SOLID-STATE NMR ANALYSIS OF ADHESIVE BONDLINES IN PILOT SCALE FLAKEBOARDS

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ABSTRACT

This work demonstrates the application of solid-state NMR to the analysis of adhesive bondlines in pilot scale flakeboards. A comparison to laboratory scale experiments is also made. Phenol-form-aldehyde resin is easily detected by using labeled formaldehyde. However, resin washout can occasionally prevent detection in pilot scale composites. The relative degree of resin cure is determined by measuring corrected signal areas and also by measuring proton longitudinal relaxation in the ro-tating frame. Such relaxation measurements were effective in laboratory scale experiments, but were much less useful for pilot scale tests. The degree of phenol-formaldehyde polymerization was not affected by changes in wood furnish moisture content; the range of furnish moisture was 13 and 24%. This suggests that phenol-formaldehyde moisture intolerance is not related to polymerization retar-dation by water. This work demonstrates the feasibility of performing detailed bondline analyses on pilot and possibly industrial scale composites.

Keywords: Adhesion, phenol-formaldehyde, solid-state NMR, isotopic labeling.

INTRODUCTION

Solid-state nuclear magnetic resonance, NMR, is effective for analyzing cured wood-adhesive bondlines (Ni and Frazier 1998; Schmidt and Frazier 1998). This approach pro-vides valuable information about resin chemis-try, and also bondline morphology via relaxation measurements. However, the published work in this area has concentrated on small flake sam-ples that have little similarity to industrial wood-based composites. The extension of solid-state NMR to pilot and industrial scale composites would be interesting and potentially useful. This work demonstrates the application of solid-state NMR to pilot scale composite flakeboards; a comparison is made to laboratory scale appli-cations. Pilot scale experiments were used to study the effects of wood furnish moisture con-tent on resin cure. Resin detection was achieved with isotopic labeling of phenol-formaldehyde. The utility and limitations of solid-state NMR for more realistic applications will be demon-strated.

MATERIALS AND METHODS

Phenol (99 + %) and 50% aqueous NaOH were purchased from Aldrich and used as re-

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ceived. Paraformaldehyde-^{13}C, phenol-d$_6$, and methanol-^{13}C-d$_2$ were purchased from Cambridge Isotopes and used as received. A molybdenum oxide–iron molybdate catalyst was obtained from Perstorp Polyols. Yellow-poplar (*Liriodendron tulipifera*) flakes were cut from 5- × 5- × 20-cm water-saturated blocks, using a disk flaker. Final dimensions of the flakes were 5 × 2.5 cm × 0.38 mm. Flakes were oven-dried at 105°C (±3°C) for 24 h and subsequently conditioned to 5% moisture content. Core flakes, 60% southern yellow pine and 40% mixed hardwoods, were obtained from Weyerhauser Corp., Elkin, NC. Flake moisture content was 5%. Phenol-formaldehyde oriented strandboard resin (Chembond 1527) was obtained from Neste Resins Corp, resin solids: 44.8%.

Resin synthesis

^{13}C labeled phenol-formaldehyde.—^{13}C labeled resole phenol-formaldehyde, PF, resin was synthesized using a P:F:Na molar ratio of 1:2:0.2. Paraformaldehyde-^{13}C (1.6 g, 0.0532 moles) was hydrolyzed in 4.2 ml of distilled water at 120°C in a sealed tube for 4 h. Phenol (2.5 g, 0.0266 moles) was added to a 10-ml round-bottom flask. The formaldehyde-^{13}C solution was added, followed by 50% aqueous NaOH (0.213 g, 0.00266 moles). The mixture was refluxed at atmospheric pressure for 30 min. The reaction was quenched by immersion into a cold water bath, and the resin was stored in a freezer. No adhesive characterization was performed.

^{13}C labeled and deuterium enriched phenol-formaldehyde.—Paraformaldehyde-^{13}C-d$_2$ was synthesized via catalytic oxidation of methanol-^{13}C-d$_2$ over a molybdenum oxide iron-molybdate catalyst; this procedure is published elsewhere (Schmidt et al. 2000). The PF polymerization was conducted as above, except that 50% of all protons were replaced with deuterium by using the following reagents: paraformaldehyde-^{13}C-d$_2$ (0.25 g, 0.0076 moles), paraformaldehyde-^{13}C (0.236 g, 0.0076 moles), phenol (0.353 g, 0.00375 moles), and phenol-d$_6$ (0.376 g, 0.00375 moles), NaOH (0.12 g, 0.0015 moles). Deuterium oxide was used as the solvent.

