J Mater Sci (2006) 41:6001–6005
DOI 10.1007/s10853-006-0497-6

^{13}C CP/MAS NMR study of a wood/phenol–formaldehyde resin bondline

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Received: 13 May 2004 / Accepted: 9 August 2005 / Published online: 1 August 2006

Abstract The dynamics and interactions of a wood powder/phenol–formaldehyde (PF) resin composite are evaluated by solid-state ^{13}C NMR. A ^{13}C labeled and perdeuterated PF resin, with low molecular weight distribution, is synthesized and cured in the neat state and also in combination with yellow-poplar wood powder. The ^{13}C NMR spectral features and cross-polarization dynamics of the PF hydroxymethyl and methylene nuclei are compared in the neat resin and in the wood powder composite. In the composite, a downfield shift of the PF hydroxyl bearing carbons suggests secondary interactions between the PF resin and wood. In addition, the PF resin methylene and hydroxymethyl carbons exhibit slower CP dynamics compared to the neat resin. Lower resin CP rates in the composite indicate lower molecular rigidity of the resin in presence of wood compared to the neat cured PF resin.

Introduction

The performance of wood-based composites is affected strongly by the interactions in, and by the morphology of, the wood/adhesive interphase [1]. Intermolecular interactions at the wood/adhesive interphase can be evaluated by monitoring molecular motions in the composite system [2–4]. Nuclear magnetic resonance with cross-polarization and magic angle spinning, CP/MAS NMR, is a technique of choice to probe molecular relaxations of the individual components of wood-based composites [2–4]. Using CP/MAS NMR, Marcinko and coworkers have demonstrated that cured polymeric diphenylmethane diisocyanate, pMDI, affects the molecular relaxation of the amorphous constituents of wood [2, 3]. Specifically, the proton rotating frame spin lattice relaxations, $^{H}T_{1\rho}$, of pine wood resonances were decreased in the pMDI bondline compared to those in control pine [2]. In aspen composites, the CP rates (T_{CH}) of lignin methoxyl (56 ppm) and aromatic carbons (150 ppm) and the CP rates of hemicellulose acetate resonances (21 and 173 ppm) were also shortened in the presence of cured pMDI resin [3] suggesting a decrease in molecular mobility of wood amorphous polymers. Both studies therefore supported the prevalence of molecular interactions between wood polymers and pMDI. On the other hand, studies on composites of pMDI and yellow-poplar [5] or spruce wood [6] did not find any significant effect on the relaxations or local mechanical properties of the woody cell wall. These differences may relate to the species dependence of pMDI penetration and performance [7]. Similarly, in composites utilizing cured urea–formaldehyde resin on pine, the resin did little to affect the molecular scale dynamics of southern pine [2].

Most CP/MAS NMR studies in wood–adhesive bondlines focus on the effect of a cured resin on the wood polymer relaxations. A few studies propose a

