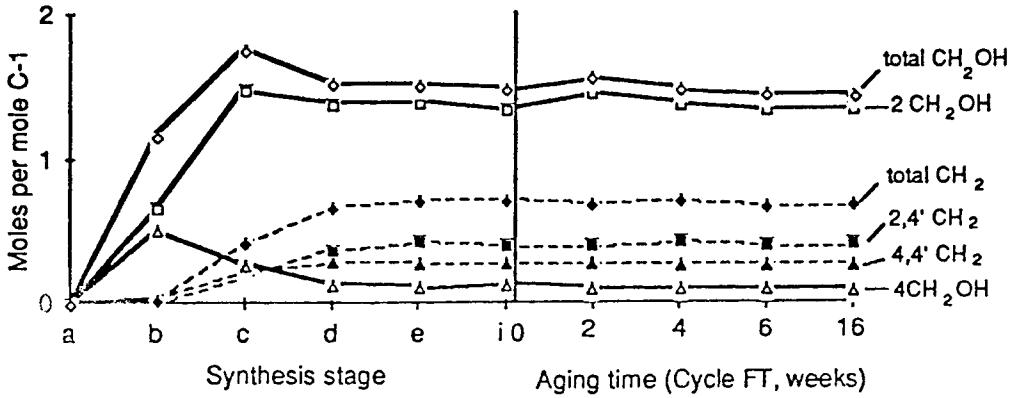

Figure 5 Composition of resin 2-B by NMR during synthesis and aging (solid points, methylene; open points, hydroxymethyl; synthesis stages identified in Table II).

idly than was the 2-position (see Fig. 5), and the resultant 4-hydroxymethyl subsequently reacted more rapidly than the 2-hydroxymethyl. In fact, the 2-hydroxymethyl maintained a high concentration throughout the later reaction steps and aging whereas the 4-hydroxymethyl decreased, especially after sample b.

3. Increasing methylene content paralleled the loss in hydroxymethyls. In both resins, the 2,4′-links were more prevalent than the 4,4′-links because of the twofold greater number of C-2's. In contrast, the 2,2′-links were not formed to a significant extent.
4. By stage d or e, all the C-4's on the rings had reacted in both resins. Simultaneously, a majority, but not all, of the C-2's had reacted.
5. No significant changes in hydroxymethyl, methylene, or unsubstituted ring sites could be detected during the aging regimes studied.
6. Whether or not methylene ether links between phenolic rings developed during the synthesis was not clear because of other possible structures that could have signals in the relevant region (about 70 ppm). As Figure 3 demonstrates, however, absorptions in that region were at best weak and transient.
7. Overall, the structural changes during synthesis, as derived from the NMR, were qualitatively consistent with those reported elsewhere; quantitative differences undoubtedly arose from the use of different synthesis conditions and compositions. For example, other authors also found no 2,2′-methylene links and faster reaction by the 4-position than by the 2-position in alkaline PF systems.[17-19] Similarly, Werstler showed the same preponderance of 2-hydroxymethyls during most of the reaction, indicating the greater reactivity of the 4-hydroxymethyls.[17]
8. Both formulas 1 and 2 had the same starting formaldehyde to phenol ratio. Therefore, the greater residual hydroxymethyl content of formula 2 is consistent with its lower methylene content, that is, with a lower degree of advancement. These NMR findings, in turn, agree qualitatively with the GPC results.

Resin Aging Behavior

Resin aging was followed by viscosity, NMR, and DSC.

Viscosity

When single containers of resin were aged and periodically sampled, the viscosity limit of 550 mPa s for resin 1-A was exceeded in only 2 weeks at 24°C, but 16 weeks were required at 5°C. The viscosity of resin 2-A increased approximately twice as fast.

Resin 2-B was then aged in separate containers at 5°C, at −20°C, and under Cycle FT (−20°C except for three periods per week of 1 h at 30°C plus 2 h at 24°C). At −20°C, no viscosity increase was observed after 16 weeks, whereas the material aged at 5°C and the freeze–thaw cycled material exceeded the 650 mPa s limit in 6–9 weeks.

