^{13}C CP/MAS NMR AS A DIRECT PROBE OF THE WOOD-PHENOL FORMALDEHYDE ADHESIVE BONDLINE

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ABSTRACT

Resole phenol formaldehyde resin was synthesized using ^{13}C labeled paraformaldehyde. Wood flake model composites were prepared with the labeled resin, cured for various times and temperatures, and then characterized by ^{13}C CP/MAS NMR. The relative degrees of adhesive cure were determined from the corrected peak areas of the methylene and hydroxymethyl carbon signals. Similar cure information was provided by measuring rotating frame proton spin-lattice relaxation times. However, cure measurements via relaxation times were less sensitive because of the effects of spin diffusion within the cured resin. Relaxation measurements revealed that wood induces heterogeneity in cured PF, whereas neat-cured PF is normally more homogeneous. This method provides cure and morphological information for intact bondlines. The procedure is readily applicable to pilot or industrial scale manufacturing processes, allowing the direct evaluation of resin cure within a wood-based composite.

Keywords: Phenol formaldehyde, adhesion, CP/MAS NMR, cure.

INTRODUCTION

Large-scale solid wood members are gradually being replaced in structural applications by wood-based composite materials. These products consist of wood in a refined form (flakes, particles, veneer, strands) bonded with a thermosetting adhesive. The most common type of adhesive used is liquid resole phenol formaldehyde (PF).

The strength and durability of wood-based composites are functions of the cured state of the adhesive. Processing variables acting during adhesive cure strongly influences the performance of the finished composite. These variables control gradients in temperature, moisture, and water vapor pressure within a composite mat. Adhesives that cure via condensation equilibria are particularly sensitive to gradients in liquid and gaseous water. Such resins produce water during cure, which means that external changes in water concentration will bear directly upon polymerization equilibria. For example, while steam accelerates cure by enhancing heat transfer, condensation equilibria are simultaneously forced backwards via the action of Le Chatlier's principle. Because PF cures by condensation equilibria, we can expect that PF performance will be sensitive to all moisture-related variables that act during cure. Unfortunately, we cannot hope to simulate these complexities in any place other than the mat itself. Consequently, a method allowing the direct characterization of the adhesive bondline would be highly valued as a tool for understanding *in situ* adhesive cure.

Solid-state nuclear magnetic resonance (NMR) employing cross-polarization and magic angle spinning (CP/MAS) is ideally suited for the characterization of intact wood-isocyanate bondlines (Wendler and Frazier 1996a, b). Information with regards to adhesive chemical structure, molecular motions, and morphology can be obtained. These methods are also applicable to other systems such as PF. In fact, recent work has shown that ^{13}C CP/MAS NMR is effective for the characterization of neat PF systems (Schmidt and Frazier 1997). It was shown that the degree of resin cure within the intact solid sample can be evaluated with two complementary NMR methods. One method involves the simple measurement of carbon signal areas. For example, since PF resoles cure by the conversion of hydroxymethyl carbons into methylene carbons, a determination of the ratio of the respective carbon signals reveals the state of cure. The second method monitors cure by measuring changes in network mobility within the resin. Molecular mobilities drop as cross-linking increases, meaning that measured relaxation times will correlate with the degree of resin cure. This was demonstrated in neat-cured PF where molecular relaxations have been correlated to glass transition temperature and cross-link density (Schmidt and Frazier 1997). These prior results suggest that ^{13}C CP/MAS NMR can directly evaluate adhesive properties within the wood-resin bondline.

This paper describes a first step towards the application of ^{13}C CP/MAS NMR to the PF-wood bondline. Wood flake sandwich composites have been prepared with a PF resin that is enriched in [13]C. Isotopic enrichment provides the required sensitivity while maintaining the low resin levels that are characteristic of wood-based composites. The greater objective is to transfer this methodology to a pilot or industrial scale hotpress operation.

MATERIALS AND METHODS

Phenol (99 + %) and 50% aqueous NaOH were purchased from Aldrich and used as re-ceived. Ninety-nine percent ^{13}C labeled para-formaldehyde was purchased from Cambridge Isotopes and used as received.