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parallel approach where the influence of wood on the cured resin relaxations is determined. In one such study, Schmidt and Frazier [4] measured the T_{CH} of the pMDI methylene carbon in a neat cured resin and also in the wood/resin bondline. In this study the pMDI was partially deuterated. Resin deuteration minimizes intramolecular CP and therefore allows for the detection of intermolecular CP between wood ^{1}H and resin ^{13}C. Because CP requires angstrom scale proximity between the interacting nuclei, the detection of intermolecular CP in the bondline may suggest some degree of miscibility and/or intimate association between wood polymers and the resin. In a bondline cured at 135 °C, faster CP was evidenced than in the corresponding neat resin [4]. Enhanced CP from wood to the resin could be ascribed to nanometer scale proximity between wood protons and the resin or enhanced molecular rigidity of the resin. In a bondline cured at 175 °C on the other hand, CP was always faster in the neat resin [4]. In this case, the neat resin appeared to have greater molecular rigidity in the neat state than in the composite. Hence at higher cure temperature, wood polymers may hinder molecular rigidity in the resin. However, no definite interpretation was possible in this study because the pMDI resin was only partially deuterated. A more specific study would require complete resin deuteration. Unfortunately, even complete resin deuteration does not completely exclude the confounding effects of intramolecular CP. For instance, in base-catalyzed phenol–formaldehyde resins (PF), proton exchange between wood and the resin acidic protons (hydroxyl and hydroxymethyl) can generate intramolecular CP. In order to detect true intermolecular CP in a wood/perdeuterated PF composite, reference to intramolecular CP in a neat perdeuterated PF resin (protonated at its exchangeable sites) is required. In addition, the resin must be enriched in ^{13}C for unambiguous resin detection in the composite. Using a ^{13}C labeled and perdeuterated phenolic resin (PF-$^{13}C_{-d/H}$), the incidence of intermolecular CP (from wood to resin) may be detected by comparing the CP rates of the neat resin and the corresponding wood/PF-$^{13}C_{-d/H}$ composite. If resin CP is enhanced by the presence of wood, then magnetization is transferring from wood protons to resin carbons, thus indicating intimate association in the wood/PF interphase which affects the bulk of the resin phase. On the other hand, if the resin CP is mitigated in the presence of wood then the mobility of the PF network is effectively increased by wood, because substantial mobility will counteract nuclear proximity and reduce the CP rate.

The objectives of this study were (1) to evaluate the applicability of intermolecular CP experiments in a wood/PF composite for detecting angstrom scale proximity and (2) to evaluate the effect of wood on the molecular rigidity of a cured PF resin.

Experimental procedure

Resin synthesis

Paraformaldehyde-^{13}C-d_2 was synthesized in the laboratory from gas phase oxidation of methanol-^{13}C, d_4 over a molybdenum oxide catalyst according to a previously published procedure [8]. The doubly labeled paraformaldehyde was utilized to synthesize a low molecular weight ^{13}C labeled and perdeuterated resin with P:F:NaOH molar ratios of 1:2:0.2. The ^{13}C labeled perdeuterated resin was synthesized under dry nitrogen gas. Phenol-d_6 (98% deuteration) was purchased from Cambridge Isotopes Inc. Sodium deuteroxide (30 wt%) and D_2O were obtained from Aldrich. Reagents were used as received. Paraformaldehyde-^{13}C-d_2 (0.5287 g) was mixed with D_2O (1.142 g) in a sealed tube filled with N_2 and submerged in an oil bath at 170 °C. The hydrolysis was complete after 10 min of stirring. The formaldehyde solution was cooled to room temperature and transferred with a cannula under N_2 atmosphere to a vial containing the sodium deuteroxide solution (0.2184 g). Phenol-d_6 (0.806 g) was placed in a triple neck flask with condenser; the flask was submerged in a silicone oil bath at 80 °C. The sodium deuteroxide/paraformaldehyde-^{13}C-d_2 mixture was transferred by cannula to the reaction flask and stirring was started under N_2 gas. After 60 min of polymerization, the reaction was quenched in an ice bath. Immediately after synthesis, the ^{13}C labeled, perdeuterated resin was acidified with a protonated acid to prepare the control PF-$^{13}C_{-d/H}$. Namely, 1 g of ^{13}C labeled, perdeuterated PF was acidified to pH 3–5 by adding 20 ± 10 μl of a 37% hydrochloric acid using a microcapillary. The resins were also prepared from unlabeled reagents and characterized by solution NMR on a Bruker 360 MHz spectrometer.

Preparation of neat cured PF-$^{13}C_{-d/H}$ resin samples and yellow-poplar/PF-$^{13}C_{-d/H}$ composites

The PF-$^{13}C_{-d/H}$ composites were manufactured with extracted 40 mesh yellow-poplar (*Liriodendron tulipifera*) powder. Prior to composite manufacture, the wood powder was Soxhlet extracted three times in 50% aqueous acetone, each for a period of 24 h.