Nuclear Magnetic Resonance

Figures 4 and 5 demonstrate virtually no changes in the NMR spectra during aging of resin 1-A for 6 weeks at 24°C or for resin 2-B for 16 weeks of Cycle FT. This constancy contrasts with Werstler's finding of major changes in hydroxymethyl and methylene contents after 60 days at 33°C.[17] Presumably, the faster aging in Werstler's work was the consequence of several factors: (a) the higher formaldehyde to phenol ratio (3.0 compared to 2.2 in our study), (b) the resultant higher concentration of residual, reactive formaldehyde in the unaged resin, and (c) the somewhat higher aging temperature.

Differential Scanning Calorimetry

No significant trends in exotherm peak temperature (Fig. 6) or heat of cure occurred during aging of either resin. For 19 measurements on resin 1-A, the mean and standard deviation for peak temperature

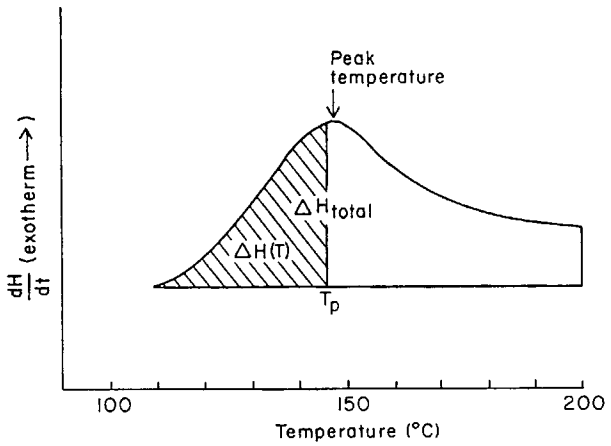

Figure 6 DSC scan for liquid resin 1-B (10°C/min) (ML89 5864).

and heat were 152.8 ± 1.2°C and 0.22 ± 0.03 J/mg (solids basis), respectively. For six measurements on resin 2-A, the comparable values were 139.8 ± 0.7°C and 0.43 ± 0.02 J/mg.

Overall, we observed no changes during aging in those attributes that depend primarily on numbers of molecular species, such as reactivity (DSC) and molecular structure (NMR). Simultaneously, however, large changes occurred in viscosity, which is dependent on large molecular species. The latter is clearly important for proper application of resin to substrate and for control of subsequent wetting, penetration, and bonding. In all subsequent testing, therefore, we stored resins in small containers at −20°C and restricted the number of times that a given container was thawed and sampled.

Resin Cure Behavior

Compared to formula 1, the higher cure reactivity of formula 2 is demonstrated by faster aging, lower DSC peak temperature, and higher heat of cure. This difference between the resins agrees with previous work that showed that higher sodium hydroxide to phenol ratios during earlier polymerization stages [as in our formula 1 (Table I)] yield resins with lower free formaldehyde, ring substitution, and reactivity.[20] In this section, we examine the cure behavior of these two formulas in greater detail. Our objectives in this phase of the study were to (a) make a preliminary judgment about which techniques (FTIR, DSC, or DMA) would be most useful to our overall program for characterizing the cure behavior and extent of cure and (b) relate differences in cure behavior to resin structure and composition.

Differential Scanning Calorimetry

Differential scanning calorimetry has often been used to establish a degree-of-cure scale by defining the degree of cure, $\alpha(T)$, as

$$\alpha_{dsc}(T) = \Delta H(T)/\Delta H_{total} \quad (1)$$

where ΔH_{total} is the total heat (total DSC area) evolved for complete cure, measured here by scanning up to 200°C (the limit for the capsules), holding for 30 min to complete cure, cooling, and rescanning to establish the cured resin baseline. The quantity $\Delta H(T)$ is the heat (area) evolved up to temperature T (Fig. 6).[21] Ideally, the heat evolution curve for the cure process should return to the baseline after complete cure is achieved. In the case of PF resoles, this does not take place, apparently because of the beginning of decomposition processes. Consequently, we define ΔH_{total} as the area enclosed by the baseline, the heat flow curve up to 200°C, and the vertical line at that final condition.

