Effect of Moisture Content on the Isocyanate/Wood Adhesive Bondline by ^{15}N CP/MAS NMR

STEVEN L. WENDLER and CHARLES E. FRAZIER*

Department of Wood Science and Forest Products, Center for Adhesive & Sealant Science, Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

SYNOPSIS

A 99% ^{15}N-labeled polymeric diphenylmethane diisocyanate (pMDI) resin was used to make a series of wood/^{15}N-pMDI composites at various wood precure moisture contents. Cure chemistry and bondline morphology was monitored using ^{15}N CP/MAS (^{15}N cross-polarization, magic-angle spinning) NMR (nuclear magnetic resonance). Biuret-type structures were identified as the predominant chemical moieties when dry wood flakes were bonded together, while urea linkages were predominant at higher precure moisture. Urea and urethane signal overlap make the unambiguous identification of urethane difficult. Relaxation studies using variable contact times were complicated by excessively long cross-polarization rates for nonprotonated nitrogens. Experiments using variable spin lock periods prior to a fixed contact time indicate that the cured resin in these composites is homogeneous. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Polymeric methylenebis(phenylisocyanate) (pMDI) is a wood adhesive which imparts excellent properties to wood-based structural composite panels.[1-6] The specific adhesive mechanism by which isocyanate resins derive superior adhesive properties has been the subject of some debate.[1-4,7,8] An examination of isocyanate chemistry reveals that multiple pathways exist for the formation of a wood/isocyanate adhesive bond (Scheme 1). The polyhydroxylic nature of wood provides ample opportunity for the formation of direct covalent linkages to wood. However, it also ensures the presence of adsorbed moisture at all times. This means that the isocyanate reaction with water to form polyureas and biuret-type structures is expected to compete with urethane formation. The extent and nature of the isocyanate/water reaction will affect the cure chemistry and, as a result, the adhesive mechanism of isocyanate-bonded wood composites. This study was undertaken to explore the influence of wood precure moisture content on the cure chemistry and bondline morphology of pMDI-bonded wood composites.

Previous studies of the wood/isocyanate reaction have utilized techniques such as Fourier transform infrared (FTIR) spectroscopy[3,7,9-11] and differential scanning calorimetry (DSC).[3,4,9] Owen and co-workers have demonstrated by FTIR that urethane bonds could be formed under anhydrous conditions when an excess of isocyanate was used.[7,10] Others have used FTIR and DSC to reveal the domination of polyurea formation when moisture is present.[2,7,9] However, there remains a shortage of published information regarding the wood/isocyanate reaction under conditions more similar to industrial wood bonding operations (e.g., the production of oriented strand board).

This article describes the use of ^{15}N cross-polarization, magic-angle spinning (CP/MAS) NMR as a technique for probing these complex composite systems. CP/MAS NMR is ideally suited for the study of cured resin systems.[12-17] Not only is CP/MAS NMR capable of elucidating fine structural information from the solid state, but relaxation phenomena can also provide information about the polymer morphology and molecular chain dynamics.[18-20] Of particular importance for the study of
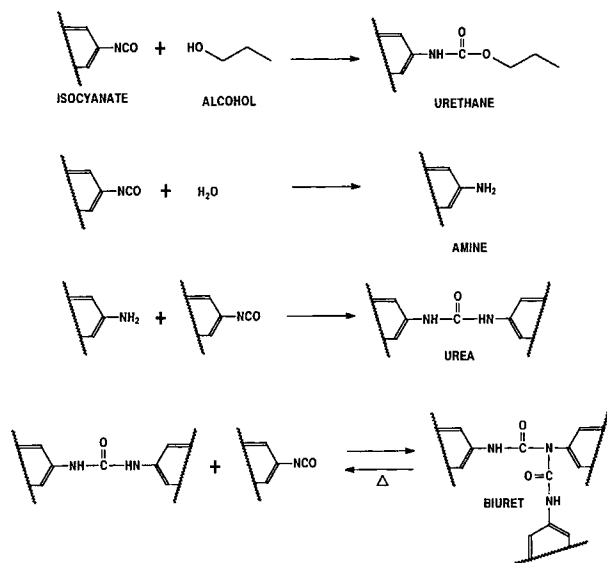
Scheme 1   Some potential reaction products in the wood/isocyanate bondline.