Laboratory scale sample preparation

Laboratory scale samples were prepared by spraying the labeled PF resin onto a single yellow-poplar flake, and then hot-pressing a second flake on top. Cure temperatures were 110, 135, and 175°C; hot-press pressure was 1.28 Mpa (184 psi). Three different cure times, 1 min, 5 min, and 10 min, were employed at each cure temperature. The average post-cure resin content was 5% of the oven-dry weight of wood, with a range of 4.2–7%. Cured samples were dried in a desiccator over anhydrous calcium sulphate and stored in a desiccator at 10°C prior to NMR analysis.

Pilot scale composite manufacture

Panels were manufactured with a target density of 0.61 g/cm^3 (38 lbs/ft^3). Resin solids content was 7%, on oven-dry wood. Two panel types were made based on total furnish moisture content, 13% and 24%. Wood flakes were sprayed with commercial liquid PF using a laboratory drum blender; no wax sizing was used. For boards with 24% MC furnish, additional water was sprayed onto the flakes prior to resin application. Afterwards, 50% of the furnish was hand-felted onto a steel caul plate, surrounded by a forming box. An uncured yellow-poplar flake composite, prepared with labeled resin as above, was placed between two pieces of teflon mesh. The labeled sample, enclosed within the teflon mesh, was positioned in the center of the panel alongside a thermocouple. The remaining 50% of the furnish was added to the forming box. A second uncured and labeled sample was placed at the center of the face of the mat, again using teflon mesh. The mat was covered with a second steel caul plate and the board was immediately hot-pressed in a 61- × 61-cm (2- × 2-ft) hydraulic press at 200°C. A displacement controlled press schedule was used: closed press time was 5 min, with 30-s compression and

decompression cycles. Final mat thickness was 1.27 cm (0.5 in.). Once the press had opened, the labeled flake samples were immediately removed from the panel face. The panels were broken in half, and the labeled core samples were removed within 90 s of hot-pressing. The samples were weighed and then stored at 10°C until NMR analysis. Samples, which contained ^{13}C and 50% deuterium labeled PF resin, were dried under high vacuum (3 mm Hg) in the presence of phosphorus pentoxide for 72 h and analyzed by ^{13}C solid-state NMR.

NMR experiments

Small disks were punched from the flake samples using a paper hole puncher. These disks were loaded into a zirconium oxide rotor and filled in and around with anhydrous aluminum oxide powder. Cross-polarization, magic angle spinning, CP/MAS, NMR measurements were performed on a Bruker MSL-300 MHZ spectrometer. The spectrometer operated at a frequency of 75.47 MHZ for ^{13}C nuclei. The proton spin-lock field strength was approximately 56 kHz. Proton spin-lattice rotating frame relaxation times were obtained by two different methods. Samples, which were made with ^{13}C labeled resin, were analyzed using a standard cross-polarization pulse with a variable contact time, 75 μs to 7 ms. Samples made with ^{13}C and 50% deuterium enriched resin were analyzed using a variable spin-lock pulse, 100 μs to 7 ms, prior to a fixed contact time. Four hundred scans were accumulated for each delay time. Recycle delay was 3.75 s and all samples were spun at 4 kHz (±20 Hz).

RESULTS AND DISCUSSION

Laboratory scale flake samples

A series of ^{13}C CP/MAS NMR spectra are shown in Fig. 1. The top two spectra are: yellow-poplar flake without resin (solid line), and neat cured ^{13}C labeled PF resin (dashed line). Only methylene carbons (28–42 ppm) and hydroxymethyl carbons (58–70 ppm) are seen in the neat resin because of formaldehyde label-
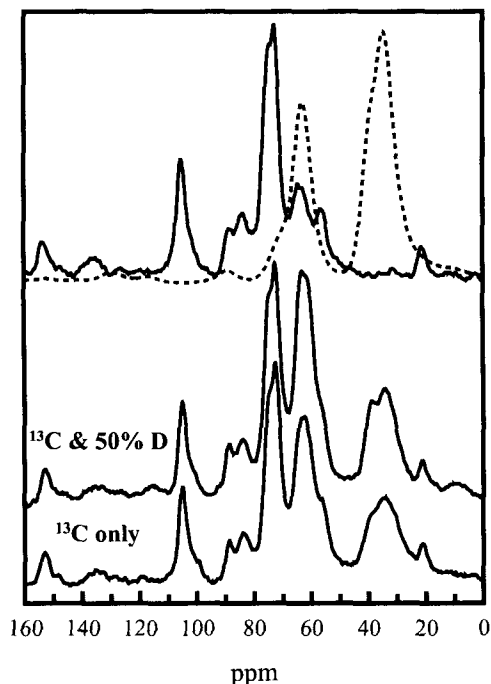