Figure 7 compares the fractional cure as a function of DSC scan temperature for one batch each of the two PF formulas. By definition, the two curves reach full cure at the same point, but, as expected, formula 2 achieved greater cure at lower temperatures.

Fourier Transform Infrared Spectroscopy

Changes in infrared spectra during cure were studied by examining samples heated in the DSC to different temperatures. Figure 8 shows spectra for resins 1-B and 2-C in the uncured state (25°C, no DSC scan) and after being scanned to the maximum DSC scan temperature (200°C). Based on previous work,[22–25] the bands of primary interest are (a) 1600 cm^{-1}, composite aromatic ring, (b) 1275 cm^{-1}, sodium salt of the phenolic hydroxyl, (c) 1205 cm^{-1}, phenolic hydroxyl, and (d) 1005 cm^{-1}, hydroxymethyl.

Several problems arose in attempting to quantify the spectra to define changes during cure. These problems included difficulties in obtaining quantitative values for either peak height or area because of uncertainties in baselines and poor resolution of bands. Because of these uncertainties, spectral subtraction techniques were unsuccessful. Attempts to improve resolution by spectral deconvolution[26,27] yielded results whose quantitative reliability was suspect. Therefore, we chose to employ peak heights rather than areas and selected the baselines as indicated in Figure 8. In some cases, these peak heights are clearly quantitatively suspect; for example, the 1275-cm^{-1} shoulder on the 1205-cm^{-1} peak in the uncured resin 2-C.

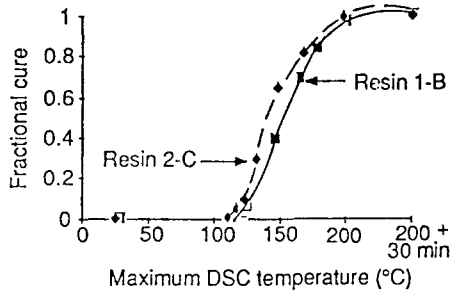

Figure 7 Degree of cure measured by DSC as a function of DSC scan temperature.

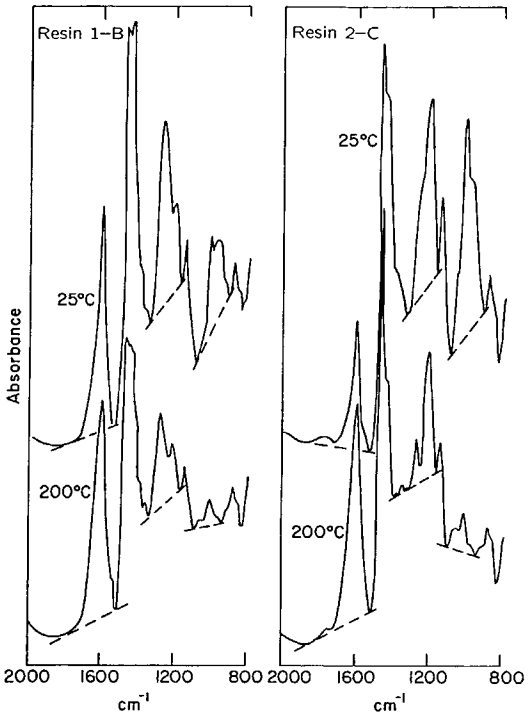

Figure 8 FTIR spectra before (25°C) and after DSC scan to 200°C for Resins 1-B and 2-C (absorbance is measured in arbitrary units) (ML89 5865).