Flakes of yellow-poplar (*Liriodendron tulipifera*) were hand-turned from 5-× 5-× 20-cm blocks using a CAE Disk flaker. The blocks had been previously soaked in distilled water for 24 h. Final dimensions of the flakes were 5 × 5 cm × 0.38 mm. Flakes were oven-dried at 105°C (±3°C) for 24 h and subsequently conditioned to a moisture content of approximately 5%. This was accomplished by placing the flakes in a sealed desiccator over a saturated sodium sulfate solution for 24 h.

Resin synthesis

Resole phenol formaldehyde resin was synthesized using a P:F:Na molar ratio of 1:2:0.2. Fifteen grams of resin was synthesized by combining the appropriate amounts of phenol, ^{13}C labeled paraformaldehyde, and 50% NaOH in a reaction vessel. Additional distilled water was added to attain a target resin solids content of 50%. The solution was brought to reflux and allowed to heat for 30 min in the open atmosphere. Subsequently, the reaction was quenched by immersing the reaction vessel in a cold water bath. No characterization of the liquid resin was performed. The resin was stored in a common freezer, and allowed to warm to room temperature for use.

Composite preparation

Flake composites were prepared by spraying resin onto a single flake, placing a second flake on top, and then hot-pressing. Cure temperatures used were 110, 135, and 175°C. At each temperature, three different cure times were employed: 1 min, 5 min, and 10 min. Replicates were made for the following cure conditions: 110°C, 1 min; 135°C, 5 min; and 175°C, 10 min. Pressing was performed on a Micromet Instruments MP-2000 Minipress with a pressure of 1.28 MPa (184 psi). The average post-cure resin content was gravimetrically determined to be 6% of the dry weight of wood; the range was from 4.5 to 7%. Cured

samples were stored over a desiccant at 10°C prior to NMR analysis. Post-cure drying of the samples was unnecessary because the specimens were fully desiccated as a result of the curing and storage procedures.

NMR experiments

Samples for NMR analysis were made by cutting small disks out of the flake composites using a paper hole puncher. These disks were randomly loaded into a zirconium oxide rotor and filled in and around with aluminum oxide powder. Kel-f caps were used to seal the rotors. Variable temperature experiments were performed using boron nitride caps.

NMR measurements were performed on a Bruker MSL-300 MHz spectrometer using a 7-mm Probenkopf MAS.07.D8 probe. The spectrometer operated at a frequency of 75.47 MHz for ^{13}C nuclei. The proton spin-lock field strength was approximately 56 kHz. The Hartmann-Hahn match was established using adamantane. Standard phase cycling was used during acquisition.

Proton spin-lattice rotating frame relaxation times ($T^H_{1\rho}$) were obtained at room temperature by employing a standard cross-polarization pulse with a variable contact time. Contact times ranged from 25 μsec to 9 msec. Six hundred scans were accumulated for each contact time. Recycle delay was 3.75 sec and all samples were spun at 4 kHz (±20 Hz). Variable temperature experiments were performed at 0, 40, and 60°C using the same procedure.

RESULTS AND DISCUSSION

A series of ^{13}C CP/MAS NMR spectra is shown in Fig. 1. Yellow-poplar flakes are compared to two cured PF resins. The only difference between the two resins is that one is enriched with ^{13}C. The peaks of interest for the cured PF are: 150 ppm (carbons attached to the phenolic hydroxyl); 130 ppm (substituted and unsubstituted aromatic carbons); 63 ppm (unreacted hydroxymethyl carbons); and 35 ppm (methylene bridges). It is evident that isotopic enrichment greatly enhances the hy-
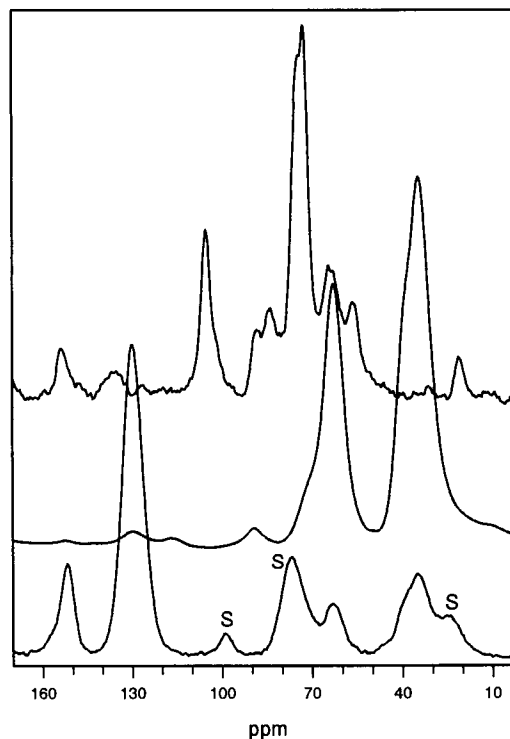