Fig. 1.   Representative ^{13}C CP/MAS spectra for this study. Top: yellow-poplar flake without resin (solid); Neat, cured ^{13}C labeled PF resin (dashed). Bottom: yellow-poplar flake cured with ^{13}C labeled PF resin as indicated.

ing. Methylene carbons do not overlap wood signals, while hydroxymethyl carbons do. The bottom two spectra are of flake composites cured under identical conditions and with similar ^{13}C labeled resins; one of the resins has had 50% of all protons replaced with deuterium. Notice that the partially deuterated resin reveals a slightly enhanced resolution of the methylene carbons as compared to the fully protonated sample. This reproducible effect was observed in all cases. Dilution by deuterium improves resolution by decreasing homonuclear dipolar broadening between adjacent protons (Fyfe 1983). Proton dilution provides additional structural information about the cured resin, probably without significant impact from isotope effects (Halevi 1963; Van Hook 1970; Shiner 1970). In other words, signal resolution is certainly enhanced by deuteration, and any structural changes caused by kinetic isotope effects are unlikely to improve

solids NMR resolution (The kinetic isotope effects of deuterium could retard PF polymerization, but a reduced polymerization rate would not affect the resulting NMR resolution. The isotope effects of ^{13}C would be insignificant as compared to deuterium, and may be ignored (Van Hook 1970)). The structural detail revealed by deuteration allows one to crudely track the changes in crosslinking. Solution NMR has shown that ortho-ortho (o–o'), para-para (p–p'), and ortho-para (o–p) methylene bridges resonate in the range of 30–32 ppm, 40–41 ppm, and 36–37 ppm, respectively (Werstler 1986). Not visible are the o–p linkages; however one can roughly approximate the relative amounts of o–o' and p–p' coupling. It was found that the ratio of o–o' to p–p' signals directly correlated with the degree of resin cure in laboratory and pilot scale samples, as expected; data not shown (Schmidt 1998). Again, this information is obtained only from partially deuterated resins.

Relaxation measurements from laboratory scale samples are shown in Fig. 2; these are proton spin-lattice rotating frame relaxation times ($^{H}T_{1\rho}$) of PF methylene carbons. Data from ^{13}C labeled samples are on the bottom, while the top graph is from samples with ^{13}C and 50% deuterium. Rising values of $^{H}T_{1\rho}$ have been positively correlated with glass transition temperature and crosslink density for neat PF (Schmidt and Frazier 1998). Labeling with ^{13}C alone provides minimal sensitivity to the state of resin cure, whereas deuteration enhances the sensitivity of $^{H}T_{1\rho}$ to cure time and temperature by reducing proton-proton interactions. These interactions cause a nonmotional relaxation because of rapid energy exchange among the normally abundant protons; the effect is referred to as spin diffusion. Spin diffusion is reduced by deuterium and therefore more of the motional aspects of relaxation are revealed as indicated in the top of Fig. 2 (Parmer et al. 1987; Schmidt and Frazier 1998).

These results demonstrate that laboratory scale samples will reveal cure and molecular mobility information from intact wood-adhe-
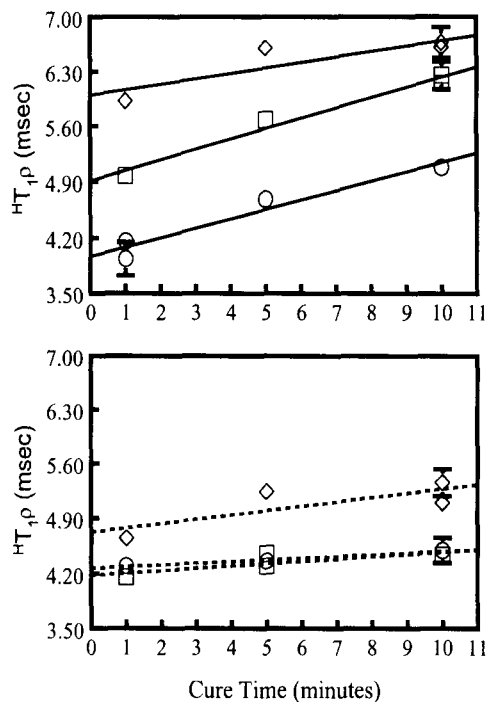