Because the spectra were obtained on different specimens of each resin, it is also necessary to normalize the observed peak heights by the height of a band that is not changed by cure. If we assume with Yamao and co-workers[25] that the 1600-cm^{-1} band is constant during cure and if we use its intensity to normalize the other bands, we arrive at the peak height ratios shown in Figures 9 and 10 as filled data points. Although the resultant decrease of hydroxymethyl was expected, the decrease of phenolic ONa and OH was not. This led to the suspicion that the 1600-cm^{-1} band might be increasing because of overlap from oxidation-produced carbonyl absorptions in the 1650- to 1700-cm^{-1} region or to ring structural changes. (We note, however, that Yamao and co-workers[25] reported that after 1 h at 160°C, the 1610-cm^{-1} band was essentially unchanged while the 1650/1610 ratio increased from zero to about 0.3.)

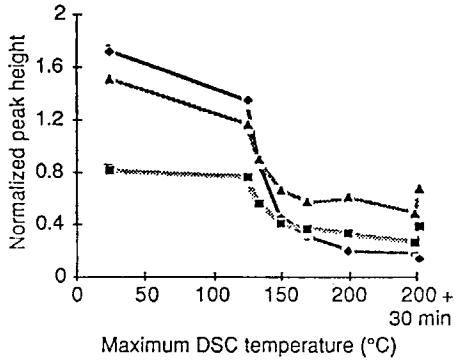

Figure 9 FTIR changes during cure of resin 2-C (samples from DSC scans; squares, 1275 cm^{-1}; triangles, 1205 cm^{-1}; diamonds, 1005 cm^{-1}; all samples unneutralized; points all normalized to 1600 cm^{-1} band).

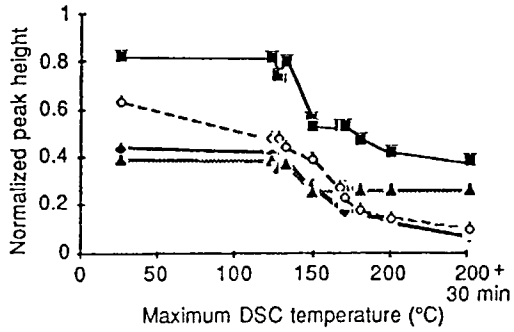

Figure 10 FTIR changes during cure of resin 1-B (samples from DSC scans; squares, 1275 cm^{-1}; triangles, 1205 cm^{-1}; diamonds, 1005 cm^{-1}; open diamonds for 1005/1205 cm^{-1} in neutralized samples; filled points all for unneutralized samples normalized to 1600 cm^{-1} band).

Consequently, we attempted an alternative approach to normalization.[24] We used the phenolic hydroxyl band (1205 cm^{-1}) after neutralizing the base, that is, after converting the sodium phenate to phenol. The resultant normalized hydroxymethyl band (1005 cm^{-1}) of resin 1-B is shown in Figure 10 by the open diamonds and closely parallels the hydroxymethyl intensities normalized by the 1600-cm^{-1} band. Because of that agreement and because normalization by the 1600-cm^{-1} band is simpler and more direct, the following comments are based on normalizing by the 1600-cm^{-1} band.

1. Because of the uncertainties that we have described, we must regard the FTIR data as semiquantitative.
2. The greater alkali content in formula 1 is evident from the higher ratio of 1275- to 1205-cm^{-1} peaks (Fig. 8). If the normalized intensities of those peaks do indeed fall with cure, as indicated in Figures 9 and 10, the reason is unknown.
3. The small peak at about 1050 cm^{-1} (Fig. 8) indicates the presence of small amounts of methylene ether bridges between the phenolic rings, although the less sensitive NMR did not reveal their presence. Because of the

overlap of this peak with the hydroxymethyl peak at 1005 cm^{-1}, we did not attempt to follow changes in the 1050-cm^{-1} peak during cure.