pMDI-bonded wood composites is the emergence of ^{15}N CP/MAS NMR for the analysis of isocyanate-based resins.[21–24] [13]C is the most common nucleus used for CP/MAS study of polymeric solids. However, the ^{13}C spectrum of pMDI-bonded wood composites is complicated by numerous overlapping resonances from the resin and the wood substrate. ^{15}N-NMR offers the advantage of direct observation of resin chemistry. No additional resonances are present from the wood substrate, and each resonance in the spectrum provides concise chemical information regarding cure chemistry. Fewer resonances combined with a broader spectral width makes interpretation of ^{15}N spectra easier for these systems. The utility of ^{15}N CP/MAS NMR for elucidating fine structural and morphological information from model ^{15}N-enriched pMDI/cellulose composites was recently demonstrated.[25] We have found that ^{15}N CP/MAS NMR does suffer from signal overlap problems; nevertheless, it has proven to be a valuable technique, as we will demonstrate.

EXPERIMENTAL

Materials

A 99% ^{15}N-labeled pMDI resin was synthesized for this study using procedures similar to industrial production.[26,27] The resin has an isocyanate content of 25.60% and is structurally similar to commercial resin according to ^{1}H and ^{13}C solution state NMR. A complete, detailed description of the resin syn-

thesis has been reported.[25] Previously, we reported an approximate number average molecular weight of the ^{15}N-labeled pMDI based on solution state ^{1}H-NMR, where the resin was thought to consist of primarily diisocyanate. Since that original report it has been discovered that the number average molecular weight based on solution state ^{1}H-NMR is badly in error. Gel permeation chromatography (using universal calibration via differential viscometry) of the resin in tetrahydrofuran reveals that the number average molecular weight is approximately 440 grams/mol with a weight average molecular weight of approximately 4500 grams/mol. Therefore, the pMDI resin used in this study has a much higher molecular weight distribution than commercial preparations. Commercial pMDI resins for wood composite manufacture typically have number and weight average molecular weights below about 500 grams/mol.

Wood flakes were cut from a block of yellow poplar, *Liriodendren tulipifera,* that was clear of visible defects and had cross-sectional dimensions of 1.90 in. by 1.95 in. The wood block was softened by immersion into water and then cut with a CAE disk flaker. All flakes were cut from the radial face of the block to a thickness of 0.012–0.015 in., followed by drying at 103 ± 2°C for 24 h. The flakes were then conditioned to various equilibrium moisture contents. In all, six wood precure moisture contents were studied: dry, 4.5%, 8%, 12%, 15%, and 31%. Flakes at 4.5% moisture were conditioned to room conditions while those at 31% were held in a sealed container over water for 24 h. Intermediate moisture contents were reached by storing over water until saturated and then removing to the open atmosphere until the desired moisture level was reached. To minimize and standardize the effects of wood surface deactivation, flakes were stored in the dark and always made into composites within 2 days of drying.

Preparation of Wood Composites

Composites were made of the ^{15}N-pMDI resin sandwiched between two wood flakes. Resin was applied in the open atmosphere using a teflon-coated spatula at a loading of 17% of the total composite weight. This resin loading was the lowest amount possible while still achieving an equal distribution of the resin over the entire surface area of one side of one wood flake. No resin was applied directly to the second wood flake. Composites were pressed between thin teflon sheets using a Micromet Instruments MP-2000 Minipress at 120°C and 50 psi platen pressure for 60 min. Samples were then placed in individual

sealed containers under anhydrous N_2 gas and stored over desiccant in a freezer to prevent postcure reactions.