FIG. 2. Proton rotating frame relaxation times for flake samples cured with ^{13}C labeled PF resin. Top: ^{13}C and 50% deuterium labeled PF resin. Bottom: ^{13}C labeled PF resin. Cure temperatures: 110°C (O), 135°C (□), 175°C (◊). Error bars not shown are smaller than the symbol.

sive bondlines. Deuteration enhances this procedure by reducing proton-proton interactions. While not mentioned here, it is also possible to evaluate resin cure by measuring corrected resin signal integrals (Schmidt and Frazier 1998). This measurement is somewhat compromised by the overlap of hydroxymethyl carbons (58–70 ppm) with wood carbons, but it does provide useful qualitative trends.

Pilot scale panel experiments

The techniques described above were employed with pilot scale flakeboards having dimensions of 61 × 61 × 1.27 cm (24 × 24 × 0.5 in.). Flake samples were prepared with labeled PF as above, and were positioned centrally in the core and on the face of panels. These were removed after panel hot-pressing and analyzed by ^{13}C CP/MAS NMR. The effects of total wood furnish moisture content,
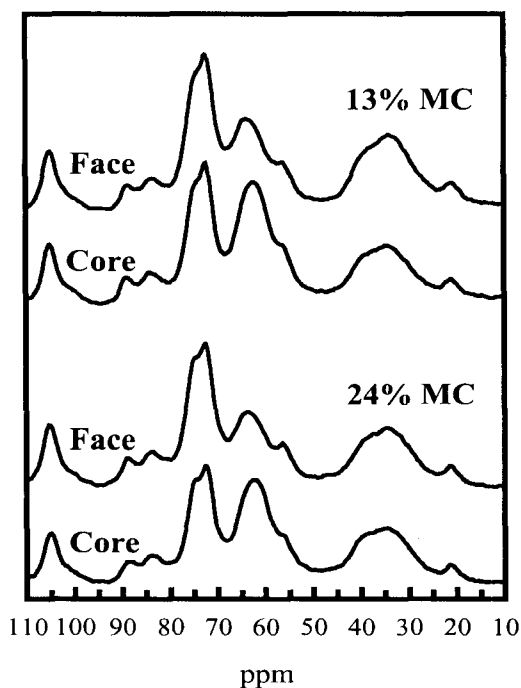
Fig. 3. CP/MAS spectra of ^{13}C labeled flake samples cured within pilot scale boards at different moisture contents as indicated.

TABLE 1. *Ratios of corrected signal integrals (methylene to hydroxymethyl carbon ratio) as a function of furnish moisture content and position in pilot scale boards for ^{13}C labeled samples.*

Furnish moisture content	Corrected ratio of CH$_2$ to CH$_2$OH in cured PF	
	Core	Face
13%	0.8	1.5
	0.8	1.3
	0.9	1.9
	mean = 0.8	Mean = 1.6
24%	0.8	1.9
	1.1	1.8
	1.0	1.8
	mean = 1.0	mean = 1.8

MC, were studied. Wood furnish MC was 13% or 24%. Final core temperatures ranged from about 137 to 150°C, and this was independent from wood furnish MC. It is probable that a state of saturated steam was present within high and low MC panels; however gas pressures were not measured.

^{13}C CP/MAS NMR spectra for ^{13}C labeled core and face specimens are shown in Fig. 3. As expected, face samples possess increased methylene (35 ppm) and diminished hydroxymethyl (63 ppm) signals as compared to core samples. The relative degree of cure is more accurately followed by correcting the peak integrals for differential cross-polarization and proton spin-lattice relaxation (Mehring 1983; Schmidt and Frazier 1998). Ratios of corrected peak integrals are shown in Table 1; this is the ratio of the methylene carbon to the hydroxymethyl carbon. The average integral ratios for core and face specimens were 0.9 and 1.7, respectively, for all panels. Integral ratios for the face and core samples are significantly different (*P* < 0.001). This is expected since the core temperatures are 50–60°C lower than the 200°C platen temperature. No significant difference in integral ratios was noted between high and low furnish moisture contents. It is generally accepted that PF resins do not perform well when hot-pressed under high moisture conditions. These findings suggest that PF moisture intolerance is not related to polymerization retardation by excess water. It may be that no moisture dependence was observed because all boards were above a critical moisture level. This is a distinct possibility given that industrial processes would normally target furnish moisture contents at below 10%. Consequently, even the low MC boards discussed here are relatively wet by industrial standards.