FIG. 1. ^{13}C CP/MAS spectra of yellow-poplar flakes (top), ^{13}C labeled, cured PF (middle), unlabeled, cured PF (bottom). Peaks labeled S are spinning sidebands.

droxymethyl and methylene peaks, so much that the other resin peaks are only slightly visible. Notice that a small peak appears near 90 ppm in the labeled resin. The chemical shift suggests that this may be residual formaldehyde in the form of low molecular weight polymethylene glycol species (Tomita and Hatono 1978; Rammon et al. 1986), and/or hemiformal species (Werstler 1981) (hemiformal results from the reaction of formaldehyde with hydroxymethyl). Evidence of the hemiformal is also seen as the shoulder at 70 ppm (Werstler 1981). The methylene carbon resonance is not overlapping with any wood signals. However, the hydroxymethyl carbon overlaps the C_6 cellulose carbon from wood. Fortunately, the intensities of the labeled peaks are so strong that overlap is not a significant problem. This means that the peaks of interest will be easily observed in a composite
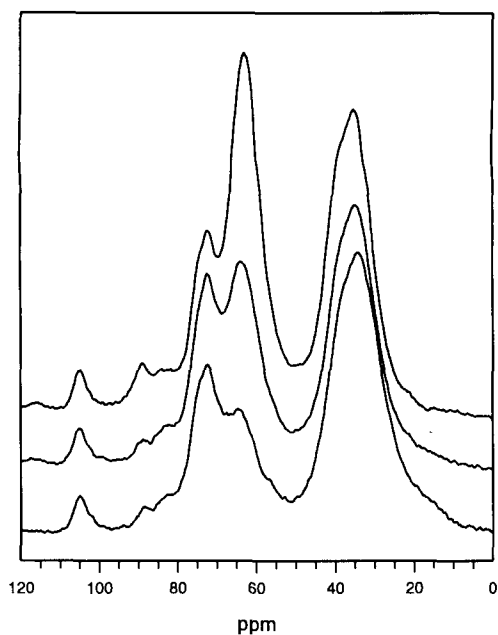
Fig. 2. [13]C CP/MAS spectra of PF-wood sample composites cured at 110°C (top), 135°C, and 175°C (bottom) for ten minutes.

Fig. 3. Ratios of corrected areas of methylene to hydroxymethyl peaks as a function of cure time. Cure temperatures: □—110°C, ▼—135°C, △—175°C.

cured with ^{13}C labeled PF, as demonstrated below.

Simple flake composites were cured at temperatures of 110, 135, or 175°C for periods of 1, 5, or 10 min. The thin samples were effectively dried during the curing process. Furthermore, they were stored over a desiccant prior to NMR analysis; consequently, no other post-cure drying was necessary. Gravimetric analysis revealed that the composites had an average post-cure resin content of 6% on dry wood; the range was from 4.5 to 7%. Figure 2 shows representative ^{13}C CP/MAS NMR spectra obtained in this study. As mentioned previously, the degree of conversion is revealed by measuring the integrated areas of the hydroxymethyl and methylene peaks as a function of cure time and temperature. Curing trends are evident in Fig. 2. However, it is incorrect to rely solely on the signals shown in these spectra. Different samples, and even different signals from within a sample, are subject to variations in the rates of cross-polarization (signal growth) and rotating frame
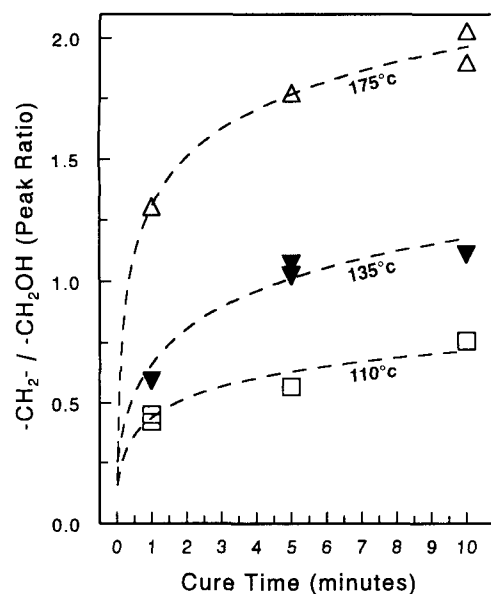
spin-lattice relaxation (signal decay). Consequently, all signals must be corrected for differential relaxation in order to obtain accurate relative concentrations. For the variable contact time experiment, a relationship exists that corrects spectral intensities (Mehring 1983).