Preparation of Catalyzed Wood Composites

Two yellow poplar flakes were dried at 103 ± 2°C for 24 h. A solution of phenylmercuric acetate (255 mg) in dry acetone (10 mL) was prepared. One milliliter of this solution was pipetted onto each wood flake. The flakes were then redried at 1 mmHg vacuum and 40°C for 36 h. The vacuum was released with dry argon gas, therefore eliminating any sample exposure to air. The flakes were transferred without exposure to the atmosphere to a dry argon filled glove bag, equipped with an analytical balance. The dry weight of the flakes indicated a catalyst concentration of 9.5 wt %. While still inside the glove bag, labeled adhesive was applied to one flake at a loading of 20 wt % of the total composite weight. The sample was quickly removed from the glove bag and then pressed at 50 psi platen pressure and 120°C for 60 min. After pressing there was no visible ooze out of the resin, which was characteristic of the other samples. The sample was stored and analyzed in the same fashion as the uncatalyzed samples.

Preparation of Wood–Urethane Model

Yellow poplar veneer was milled through a 60-mesh screen. The resulting powder was dried overnight at 50°C under approximately 1 mmHg vacuum. The dried wood powder (165 mg) was placed in a tripleneck flask which was equipped with a thermometer, a septum, a magnetic stir bar, and a 20-cm vigreux column. At the top of the vigreux was a short path equipped with thermometer, cooling water, vacuum, and a cow with receiving flasks. After placing the wood powder into the glassware, the entire apparatus was flamed under dry nitrogen purge, taking care not to overheat the wood powder. The wood powder was redried in the glassware under a 2 mmHg vacuum, with the flask immersed in a silicone oil bath heated to 100°C for about 3.5 h. Afterward, the flask was allowed to cool to room temperature whereupon dioxane (50 mL, freshly distilled under dry nitrogen using potassium metal) was added to the wood powder. The dioxane–wood powder suspension was heated to 80°C and stirred for 1 h under dry nitrogen. The suspension was allowed to cool and 15 mL of dioxane was removed from the flask via distillation. ^{15}N-labeled pMDI (about 490 mg) was dissolved in dry dioxane (15 mL), and phenyl mercuric acetate (25 mg) was added to the pMDI solution. This so-

lution of catalyst and pMDI was added to the reaction flask via syringe. The suspension was stirred and heated to 50°C for 18.5 h under dry nitrogen. The wood powder was then collected, filtered, and rinsed with excess acetone and dried at room temperature under about 1 mmHg vacuum overnight. No yield was determined.

NMR Measurements

^{15}N CP/MAS NMR spectra were obtained on a Bruker MSL-300 MHz spectrometer using a 7-mm Probenkopf MAS.07.D8 probe. Small circles were punched out of the composites using a paper hole puncher, randomly inserted into a zirconium oxide rotor, and filled in and around with powdered aluminum oxide to facilitate rapid spinning. Rotors were sealed with Kel-f caps. The ^{1}H channel was tuned using adamantane while ^{15}N-glycine was used to set the Hartmann-Hahn condition. Standard phase cycling was used during acquisition. CP variable contact time experiments were performed with contact times ranging from 0.2 ms to 18 ms. The proton 90° pulse was 8 μs in duration. Four hundred scans were collected for each contact time with a repetition time of 6 s. Samples were spun at 4.1 kHz, and all spectra were referenced externally to ^{15}N-glycine at 31 ppm. An additional experiment using a variable spin lock period prior to a fixed contact time of 5 ms was performed for the composites cured dry and at 8, 15, and 31% moisture. All other acquisition variables were the same as in the variable contact time experiments.

RESULTS AND DISCUSSION

Effect of Moisture on Cure Chemistry

A series of wood/^{15}N-pMDI composites were cured as a function of wood precure moisture content using 17 wt % resin, 50 psi platen pressure, and 120°C for 60 min. Yellow poplar was chosen as the wood species because its uniform texture facilitates the rapid spinning that is required for solid-state NMR. Random stacking of the composite disks inside the rotor followed by packing with powdered aluminum oxide proved effective in spinning the samples to high frequency. This affords the opportunity to study the intact bondline without disrupting the composite, as would be the case if sample grinding was necessary. While a resin loading of 17 wt % may seem high for wood-based composites, these composites have continuous bondlines. As a result, they are

probably not very different from the localized, "spot-weld" resin loadings that are characteristic of industrial wood composites which have discontinuous bondlines.