A second series of panels was manufactured in hopes of using relaxation measurements (^{1}T$_{1\rho}$) as a measure of cure. In this case, the core and face samples were prepared with ^{13}C and deuterium labeled resin in order to enhance sensitivity to molecular motions. As in the case of corrected integral ratios, relaxation measurements did not reveal significant differences between the high and low MC boards (Table 2). Nevertheless, face and core samples exhibit different mobilities, which reflect the difference in cure state. Pilot scale relaxation measurements appear to be less sensitive than those for laboratory scale samples. However, the pilot and laboratory scale samples were

TABLE 2. *Proton spin-lattice rotating frame relaxation times, $^{H}T_{1}\rho$, for ^{13}C and deuterium labeled samples as a function of furnish moisture content and position in pilot scale boards; determined from methylene carbon. Samples were dried thoroughly before NMR analysis. Standard errors appear in parentheses.*

Furnish moisture content	$^{H}T_{1}\rho$ (msec)	
	Core	Face
13%	6.4 (0.2)	6.4 (0.2)
	6.3 (0.3)	7.0 (0.2)
	5.2 (0.3)	7.2 (0.4)
	6.4 (0.3)	6.8 (0.3)
	mean = 6.1	mean = 6.9
24%	6.5 (0.3)	6.8 (0.3)
	6.5 (0.3)	6.9 (0.3)
	6.4 (0.3)	6.7 (0.1)
	5.8 (0.3)	6.5 (0.2)
	6.2 (0.3)	7.0 (0.3)
	mean = 6.3	Mean = 6.8

cured at different temperatures, so a direct comparison is invalid. Nevertheless, it seems that pilot scale $^{H}T_{1}\rho$ measurements have little value because of the low sensitivity to differences between core and face cure states. Carbon laboratory frame longitudinal relaxation measurements may be of greater value, and this possibility deserves further investigation.

Again, it appears that the NMR analyses employed here are insensitive to changes in furnish MC above 13%. If adhesion is adversely affected over the MC range studied, it would not be related to the degree of cure (However, moisture related changes in network structure may occur, remaining undetected by this analysis). Degrees of cure revealed by corrected signal integrals and relaxation measurements were identical for both high and low MC boards. It was only possible to reveal cure differences between face and core samples. Any hypothetical adhesion differences in these boards may be related to surface and/or viscosity effects. A possible surface effect could be impaired adhesive adsorption because of excess moisture. Likewise, excess moisture could reduce resin viscosity and cause excessive resin penetration or adhesive washout. Indeed, resin washout was noted in the pilot scale experiments. Significant varia-

tions were noted for resin signals from core samples. In fact, one sample retrieved from the core of a low MC board had no detectable resin. Consequently, it was clear that resin washout was occurring randomly in this study with no apparent relation to furnish MC. Finally, the reader will notice that this report has not touched upon other issues and techniques that are available with solid-state NMR. For example, no attempts were made to evaluate wood-resin interactions, and no detailed morphological information was sought. Such analyses are possible as demonstrated recently (Marcinko et al. 1998; Marcinko et al. 1999). This work merely demonstrates the feasibility of applying NMR techniques to pilot and possibly industrial scale applications. Consequently, more detailed and revealing studies are possible, and will no doubt arise in the future.

CONCLUSIONS

Solid-state NMR is effective for evaluating relative degrees of adhesive cure in laboratory scale and pilot scale wood-based composites. Isotopic enrichment simplifies resin detection, although steam condensation and washout can occasionally prevent resin detection in pilot scale experiments. Relative degrees of resin cure are measurable through ratios of resin integrals, and by proton longitudinal relaxation in the rotating frame. However, relaxation measurements were relatively ineffective for pilot scale experiments. The state of resin cure was not affected by large changes in wood furnish moisture content. Consequently, any moisture-related impact on adhesion was not caused by retardation of PF polymerization. Instead, adverse effects on adhesion might result from surface and/or viscosity effects caused by excess moisture. Moisture-dependent changes in PF network structure may also occur. Such effects would not be detected by the method used here, so definitive conclusions about PF moisture intolerance elude us here. Nevertheless, this methodology could be useful for more detailed studies of resin cure

and bondline morphology in pilot scale or even industrial scale experiments.

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