Extractions in 50% aqueous methanol and 50% aqueous tetrahydrofuran were subsequently performed over 12 h. The extracted yellow-poplar powder was then dried in a desiccator over calcium sulphate for 48 h to a moisture content of approximately 1.5%. Composites were manufactured by mixing extracted yellow-poplar powder (0.410 g) with PF-^{13}C-$_{\mathrm{d/H}}$ (0.604 g) in a vial thereby yielding 65% theoretical resin solids on dry wood mass. In order to enhance resin diffusion and penetration into wood, the mixture was allowed to stand at room temperature for 30 min prior to cure. Cure was then performed by submerging the sample vial in a silicone oil bath at 150 °C for 15 min. Neat PF-^{13}C-$_{\mathrm{d/H}}$ samples were cured in the same fashion. These cure conditions resulted in resin vitrification, as was previously determined using dynamic mechanical analysis [9]. The cured resin was then ground with a mortar and pestle. Resin and composite samples were vacuum dried overnight and stored in a dessicator over calcium sulphate until CP/MAS NMR analysis.

^{13}C CP/MAS NMR measurements

Cross-polarization experiments were performed on a Bruker MSL-300 MHz spectrometer using a 7 mm probenkopf MAS.07.D8 probe. The spectrometer frequency was 75.47 MHz for ^{13}C Nuclei and the spin locking frequency for the proton channel was approximately 56 kHz. Adamantane was utilized for establishing the Hartmann–Hahn match. Neat resin and composite powdered samples were packed in a zirconium oxide rotor, sealed with a Kel-f cap. The samples were spun at 5 kHz ± 20 Hz. Standard CP pulses with variable contact times were performed. As many as 12 contact times were utilized in the 0.1–12 ms range. For each contact time, 600 scans were accumulated utilizing a recycle delay of 3.75 s and an acquisition time of 50 ms. Three replicates of neat PF-^{13}C-$_{\mathrm{d/H}}$ resin and wood/PF-^{13}C-$_{\mathrm{d/H}}$ composites were analyzed.

Results and discussion

Characterization of the liquid resins by solution NMR

In order to assess the applicability of intermolecular CP experiments in the wood/PF composite, adhesive penetration into the woody cell wall must be maximized. Adhesive penetration into the wood cell wall is favored for low molecular weight resins, particularly if several minutes of diffusion time are allowed prior to cure. Based upon prior experience, the PF preparation conditions used here were devised to provide a low molecular weight system which would readily penetrate the cell wall. While no molecular weight analysis was conducted, the ^{13}C NMR spectrum in Fig. 1 reveals that an unlabeled model resin shows no detectable methylene signal in the 30–40 ppm range; the resin is predominately monomeric. Note also that no significant polymerization advancement is caused by the acidification procedure (Fig. 1). Again the resin acidification is intended to mimic the partial protonation that would occur when a fully deuterated PF resin is cured in the presence of wood. Consequently, the acidified neat cured resin (PF-^{13}C-$_{\mathrm{d/H}}$) provides a measure of the maximum intramolecular CP that would be expected to occur in the composite sample. Furthermore, note that the resin was also acidified prior to its curing with wood, again to maximize the possible intramolecular CP; any CP above this level would be attributed to magnetization transfer from wood to resin.