Figure 1 displays the ^{15}N CP/MAS NMR spectra of these composites as a function of wood precure moisture content. As reported for the model cellulose/^{15}N-pMDI composites,[21,25] there are four major resonances in the spectra: residual isocyanate (44 ppm), urea (104 ppm), and the amide (111 ppm) and imide (138 ppm) nitrogens of a biuret-type network. Note that there is occasionally a small shoulder at about 52 ppm present to the left of the isocyanate peak, especially in the composites cured above 12% moisture. The chemical shift of this shoulder is characteristic of an amine functional group.[21] Also present in the spectra is a minor resonance at about 130 ppm that was also noted in the model cellulose composites.[25] The identity of this signal is unknown; however, its chemical shift rules out assignment as an isocyanurate or uretidione linkage.

The spectra clearly show the dominance of water on the cure chemistry. The significant amount of biuret formation in the composite cured "dry," as shown by the intense amide and imide resonances, demonstrates the difficulty of achieving and/or maintaining complete dryness in wood. The flakes for this composite were taken directly from the oven after drying for 24 h at 103 ± 2°C; resin was then quickly applied in the open atmosphere. The total atmospheric exposure is estimated to have been 3–5 min. Nevertheless, Figure 1 shows that the moisture taken up by the flakes during that time was enough to influence the cure. That is, a small amount of urea resulted from a limited isocyanate–water reaction which then ultimately led to biuret formation. Some residual polyurea remains in the bondline, as shown by a very slight shoulder on the amide nitrogen resonance at 104 ppm (Fig. 1, Dry). There is also a significant amount of residual isocyanate.

When moisture is present at 4.5% or more, the cure is dominated by the isocyanate–water reaction and polyurea is most prevalent. However, note that biurets persist even with 31% precure moisture. The primary reaction product is polyurea, with significantly less biuret formation and residual isocyanate than in the composite cured "dry." It is interesting to note that the cure chemistry does not visibly change beyond 4.5% moisture, not even when cured as high as 31%. There does appear to be slightly more residual amine at the high precure moisture contents, but the levels of biuret formation and residual isocyanate do not appear to decrease any further.
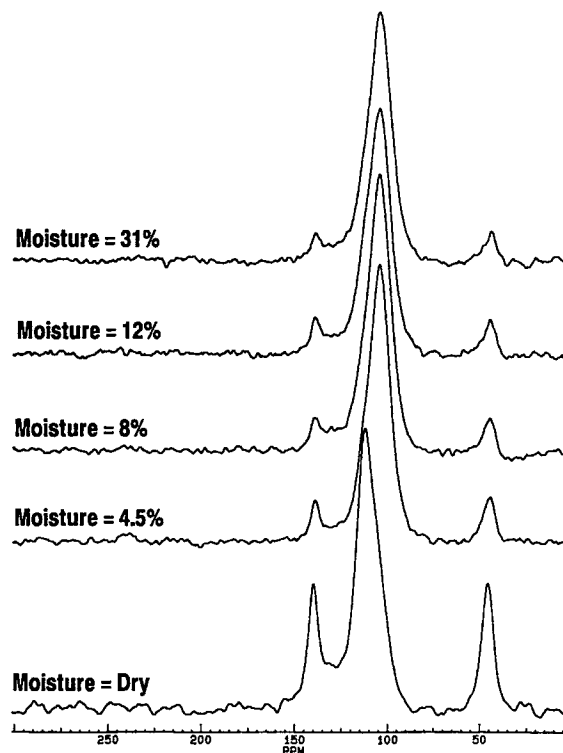

Figure 1 ^{15}N CP/MAS NMR spectra of wood/^{15}N-pMDI composites as a function of wood precure moisture content. Contact time is 2 ms and spectra are referenced to ^{15}N-glycine at 31 ppm. The spectrum for the composite cured at 15% moisture has been omitted but is identical in appearance to the composite cured at 12% moisture.