4. The much higher hydroxymethyl content observed in the FTIR spectrum (1005 cm^{-1}) for uncured formula 2, compared with uncured formula 1, agrees with the NMR results.
5. The strong loss of hydroxymethyl during cure is obvious from the behavior of the 1005-cm^{-1} peak, which has been used in the past as a measure of extent of cure.[24] For example, we can define the fractional cure by FTIR as

$$\alpha_{ir}(T) = \frac{r(T) - r(200°C \text{ for } 30 \text{ min})}{r(25°C) - r(200°C \text{ for } 30 \text{ min})} \quad (2)$$

where $r(T)$ is the 1005-cm^{-1} peak height normalized by the 1600-cm^{-1} peak for specimens from the DSC scans to temperature T. The zero and complete cure states are identical to those used in establishing the DSC cure scale (Fig. 7). Despite the FTIR approximations, the resultant degree of cure curves by FTIR (Fig. 11) are very similar to those from DSC (Fig. 7) and confirm the greater reactivity of formula 2.

Dynamic Mechanical Analysis

Figure 12 shows the changes in dynamic storage modulus of resins 1-B and 2-C during temperature scans up to 160°C, after a pretreatment consisting of 2 min at 105°C plus overnight equilibration at 91% relative humidity and room temperature. When the sample is heated in the DMA, the modulus initially increases, presumably because the sample

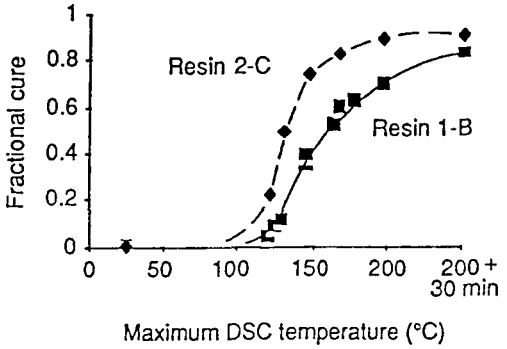

Figure 11 Degree of cure measured by FTIR as a function of maximum DSC scan temperature.

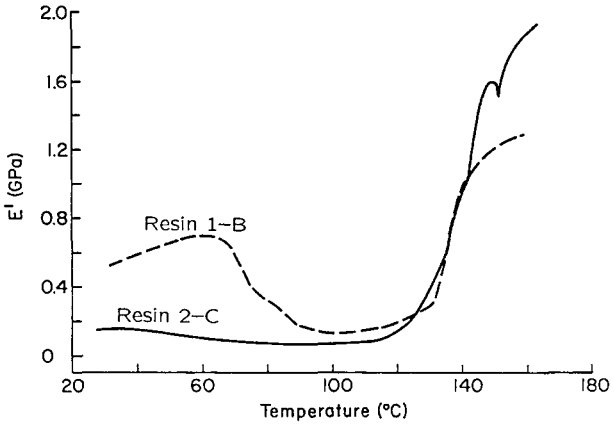

Figure 12 Dynamic storage modulus during scan at 5°C/min and 1 Hz for resins 1-B and 2-C impregnated in glass filter cloth, after exposure to 105°C for 2 min and subsequent equilibration overnight at 91% RH (ML89 5866).

hardens as some water is lost. The modulus then decreases as the effect of thermal softening becomes more important than water loss. Beyond 120°C, the modulus rises, and it reaches a plateau above 160°C.

The behavior depicted in Figure 12 raises three questions about the effects of resole resin structure and chemistry on mechanical response. First, does the increasing modulus above 120°C solely reflect crosslinking or does loss of moisture contribute to the greater stiffness? Second, why is there such a large difference in starting moduli? Third, why does resin 2-C achieve a higher plateau modulus than does resin 1-B?

To attempt to answer these questions, we conducted two additional series of experiments. The first involved measuring moisture content of resin samples at two times: (1) after a 1-min precure at 105°C plus equilibration at 91% relative humidity (RH) and (2) after attaining various temperatures in DMA temperature scans. The results (Table IV) show that although resin 1-B contained much more water than did resin 2-C at the beginning of the DMA scan (70% compared to 29%), both resins had lost a large portion of that water by the time the samples reached 70°C and were virtually dry by 110°C. Thus, the answer to the first question is that moisture loss does not contribute directly to the high temperature buildup in modulus because the moisture is lost at lower temperatures.