Characterization of cured samples by ^{13}C CP/MAS NMR

^{13}C CP/MAS NMR spectra for the neat PF-^{13}C-$_{\mathrm{d/H}}$ resin and the wood/PF-^{13}C-$_{\mathrm{d/H}}$ composite are presented in Fig. 2. Owing to ^{13}C enrichment, the resin methylene carbons are clearly detected in the 30–40 ppm region in both spectra. The methylene carbon region comprises two overlapping resonances, one around 31 ppm, which corresponds to ortho–ortho methylene bridges and the other centered at 40 ppm, characteristic of para–para methylene bridges [10]. Figure 2 demonstrates that the methylene carbon signals are better resolved in the composite specimen, suggesting that wood modifies the resin conformation. A broad resonance centered at 63 ppm and presenting a shoulder at 70 ppm arises from PF hydroxymethyl carbons and hemiformal or dibenzyl ether linkages, respectively [11] (Note again that in the composite the two resonances are better resolved than in the neat resin). Dibenzyl ether linkages are scarce in based-catalyzed PF but become favored under acidic condensation of PF resins [12]. In addition the small peak centered at 90 ppm confirms the presence of hemiformal species [10]. Furthermore, the 63 and the 71 ppm resonances are shifted downfield in the composite by approximately 1–3 ppm. In blends of novolacs and poly(methylmethacrylate), a downfield shift of the hydroxyl substituted carbon has been previously observed; it was ascribed to the stronger intermolecular hydrogen bonding in the blend than in the neat resin [11]. Similarly, the downfield shift observed

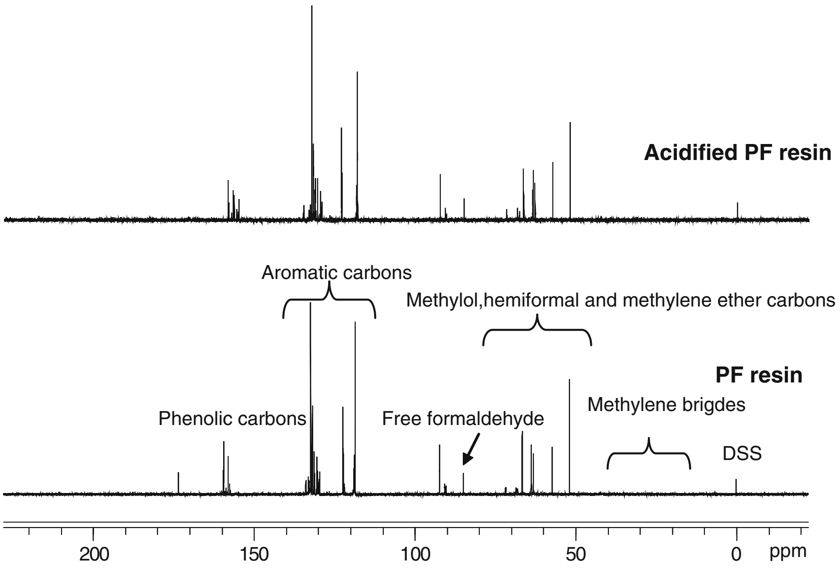

Fig. 1 ^{13}C NMR spectra of the unlabeled model PF resin in D_2O before (bottom) and after acidification (top) (internally referenced to DSS)

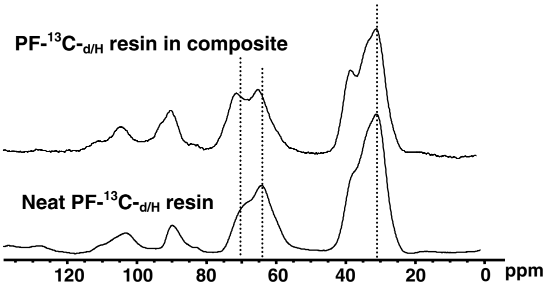

Fig. 2 ^{13}C CP/MAS NMR spectra for the neat PF-^{13}C-$_{d/H}$ resin and the wood/PF-^{13}C-$_{d/H}$ composite (3 ms contact time which corresponds to maximum resin signal intensity in both spectra)

for the hydroxyl substituted resin carbons in the composite (Fig. 2) may arise from strong wood/resin interactions. Secondary interactions through the PF resin hydroxyl group have recently been observed by Fourier Transform IR spectroscopy [13].