The peak intensities shown in Figure 1 can be used to approximate the relative concentrations of the various species present in the bondline. However, for a given contact time the cross-polarization and rotating-frame relaxation rates are not the same for all types of nitrogen. For variable contact time experiments, a useful equation exists for converting intensities at a given contact time to a standardized value corrected for variations in cross-polarization and rotating-frame relaxation[21,28]:

$$I_{(\tau)} = I^*(T_{1\rho H}/T_{1\rho H} - T_{NH})$$

$$\times (\exp^{-\tau/T_{1\rho H}} - \exp^{-\tau/T_{NH}}) \quad (1)$$

$I_{(\tau)}$ is the peak intensity at a given contact time, τ, and I^* is the corrected peak intensity one would obtain if cross-polarization were instantaneous and rotating-frame relaxation were infinitely slow. $T_{1\rho H}$ is the proton spin-lattice relaxation time constant in the rotating frame, and T_{NH} is the ^{1}H-^{15}N cross-polarization time constant.

Table I provides the relaxation parameters and corrected relative intensities for the major peaks of each composite. Note that only the major peak of the overlapping urea and amide resonances was assessed. Deconvolution of the resonances was not attempted. The relaxation parameters, $T_{1\rho H}$ and T_{NH}, were obtained by fitting the signal intensity versus contact time data to eq. (1). The corrected relative intensity is simply the corrected intensity for a given peak divided by the sum of all corrected intensities in that spectrum. It is in essence the relative concentration of that species in the bondline. A plot of the corrected relative intensities is shown in Figure 2. This plot corresponds to the trends observed in the ^{15}N spectra. The composite cured "dry" has a significant amount of residual isocyanate and imide-type nitrogens. When the wood precure moisture
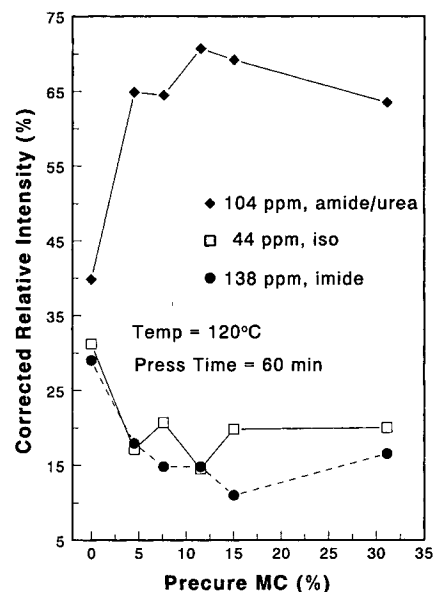

Figure 2   The corrected relative intensity, or percent composition, of the major chemical moieties present in the bondline of wood/^{15}N-pMDI composites as a function of wood precure moisture content. Values obtained from variable contact time experiments.

Table I   Relaxation Parameters and Relative Intensities Obtained from ^{15}N CP/MAS NMR as a Function of Precure Wood Moisture Content

Moisture (%)	Peak[a] (ppm)	T_{NH}[b] (ms)	$T_{1\rho H}$[b] (ms)	Corrected Relative Intensity (%)[c]
Dry[d]	44	2.8	17.4	31.2
	104	—	—	—
	111	0.10	5.8	39.8
	138	2.4	9.4	29.0
4.5	44	3.4	11.7	17.1
	104	0.11	5.3	64.9
	111	—	—	—
	138	3.7	6.6	17.9
8	44	6.6	6.5	20.7
	104	0.18	4.7	64.5
	111	—	—	—
	138	4.8	6.3	14.8
12	44	3.1	14.9	14.5
	104	0.10	5.3	70.7
	111	—	—	—
	138	2.8	9.8	14.8
15	44	6.8	6.7	19.8
	104	0.09	5.0	69.2
	111	—	—	—
	138	2.6	9.3	11.0
31	44	6.6	6.4	20.0
	104	0.09	4.9	63.5
	111	—	—	—
	138	5.7	5.6	16.5

