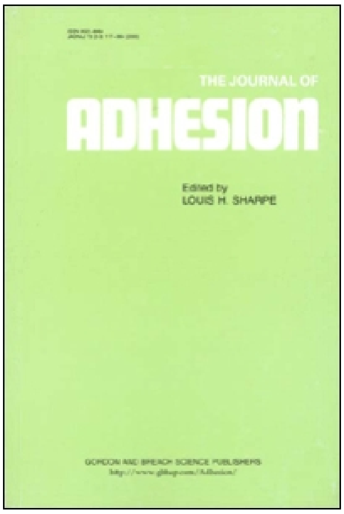

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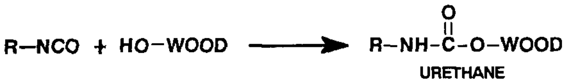
A 99% ^{15}N-labeled polymeric diphenylmethane diisocyanate (pMDI) resin with desirable adhesive properties was synthesized. This adhesive was used to make a series of cellulose/^{15}N-labeled pMDI composites at various cellulose precure moisture contents. Cure chemistry and bondline morphology were monitored using ^{15}N CP/MAS NMR. Biuret-type structures were identified as the predominant chemical moieties at low precure moisture conditions, while urea linkages were predominant at higher precure moisture. Significant amounts of urethane were not detected, however low amounts could be obscured by signal overlap. Relaxation studies using variable contact times were complicated by excessively long cross-polarization rates for nonprotonated nitrogens. Experiments using variable spin lock times prior to fixed contact periods suggest that the cured resin is homogeneous. The utility of ^{15}N CP/MAS for elucidating fine structural and morphological information from complex isocyanate-cured composites is clearly demonstrated.

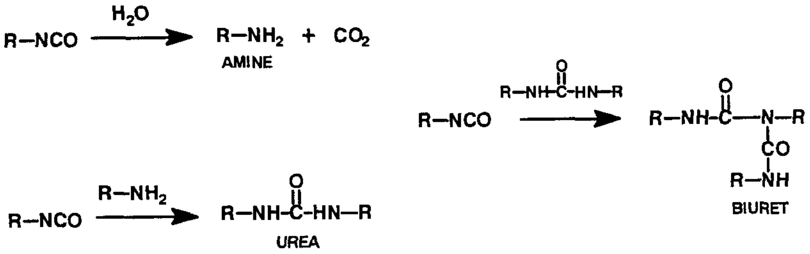
KEY WORDS: wood; polymeric methylene bis(4-phenylisocyanate); ^{15}N CP/MAS NMR; cellulose; cross-polarization; proton rotating frame T_1 relaxation; solid-state NMR; wood composites

INTRODUCTION

Polymeric methylene bis(4-phenylisocyanate), pMDI, is a wood adhesive which has been shown to provide excellent composite board properties.[1–5] The mechanism of pMDI-to-wood adhesion likely involves molecular entanglements[1] as well as secondary interactions between the adhesive and the wood substrate.[6] It has also been postulated that covalent linkages between isocyanate and wood contribute to the excellent adhesive properties found in pMDI-based resins.[2,3] Certainly, the polyhydroxylic nature of wood provides ample opportunity for these reactions (Scheme I). However, it also ensures the presence of adsorbed moisture at all times. This means that the isocyanate reaction with water to form ureas and various biuret-type structures (Scheme II) 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. In response to these issues, this study was undertaken for the purpose of developing a method for probing the isocyanate cure chemistry and morphology in pMDI bonded wood composites.



SCHEME I The proposed reaction between isocyanate and wood.



SCHEME II The expected products from the isocyanate reaction with water.

The study of isocyanate-wood adhesion began with the work of Morak and coworkers.[7–9] They learned that diisocyanates readily reacted with cellulosic fibers, thus increasing the strength of paper products. Rowell *et al.* extended this by demonstrating the stability of urethane bonds formed between wood and isocyanates under specialized conditions.[10–12] Later, Owen and coworkers founded some of the first chemical analyses that had a direct bearing upon the adhesive mechanism in wood-isocyanate bonding.[6,13] They demonstrated by infrared spectroscopy that urethane bonds could be formed under anhydrous conditions when an excess of isocyanate was used on powdered wood.[6] Others have used FTIR and DSC to reveal the domination of polyurea formation when moisture is present.[6,14] Most studies to date, however, have utilized special conditions such as small, monofunctional isocyanates[10–13] and the use of wood-swelling solvents as a carrier of the isocyanate into the wood microstructure.[13] Studies of the wood-isocyanate reaction under conditions common to gluing operations (*i.e.*, the production of oriented strand board) are lacking. This shortage of information is likely due to the chemical complexity of wood and the associated problems with techniques such as infrared spectroscopy which gives multiple overlapping signals in the carbonyl region when observing isocyanate-bonded wood.