The CP rates of the PF methylene and hydroxymethyl carbons were monitored in both the neat resin and the composite. Figure 3 presents the normalized signal intensity of the PF methylene and hydroxymethyl carbons as a function of contact time. The signals build up rapidly during CP; however, the subsequent rotating frame relaxation is greatly delayed by the effects of deuteration. For both the methylene and hydroxymethyl carbons, signal build up is faster in the neat resin than in the composite (Fig. 3). In other words CP is slower in the composite than in the neat resin. CP efficiency depends on proton abundance and spatial proximity, and also on the mobility of the interacting nuclei [14, 15]. Hence, slower CP could theoretically stem from a reduced and remote proton reservoir or from enhanced molecular mobility. In the wood/PF composite, the resin is in contact with more protons than in the neat state and therefore slower CP in the composite cannot be ascribed to a reduced proton reservoir. More likely, slower resin CP in the composite indicates that the resin molecular mobility is enhanced by the presence of wood. In other words, a low molecular weight PF resin cured in-situ achieves lower rigidity, maybe as a result of lower crosslink-density, than the corresponding neat PF resin. This interpretation is consistent with other studies [13, 16]. Namely, Schmidt demonstrated that wood has a substantial influence on PF network molecular structure and dynamics [16]. Furthermore, a recent cure kinetic study of PF resins supports that lower final degrees of conversion are achieved when a PF resin is cured in the presence of wood [13]. The present results are consistent with these studies, namely that intimate wood/resin interactions do occur, but also that wood reduces the PF network rigidity. Finally, this study also demonstrates that intermolecular CP from wood protons to the resin nuclei cannot be detected in such composite systems.

Conclusion

Comparison of the CP/MAS NMR features of a ^{13}C labeled and perdeuterated PF resin cured in the neat state and in presence of yellow-poplar indicated that wood changes the resin conformation and molecular dynamics. Intermolecular CP from wood protons to the resin nuclei could not be detected in the composite. On the other hand, a downfield shift in the PF hydroxyl

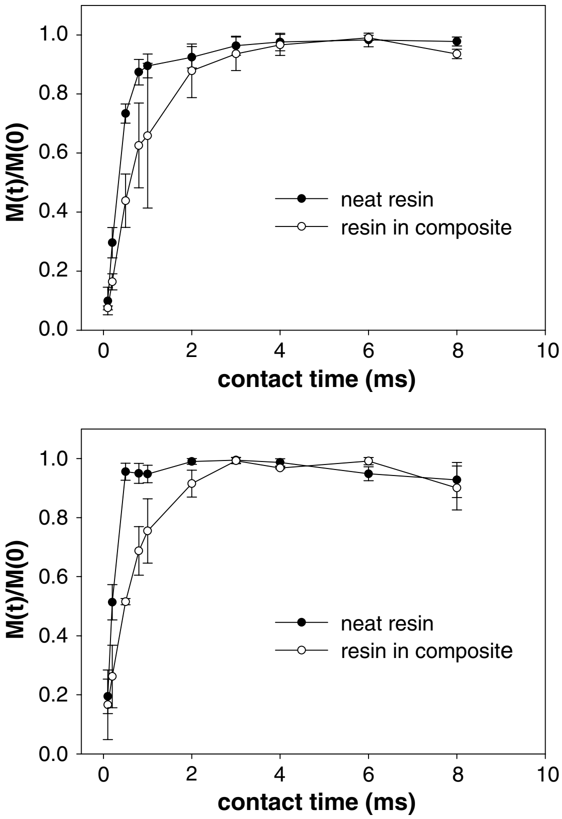

Fig. 3 Carbon magnetization as a function of contact time, $M(t)$, for PF methylene (top) and hydroxymethyl (bottom) resonances normalized to the zero contact time maximum $M(0)$ (data are average of 3 samples)

bearing carbons in presence of wood suggested secondary interactions between the resin hydroxyl groups and wood constituents. In addition, slower CP of PF resonances in the composite compared to the neat resin indicated enhanced resin molecular mobility in presence of wood. Wood/resin interactions were proposed to hinder the molecular rigidity of the PF network that would develop in a neat PF resin.

Acknowledgements Financial support from the Center for Adhesive and Sealant Science and technical support from Tom Glass for NMR measurements, all at Virginia Tech, are greatly appreciated. The solution NMR spectra have been processed with MestRe-C software.

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