However, the much greater starting moisture content of resin 1-B makes its higher initial modulus even more perplexing (question 2). That this resin should contain more moisture is consistent with its higher alkali content (Table I), but Bolton reports

Table IV Resin Moisture Contents after Exposure to Different Temperatures

Treatment	Resin Moisture Content[a] (%)	
	Resin 1-B	Resin 2-C
Precure 1 min at 105°C + equilibrate at 91% RH	70	29
DMA scan at 5°C/min to		
70°C	9	12
110°C	2	1
140°C	0	0

[a] Percentage calculated on a dry weight basis.

that resoles containing more alkali (and thus more moisture) are more highly plasticized and exhibit greater creep.[28] At this time, we can only offer two speculations to explain the initial modulus difference for resins 1-B and 2-C. First, all the water absorbed by the alkali may not be available for polymer plasticization, and the higher molecular weight of resin 1-B (Fig. 1) provides greater elasticity. Second, the higher alkali and water contents of resin 1-B lead to higher ionization of its phenolic hydroxyls, and the greater resultant charge density leads to more extended, stiffer polymer chains. (Note in this connection that FTIR showed greater conversion of phenolic hydroxyls to phenate in resin 1-B.)

A second series of experiments was directed towards answering the third question, regarding the attainment of a greater high temperature plateau modulus for resin 2-C. Several samples of resins 1-B and 2-C were heated in the DMA to various temperatures, after being heated at 105°C for 2 min and equilibrated overnight at 91% RH. The degree of cure achieved in each case was determined by subsequently measuring the residual cure heat liberated by scanning in the DSC to 200°C and holding for 30 min. Prior to the DSC scans, the approximate original water content was added to the samples in the DSC capsules, the capsules sealed, and the samples equilibrated at room temperature overnight to approximate the moisture content present in our previous DSC samples that started with liquid resins. Substantial amounts of residual heat were found, and these were converted to the degrees of cure achieved in the original DMA scans, using eq. (1). Figure 13 shows the calculated degrees of cure from the DSC plotted against the maximum previous temperature experienced by each sample. The plot includes data points for zero precure (squares at 25°C), as well as data points (triangles) for the samples that were not scanned in the DMA but received only the pre-DMA exposure to 105°C for 2 min. By this DSC measure of cure, resin 2-C (filled data points) achieved about 85% of complete cure by the time the DMA scan reached 200°C, whereas resin 1-B (open data points) only achieved about 45% of complete cure. Thus, the higher modulus developed by resin 2-C in a DMA scan (Fig. 12) is indeed consistent with a higher degree of chemical cure in that resin.

The substantial reactivity that is retained after scanning in the DMA to 200°C may be partly due

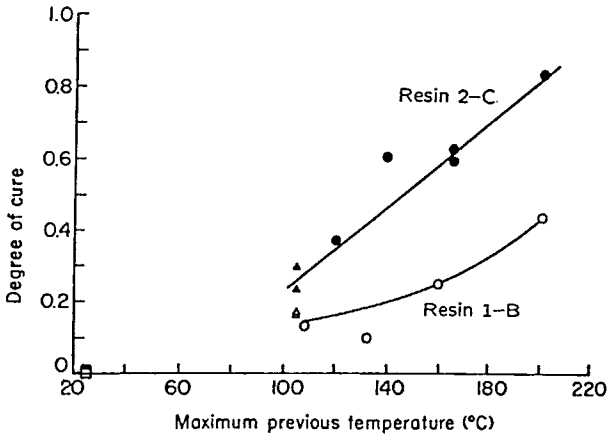

Figure 13 Degree of cure measured by DSC for samples on glass filter cloth after exposure to various temperatures. Squares, liquid resins with no previous exposure to elevated temperature; triangles, samples exposed to 105°C for 2 min plus equilibration at 91% RH, but not scanned in DMA. All other samples were exposed to 105°C for 2 min, equilibrated at 91% RH, then scanned in DMA at 5°C/min to indicated temperatures and cooled rapidly. At this point, water was added to attain approximate original resin solids content before capsule was sealed and equilibrated overnight (ML89 5867).