$$I(\tau) = I^*\left(\frac{T^H_{1\rho}}{T^H_{1\rho} - T_{CH}}\right)(\exp^{-\tau/T^H_{1\rho}} - \exp^{-\tau/T_{CH}})$$

$$(1)$$

where $I(\tau)$ is the intensity at contact time τ, I^* is the corrected intensity, $T^H_{1\rho}$ is the rotating frame proton spin-lattice relaxation time, and T_{CH} is the cross-polarization, CP, time. The correction gives a theoretical signal intensity, I^*, at instantaneous CP and infinitely long $T^H_{1\rho}$. This correction was applied to the integrated areas of the peaks of interest.

The ratio of corrected signal areas for methylene and hydroxymethyl carbons is plotted versus cure time in Fig. 3. Increasing ratios indicate increasing resin conversion resulting from the effects of time and temperature, as expected. Figure 3 shows that the ratio of cor-

TABLE 1. *Proton Rotating Frame Spin-Latice Relaxation Times (in milliseconds) for adhesive resonances from sample composites cured with ^{13}C labeled PF. Values in parentheses are standard errors for the measurements.*

Cure temperature	Peak ppm	Cure time (minutes)		
		1	5	10
110°C	63	4.1 (0.1)	4.3 (0.2)	4.7 (0.1)
		4.1 (0.1)		
	35	4.3 (0.1)	4.4 (0.1)	4.4 (0.1)
		4.3 (0.3)		
135°C	63	4.6 (0.1)	4.9 (0.1)	5.1 (0.1)
			4.5 (0.1)	
	35	4.2 (0.1)	4.4 (0.1)	4.4 (0.1)
			4.3 (0.1)	
175°C	63	5.4 (0.1)	6.1 (0.3)	5.9 (0.2)
				5.7 (0.1)
	35	4.7 (0.1)	5.2 (0.1)	5.4 (0.2)
				5.1 (0.1)

rected signal areas is sensitive to both cure time and temperature; the effects of temperature are more evident. Recall that the PF hydroxymethyl carbon overlaps the C_6 signal from wood. No corrections were made for this effect. The resulting error is minimal at low degrees of resin cure because the hydroxymethyl peak is quite strong. However, at higher degrees of cure the hydroxymethyl peak becomes weak as shown in Fig. 2. In this case, signal overlap deflates the value of the methylene : hydroxymethyl carbon ratio shown in Fig. 3. Consequently, cure is underestimated at higher resin conversions.

Values of $T^H_{1\rho}$ calculated from Eq. (1) are shown in Table 1 for the hydroxymethyl and methylene resonances. Rotating frame spin-lattice relaxation times such as $T^H_{1\rho}$ characterize molecular motions in the midkilohertz frequency range (Shaefer et al. 1980). These relaxations normally result from two processes: 1) the coupling of local dipolar fields through spin-lattice effects, or motional processes in the solid, and 2) static transfer of magnetization between nearby protons, a process known as spin diffusion. Spin diffusion is non-motional in origin and can mask the motional contribution to $T^H_{1\rho}$. Spin diffusion occurs in cured PF, however, not to the extent that all motional information is obscured. In fact, a significant degree of motional information is revealed through the measurement of $T^H_{1\rho}$