Cured at 17 wt % resin, 120°C, 50 psi, for 60 min.
[a] Chemical shifts of ^{15}N resonances referenced to glycine at 31 ppm.
[b] Calculated from CP variable contact time experiments. Mean error is ±15% for T_{NH} and ±16% for $T_{1\rho H}$.
[c] Calculated from corrected peak intensities at a contact time of 4 ms.
[d] Wood flakes were dried at 103 ± 2°C for 48 h.

content is increased to 4.5%, a large increase in the polyurea concentration is noted along with accompanying decreases in the imide nitrogen and residual isocyanate concentrations. The relatively flat slopes in Figure 2 for all nitrogen species beyond 4.5% moisture are consistent with the earlier observation that the cure chemistry remains relatively unchanged beyond this moisture level.

In the previous work on ^{15}N CP/MAS NMR of pMDI-bonded cellulose composites, the unusual cross-polarization behavior of nonprotonated nitrogens was first noted.[25] The same effect has been found for the data presented here, which renders the information in Figure 2 as only qualitative. The signal correction employed for the corrected relative intensities normally provides accurate quantitative information, as in the case of ^{13}C-NMR. However, the extremely slow cross-polarization of nonprotonated nitrogens in these samples compromises the accuracy of this correction. Previous variable contact time experiments have demonstrated that the nonprotonated isocyanate and imide nitrogens cross-polarize very slowly with T_{NH} constants of the same magnitude as the $T_{1\rho H}$.[25] The same is true of the samples shown in Table I. In a variable contact time experiment, the very slow cross-polarization of nonprotonated nitrogens artificially inflates the $T_{1\rho H}$ relaxation.[25] We were first alerted to this effect when noticing the $T_{1\rho H}$ values listed for the sample cured

"dry" (Table I). The imide and amide biuret nitrogens of the cured dry sample have significantly different values for $T_{1\rho H}$. This typically implies that the two nuclei reside in separate phases with distinct mobilities and/or spin coupling. However, this conclusion seems unlikely when considering that the imide and amide nitrogens of a biuret are separated by no more than a single carbon atom. Four of the same samples shown in Table I were reanalyzed using a variable spin locking period prior to a fixed contact time. This experiment eliminates the convolution of cross-polarization and proton rotating-frame relaxation processes. The results of these experiments (Table II) indicate that all protons relax rapidly over a range of 3.2 to 4.0 ms. Especially notable is the comparison of the results in Tables I and II for the sample cured dry (note that these results represent two experiments performed on the same sample). Table I suggests that the cured dry sample has a phase-separated bondline with three motionally distinct domains. However, Table II demonstrates that all three nitrogens in the cured dry sample exhibit the same $T_{1\rho H}$, indicating that they probably exist within a homogeneous continuum. Clearly, the samples that were reanalyzed (with the variable spin lock prior to a fixed contact time) are motionally homogeneous and appear not to be phase separated. This must also apply to all of the samples discussed here. Comparison of Tables I and II shows that variable contact time experiments give approximately correct values of $T_{1\rho H}$ for protonated nitrogens, and often give severely inflated values of $T_{1\rho H}$ for nonprotonated nitrogens. Consequently, the absolute values of the corrected relative intensities listed in Table I must be suspect; therefore, only the trends in Figure 2 should be considered reliable.