to slow heat transfer within the sample in the DMA after drying, possibly leading to significant temperature lag in the samples. However, a more likely explanation for the incomplete reaction is that the sample in the DMA loses its initial water content near 100°C; the glass transition is thereby increased and the mobility of catalyst species and polymer chains is decreased. Continuing with our earlier speculation, perhaps the lower degree of cure developed in resin 1-B is also due to the constraints on molecular mobility caused by the greater charge density of the more ionized polymer chains.

We have also seen strong effects of moisture content on resin reactivity in DSC experiments. For example, after the solids concentration of a commercial PF resin was raised from 45 to 70%, the resin showed increased reactivity as indicated by a 4°C lower exotherm peak temperature and a 44% higher cure heat. However, after another sample was further concentrated to about 98% solids, the peak temperature was 6°C higher than the original temperature, and the cure heat was decreased by 33%. In fact, these findings led to the standard procedure of remoistening the DMA samples prior to running the DSC scans.

Whatever the explanation may be for the differences in behavior of resins 1-B and 2-C, DMA behavior under conditions where drying can occur apparently may not adequately reflect cure behavior within a flakeboard or in a plywood bondline when moisture is present. This is, of course, particularly true with regard to steam-injection pressing.

CONCLUSIONS

Two quite different PF resoles are being used as model resins in a study aimed at establishing the effects of steam-injection pressing on PF resin cure and bonding in flakeboard. As necessary background for that study, we characterized the chemistry and behavior of the two resin formulas during synthesis, aging, and cure, using such techniques as viscosity measurement, GPC, NMR, DSC, FTIR, and DMA.

The two PF resole resins differ greatly in structure, composition, and reactivity. Thus, they should be excellent subjects for subsequent program phases in which we expect to explain trends in board behavior in terms of differences in resin cure and bonding.

When resin is stored at −20°C and thawed for 2 h each week, it will age as quickly as resin that has been refrigerated at 5°C. Thus, to perform multiple analyses over several months on resin that could be considered reasonably fresh, it is better to initially divide the resin up into small quantities before freezing and to then sample each resin in a small container a limited number of times.

With regard to our evaluation of techniques for studying the cure process in aqueous PF resins, our conclusions are as follows. Dynamic mechanical analysis possesses the singular advantage of reflecting the development of mechanical integrity and response during the resin cure process. However, for our instrument and sample configuration, DMA is difficult to perform without simultaneous loss of water. Water loss greatly complicates interpretation of DMA temperature scans in terms of the governing cure processes in actual wood bonding, where significant moisture may be present.

Results from the combined DSC–DMA experiments emphasize the necessity for studying the cure and bonding of adhesive resins under conditions that closely approximate those existing during real bonding conditions. We believe the incomplete cure developed in the DMA is primarily the consequence of moisture loss, with attendant loss in molecular mobility. Intermediate water content during resole phenolic cure can probably lead to more highly cured resins with more stable properties.

Infrared spectroscopy (FTIR) can provide useful semiquantitative information to supplement other techniques. Differential scanning calorimetry provides quantitative information on the development of cure in the presence of water, but the interpretation of the data in terms of mechanical properties is not clear. In future work, therefore, we plan to employ DMA, FTIR, and DSC to examine the degree of cure achieved in a high-temperature, high-humidity environmental chamber. We also hope to extend the DMA capability to permit high temperature measurements in moist environments *in situ.*

This material is based upon work supported by the U.S. Department of Agriculture Competitive Research Grants Program under Agreement 85-FSTY-9-0079. This work would not have been possible without the efforts and counsel of Virgil H. Schwandt, Martin F. Wesolowski, Lawrence L. Landucci, and Roger C. Pettersen in GPC, NMR, and FTIR. Jill Wennesheimer, Ralph E. Schaeffer, and Richard Pappas provided valuable resin synthesis, laboratory testing, and data analysis. W. Detlefsen of Borden Co. was extremely helpful in regard to resin synthesis and properties.