(Schmidt and Frazier 1997). We should therefore expect the $T^H_{1\rho}$ to correlate with network parameters such as cross-link density and glass transition temperature. Indeed, this was found to be true in the case of neat PF (Schmidt and Frazier 1997). This relationship also holds within the wood-PF bondline as shown in Figs. 4 and 5. Figure 4 shows $T^H_{1\rho}$
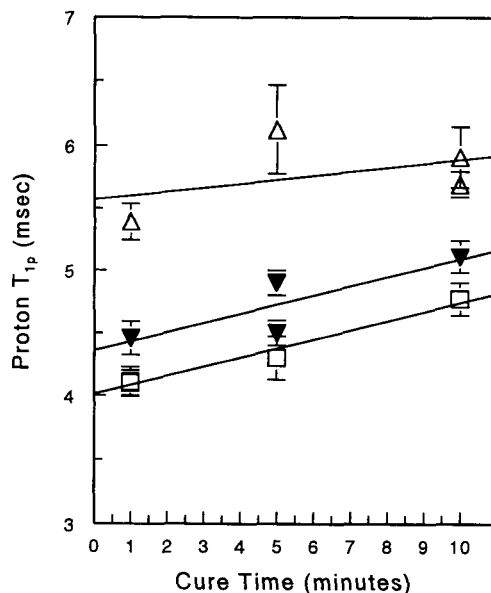

FIG. 4. Proton rotating frame spin-lattice relaxation times for the hydroxymethyl carbon (63 ppm) as a function of cure time. Cure temperatures: □—110°C, ▼—135°C, △—175°C.
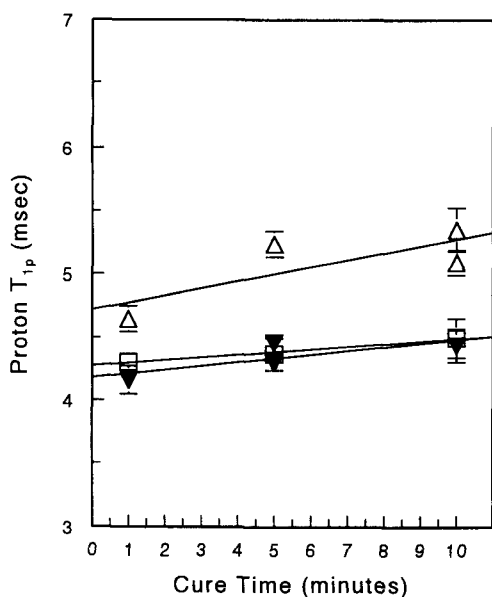
FIG. 5. Proton rotating frame spin-lattice relaxation times for the methylene carbon (35 ppm) as a function of cure time. Cure temperatures: □—110°C, ▼—135°C, △—175°C.

for hydroxymethyl carbons in sample wood composites as a function of cure time and temperature. $T^H_{1\rho}$ increases steadily with time at all cure temperatures, indicating that the network is becoming more rigid. Increases in $T^H_{1\rho}$ follow the trends seen for the ratio of corrected signal areas shown in Fig. 3.

Figure 5 shows analogous trends for the methylene carbon; however, relaxations for this carbon appear much less sensitive to the degree of cure. This lack of sensitivity is a clear example of how spin diffusion may conceal the motional information contained within $T^H_{1\rho}$. The non-motional effects of spin diffusion accelerate relaxation, thereby lowering the numerical value of $T^H_{1\rho}$. This numerically cancels the increases in $T^H_{1\rho}$ that generally occur as sample rigidity rises, for example, as a thermoset becomes more cross-linked. This complexity masks cure information, as Figs. 3–5 demonstrate. Even the hydroxymethyl relaxations appear slightly less sensitive than the trends shown for corrected signal intensities. We must conclude that corrected signal areas

provide the best method for determining cure within this system. However, remember that corrected signal areas are calculated from measured CP and $T^H_{1\rho}$ relaxation times. So the use of corrected signal areas does not free us from these measurements. Furthermore, it is preferable to use relaxation times as a measure of cure because these measurements reveal other phenomena, as will be discussed below. Consequently, we should strive for the use of $T^H_{1\rho}$ as a measure of cure, but we must eliminate the confounding effects of spin diffusion. Fortunately, this complication is avoided by simply diluting the proton reservoir with deuterium (Schmidt and Frazier 1997). Deuterium is not active in the ^{13}C CP/MAS NMR experiment and serves to physically separate the remaining protons, while not affecting the chemistry of the system. By diluting the protons with deuterium, the static transfer of magnetization between protons can be reduced or eliminated (Parmer et al. 1987). Dilution with deuterium will enhance the use of $T^H_{1\rho}$ for cure measurement, and this will be the subject of future studies.