Notably absent from Figure 1 is any clear indication of urethane formation. As previously mentioned, urea, biuret, and residual isocyanate are identified. Even the composite that was cured dry appears to be dominated by the small amount of moisture that was present. A suitable catalyst, phenylmercuric acetate, was employed in an attempt to force the isocyanate/wood reaction so that a representative urethane resonance could be obtained for comparison. Phenylmercuric acetate has been demonstrated to promote effectively the isocyanate/ hydroxyl reaction (even secondary hydroxyls) in urethane systems while hindering the isocyanate/ water reaction.[29] The ^{15}N CP/MAS spectrum of this composite displays a prominent resonance centered at 103 ppm, and also peaks for residual isocyanate and biuret (Fig. 3, middle). The biuret linkage in this catalyzed composite indicates that this sample

Table II $T_{1\rho H}$ Values Measured Using a Variable Spin Lock Period Prior to a Fixed Contact Time for Several Wood/^{15}N-pMDI Composites

Precure Moisture Content	^{15}N Resonance[a]		
	44 ppm	104/111 ppm	138 ppm
Dry[b]	3.7[c]	4.1 (111 ppm)	4.0
8%	3.5	3.7 (104 ppm)	3.6
15%	3.2	3.7 (104 ppm)	3.3
31%	3.4	3.3 (104 ppm)	3.5

A contact time of 5 m was used for these experiments.
[a] Chemical shifts of ^{15}N resonances referenced to glycine at 31 ppm.
[b] Composites were cured at 17 wt % resin, 120°C, and 50 psi platen pressure for 60 min.
[c] All $T_{1\rho H}$ measurements are listed in ms. Mean error of these values is ±6%.

is still affected by the isocyanate–water reaction. Therefore, it became necessary to take great care in the preparation of strictly anhydrous conditions for the synthesis of a wood–urethane model compound that is not affected by water. The conditions for the preparation of this model compound are listed in the experimental section. Figure 3 compares three spectra: (1) a composite that was cured at 4.5% moisture, (2) the phenyl mercuric acetate catalyzed composite, and (3) the wood–urethane model compound that was prepared under extremely anhydrous conditions. Figure 3 indicates that the wood–urethane model compound appears unaffected by water since the biuret signal is absent. The comparison in Figure 3 demonstrates that the urea and urethane resonances are almost perfectly overlapping. Even though the wood–urethane chemical shift is slightly lower than urea, it is evident that very large amounts would have to be present before it would be noticeable in the spectrum. Significant quantities of urethane formation might become evident as a broadening on the right of the urea resonance (in fact, this is a finding that we have observed under different curing conditions, as will be reported in a subsequent publication). Nevertheless, it is reasonable to conclude that very little urethane formation is taking place in these samples. That is, the conditions which are most likely to permit urethane formation are those where the more competitive moisture reaction is inhibited. This is when wood is dry. Notice that no signal is present at 100 ppm for the composite cured dry. Because the urethane reaction is most probable when the substrate is dry, and because the urethane is absent for the sample cured dry, it is reasonable to conclude that urethane formation
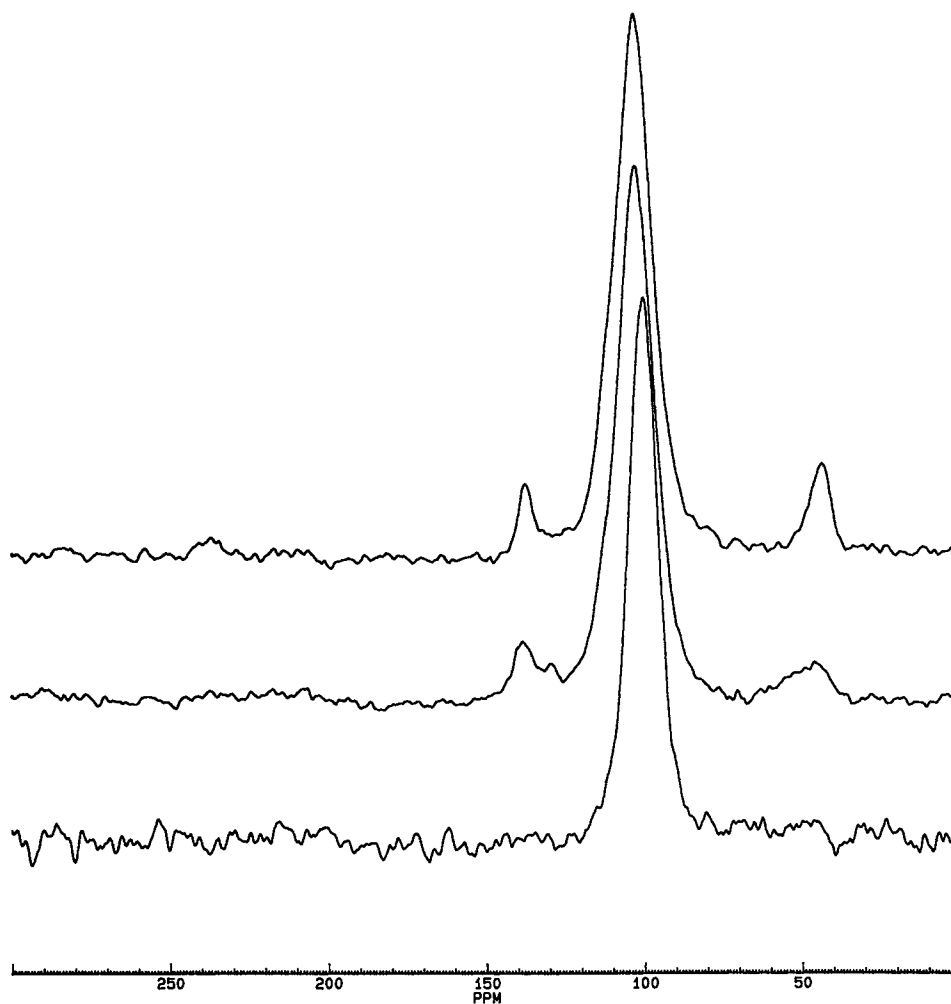
Figure 3 ^{15}N CP/MAS NMR spectra of a wood/^{15}N-pMDI composite cured at 4.5% moisture (top) and a wood/^{15}N-pMDI composite cured dry with 9.5% phenylmercuric acetate catalyst (middle). The bottom spectrum is the ^{15}N CP/MAS NMR spectra of a model wood–urethane synthesized under extremely anhydrous conditions.