This paper introduces ^{15}N CP/MAS NMR as a technique for probing these complex composite systems. Model cellulose/pMDI composites were chosen for study prior to wood composites in order to establish the feasibility of this technique. CP/MAS NMR is ideally suited for the study of cured resin systems.[15–19] In particular, the usefulness of this technique for studying wood adhesives has been expressed.[20] CP/MAS NMR allows the study of molecular phenomena within the composite without disrupting the solid state. Molecular events in the solid give rise to the macroscopic performance of materials and, as such, makes study of the intact solid most interesting.

^{13}C CP/MAS is the most common magnetic resonance technique used to probe polymeric solids. However, the ^{13}C spectrum of a pMDI composite is complicated by overlapping resonances from the resin and the substrate. For example, Figure 1 shows

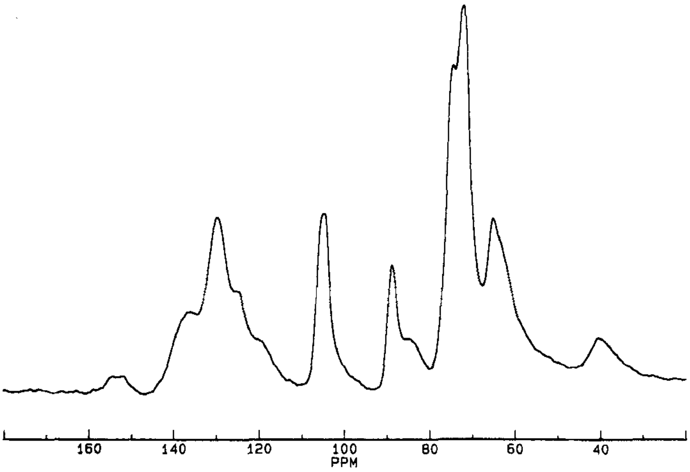
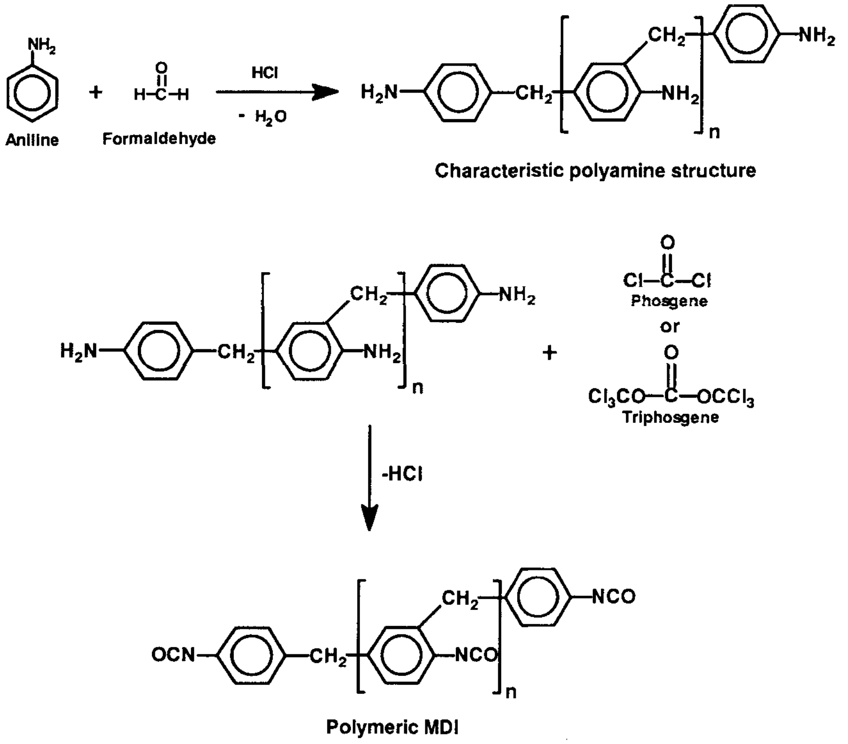


FIGURE 1 ^{13}C CP/MAS NMR spectrum of cellulose/^{15}N-enriched pMDI composite. The resin loading was 43 weight %. The composite was cured at 120°C for 60 minutes under 88 psi of platen pressure.