It was shown above that $T^H_{1\rho}$ for the hydroxymethyl and methylene carbons provides different sensitivities to the degree of PF cure. This disparate behavior indicates that the two carbon atoms relax independently of one another. In other words, the values of $T^H_{1\rho}$ for the two types of carbon diverge under certain curing conditions. For example, Table 1 shows that the $T^H_{1\rho}$ for the hydroxymethyl and methylene carbons become dissimilar at higher cure temperatures and times. This is in contrast to the behavior of neat PF resin, cured in the absence of wood. Neat-cured PF relaxes homogeneously, meaning that $T^H_{1\rho}$ is the same for all carbon atoms (Schmidt and Frazier 1997). When PF is cured with wood, chemically different resin carbons vary in their relaxation behavior. In this case, it is evident that the hydroxymethyl groups are in a different motional environment than the methylene groups. The circumstances that create this motional heterogeneity are unknown. However, one could postulate that the heterogeneity re-
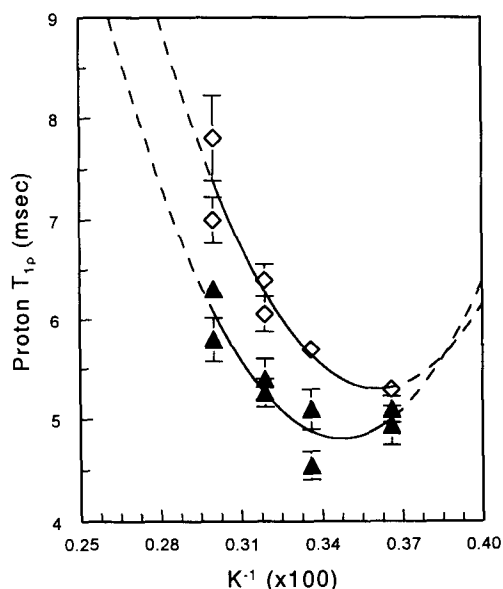
FIG. 6. Proton rotating frame spin-lattice relaxation times for the hydroxymethyl carbon (63 ppm) as a function of NMR acquisition temperature for two samples cured as follows: ▲—135°C, 1 min, ◊—175°C, 10 min.
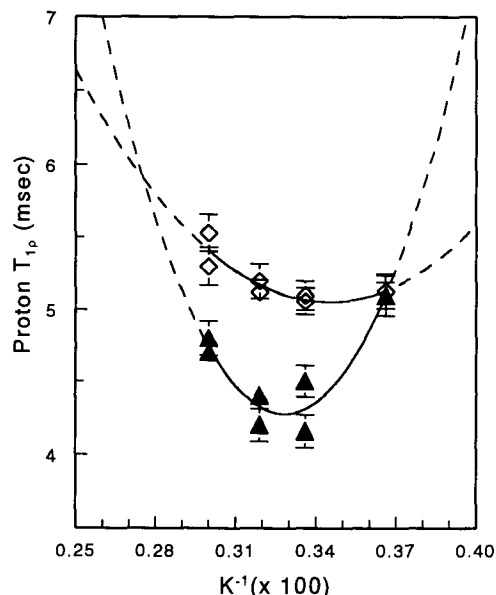

FIG. 7. Proton rotating frame spin-lattice relaxation times for the methylene carbon (35 ppm) as a function of NMR acquisition temperature for two samples cured as follows: ▲—135°C, 1 min, ◊—175°C, 10 min.

sults from the preferential association of hydroxymethyl groups with the wood surface via hydrogen bonding. Other explanations are also feasible.

Motional heterogeneity within this system is more apparent from variable temperature NMR acquisitions, the results of which are shown in Figs. 6–8. These figures show how $T^H_{1\rho}$ varies with changes in the NMR *acquisition temperature*; data are presented for adhesive and wood at the lowest and highest degrees of cure, respectively. $T^H_{1\rho}$ is plotted versus the reciprocal of NMR acquisition temperature. Experimental observations of $T^H_{1\rho}$ as a function NMR acquisition temperature typically reveal minima in $T^H_{1\rho}$. A local minimum occurs when the frequency of a molecular motion is equal to the nuclear precessional frequency, also known as the Larmor frequency, ω_0 (Fyfe 1983). When the frequencies of molecular motion and nuclear precession couple in this fashion, the excited nucleus is afforded an efficient relaxation mechanism. Nuclear magnetization is rapidly dissipated to the sur-
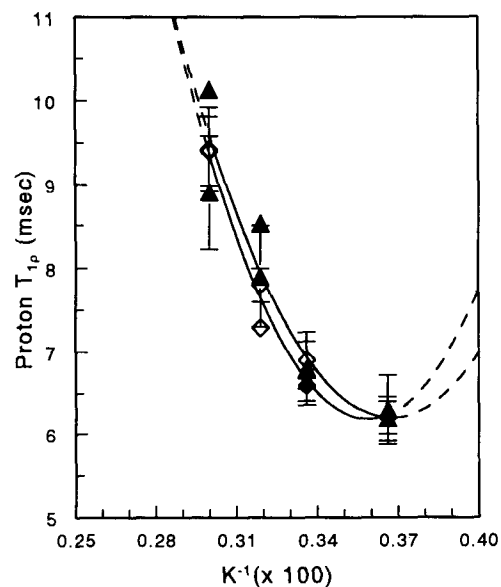