is minimal or absent in these samples. These conclusions are consistent with the recent findings of Weaver and Owen, who state that the isocyanate–water reaction is dominant.[7] Of course, the overlap of the urea and urethane signals, as demonstrated in Figure 3, prevents us from excluding the possibility of urethane formation in those composites cured at 4.5% and higher moisture contents. One should note that at 4.5% moisture, there are about 2.4 equivalents of water per equivalent of isocyanate functional group.

CONCLUSIONS

1. Wood/^{15}N-pMDI composites were cured as a function of wood precure moisture content.

^{15}N CP/MAS NMR spectra show four prominent resonances: residual isocyanate (44 ppm), polyurea (104 ppm), and the amide (111 ppm) and imide (138 ppm) nitrogens of a biuret type network.

2. Dry wood flakes did bond together, but the cure chemistry is primarily biuret-type structures from the isocyanate reaction with small amounts of moisture.

3. When the precure moisture content is increased to 4.5%, the cure chemistry is primarily polyurea-type structures with less biuret formation and residual isocyanate. There does not appear to be much change in the cure chemistry beyond 4.5% moisture.

4. It is unlikely that urethane formation can be detected in wood/^{15}N-pMDI composites by

this technique unless present in very significant amounts. Overlap with the urea resonance makes it otherwise unresolvable.

5. Variable contact time experiments produce artificially inflated $T_{1\rho H}$ values for nonprotonated nitrogens due to the interaction of cross-polarization and rotating-frame relaxation processes.

6. $T_{1\rho H}$ values obtained from experiments using a variable spin lock period prior to a fixed contact time indicate that the cured resin in these composites is probably a homogeneous continuum.

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