REFERENCES

1. R. L. Geimer, in *Proc. 16th Wash. State Univ. Int. Symp. on Particleboard,* Washington State Univ., Pullman, WA, 1982, pp. 115–134.

2. R. A. Follensbee, J. A. Koutsky, A. W. Christiansen, R. L. Geimer, and G. E. Myers, *J. Adhes. Sci. Technol.*, to appear.
3. J. F. Walker, *Formaldehyde*, 3rd ed., Krieger, Huntington, NY, 1975, Chap. 18.
4. West Coast Adhesive Manufacturers Association, Method 2.2, Determination of Per Cent Non-Volatile Content in Liquid Phenolic Resins, Seattle, WA, 1957.
5. J. Tice, Personal communication, Georgia Pacific Corp., Decatur, GA, 1986.
6. J. D. Wellons and L. Gollob, *Wood Sci.*, **13**(2), 68 (1980).
7. T. J. Wenzel, M. E. Ashley, and R. E. Sievers, *Anal. Chem.*, **54**, 615 (1982).
8. W. Detlefsen, Personal communication, Borden Co., Springfield, OR, 1987.
9. A. Rudin, C. A. Fyfe, and S. M. Vines, *J. Appl. Polym. Sci.*, **28**, 2611 (1983).
10. F. P. B. Van der Maeden, M. E. F. Biemond, and P. C. G. M. Janssen, *J. Chromatogr.*, **149**, 539 (1978).
11. T. Takeuchi and D. Ishii, *J. Chromatogr.*, **257**, 327 (1983).
12. G. E. Troughton and L. Rosen, *Wood Sci.*, **4**(4), 219 (1972).
13. L. Prokai, *J. Chromatogr.*, **331**, 91 (1985).
14. M. G. Kim, G. T. Tiedeman, and L. W. Amos, *Phenolic Resins: Chemistry and Applications*, Weyerhaeuser Science Symp., Weyerhaeuser, Tacoma, WA, 1981, p. 263.
15. B. Mechin, D. Hanton, J. Le Goff, and J. P. Tanneur, *Eur. Polym. J.*, **20**(4), 333 (1984).
16. R. A. Pethrick and B. Thomson, *Br. Polym. J.*, **18**(3), 171 (1986).
17. D. D. Werstler, *Polymer*, **27**(5), 750 (1986).
18. H. Kammerer and M. Grossmann, *Makromol. Chem.*, **140**, 131 (1970).
19. L. M. Yeddanapalli and D. J. Francis, *Makromol. Chem.*, **55**, 74 (1962).
20. A. W. Christiansen and L. Gollob, *J. Appl. Polym. Sci.*, **30**, 2779 (1985).
21. T. Provder, *J. Coatings Technol.*, **61**(770), 33 (1989).
22. P. J. Secrest, Official Digest, *J. Paint Technol. Eng.*, **37**, 187 (1965).
23. Z. Katovic, *J. Appl. Polym. Sci.*, **11**, 85 (1967).
24. R. C. Vasishth, W. C. Ainslie, and S. Y. Leong, *Polym. Prepr. Div. Polym. Chem., 155th Natl. ACS Meeting*, p. 712 (1968).
25. M. Yamao, S. Nukui, T. Yamada, and S. Tanaka, *Kogyo Kagaku Zasshi*, **74**, 2571 (1971).
26. J. K. Kauppinen, D. J. Moffatt, H. H. Mantsch, and D. G. Cameron, *Appl. Spectros.*, **35**(3), 271 (1981).
27. D. I. James, W. F. Maddams, and P. G. Tooke, *Appl. Spectrosc.*, **41**(8), 1362 (1987).
28. M. A. Irle and A. J. Bolton, *Holzforschung*, **42**(1), 53 (1988).

Received March 15, 1990
Accepted December 4, 1990