FIG. 8. Proton rotating frame spin-lattice relaxation times for wood signal at 72–75 ppm as a function of NMR acquisition temperature for two samples cured as follows: ▲—135°C, 1 min, ◊—175°C, 10 min.

roundings; thus, a minimum in $T^H_{1\rho}$ is detected. In Figs. 6–8, each data set has been fitted to a second-order polynomial curve. These curves demonstrate the idealized structure of a minimum in $T^H_{1\rho}$. They also serve to accent the sensitivity (or lack of sensitivity) of $T^H_{1\rho}$ to the NMR acquisition temperature. By sweeping the NMR acquisition temperature, we can control the frequency of molecular motion. Accordingly, the right side of the minimum corresponds to low frequency motion, or low NMR acquisition temperatures. The left side of the minimum corresponds to high motional frequencies, or high temperatures. In this case, high or low is relative to the nuclear precessional frequency. The minimum in $T^H_{1\rho}$ reveals some discreet molecular motion, such as side group rotation or backbone crankshaft motion. Whatever the motion may be, it possesses a characteristic correlation time that is related to the precessional frequency as follows:

$$\omega_0 \simeq \frac{1}{\tau_c} \qquad (2)$$

τ_c, the correlation time, is also a direct function of $T^H_{1\rho}$ (Slichter and Ailion 1965). Consequently, the characteristics of a particular motional process are revealed through $T^H_{1\rho}$ and the temperature dependence of $T^H_{1\rho}$. A comparison of Figs. 6 and 7 demonstrates the dissimilar temperature sensitivities of the hydroxymethyl and methylene carbons in PF cured with wood. In other words, the respective motions are quite different, as might be expected. In both cases, the values of $T^H_{1\rho}$ are larger for the more fully cured sample. This indicates that the correlation time for molecular motion is increasing, consistent with a state of advanced cure.

Figure 6 also shows that the temperature sensitivity of the hydroxymethyl motion is not substantially altered by advanced cure. In contrast, the temperature response of the methylene carbon flattens out with advanced cure (Fig. 7). This flattened response is thought to result from a broadening of correlation times

for the motional process (McBrierty and Douglass 1981), indicating that the characteristics of the motion are changing with advanced cure. The temperature dependence of $T^H_{1\rho}$ for the 72–75 ppm wood resonance (C_2, C_3 and C_5 of cellulose and hemicellulose) demonstrates little or no difference between the two cure conditions (Fig. 8). This indicates that there is no significant difference in the motional character of holocellulose chains between these two cure conditions.

CONCLUSIONS

^{13}C CP/MAS NMR is effective for revealing molecular structure and dynamics of cured phenol formaldehyde in the wood-adhesive bondline. The relative state of cure may be determined by measuring the corrected peak areas of hydroxymethyl and methylene bridge carbons. Proton rotating frame spin-lattice relaxation times ($T^H_{1\rho}$) reveal similar cure information by monitoring changes in network motions. However, the latter method is complicated by the effects of spin diffusion, which reduces the sensitivity of $T^H_{1\rho}$ as a measure of cure. Dilution of the proton reservoir by deuterium should alleviate this problem. $T^H_{1\rho}$ measurements for resin carbons indicate that wood induces a significant heterogeneity in the motions and/or morphology of cured PF. This is in contrast to PF that is cured neat, which relaxes homogeneously. Variable temperature $T^H_{1\rho}$ experiments can offer insight into changes in the distribution of molecular motions for both adhesive and wood components. These results demonstrate that resin cure and morphological information may be obtained directly from within a wood-based composite material.

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