the ^{13}C solid-state NMR spectrum of a cellulose composite (Fisher brand cellulose filter paper, type P8) cured with pMDI (resin content 43 weight % of total composite). Cellulose resonances are confined to the area between 110 and 60 ppm. The cured resin is observed at 40 ppm (methylene carbon), 115 to 145 ppm (isocyanate carbonyl, 125 ppm, and aromatic carbons) as well as from 148 to 158 ppm (urea and biuret carbonyl). Figure 1 demonstrates that structural information is obscured by signal overlap within the resin. The complexity is greater when the substrate is wood, where lignin resonances will completely obscure the carbonyl signals of the resin. Furthermore, isotopic enrichment is required in order to enhance detection at the low resin loadings typical of industrial practice. From this point alone, ^{15}N-labeling is preferred because of the relative simplicity of placing the nitrogen label directly in the isocyanate functional group. Placement of ^{13}C within the isocyanate functional group is possible, but much more synthetically challenging. In addition, ^{15}N NMR offers the advantage of direct observation of the resin chemistry. No additional resonances are present from cellulosic or wood substrates, and each resonance from the resin provides concise information regarding cure chemistry. Fewer resonances, combined with a broad spectral width, makes interpretation of ^{15}N spectra easier for these systems. Indeed, the advantages of ^{15}N CP/MAS over ^{13}C experiments have recently been demonstrated for the study of MDI-based resin systems.[21–24] The disadvantages associated with using the ^{15}N nucleus include low natural abundance (0.37%) and a small magnetogyric ratio, both of which usually make isotopic enrichment necessary in order to increase sensitivity.

As a result, this project began by studying the variables of pMDI synthesis so that a 99% ^{15}N-enriched pMDI resin with good adhesive properties could be made. The synthesis of pMDI is a two-step reaction beginning with the HCl catalyzed condensation of aniline with formaldehyde. The second step is the conversion of the resulting polyamine to polyisocyanate by phosgenation (Scheme III). Much of the information



SCHEME III The simplified, overall reaction pathway for pMDI synthesis.

regarding the aniline/formaldehyde condensation is proprietary and the literature that is available is lacking in detail.[25–29] Since the formation of a suitable polyamine is critical for the synthesis of a fluid resin, it was necessary to begin this study with a cursory examination of the aniline/formaldehyde condensation reaction.

EXPERIMENTAL

Materials

For the initial study of the aniline/formaldehyde condensation reaction, aniline was purchased from Aldrich Chemical and distilled under vacuum. 37% aqueous formaldehyde solution and 37% aqueous hydrochloric acid were purchased from Aldrich Chemical and used as received. 99% ^{15}N-enriched aniline was purchased from Cambridge Isotope Laboratories and used as received to prevent loss of the starting material. The labeled aniline was deep yellow in color, indicating that some impurities were present. Phosgenations were carried out using triphosgene purchased from Aldrich Chemical. Cellulose substrates were Fisher brand cellulose filter papers, Type P8. A commercial pMDI resin (Rubinate, MF-184, NCO content: 31.5%) was obtained from ICI Polyurethanes for purposes of comparison with the labeled resin made here using solution state NMR.

METHODS

Polyamine Synthesis

Three aniline: HCl molar ratios were studied prior to synthesis of a ^{15}N-enriched material: 1.0:1.5, 1.5:1.0, and 3.0:1.0. In all cases, 4g (0.043 mol) aniline were used while the amount of 37% aqueous HCl solution was varied from 5.3 ml (0.0645 mol) to 2.4 ml (0.0287 mol) to 1.2 ml (0.0143 mol). The reaction apparatus was a 50 ml, 3-neck, round-bottom flask equipped with a magnetic stir bar, septum, thermometer, condenser, and dry N_2 gas source. The HCl solution was added first and diluted to 6N with distilled water. The reaction flask was submerged in a cold water bath to maintain the flask temperature below 50°C. Aniline was added slowly with stirring, followed by 37% aqueous formaldehyde (1.45 ml, 0.0194 mol) added dropwise with rapid stirring. Reaction mixtures were then refluxed for lengths of 2, 12, 17, and 24 hours. The reaction mixtures were allowed to cool to room temperature and then added to a separatory funnel containing 30 ml chloroform. The aqueous layer was neutralized with 10 N NaOH and then extracted with three 25 ml portions of chloroform. The combined organic phase was washed thoroughly with water and then dried over excess Na_2SO_4. Residual aniline was removed by vacuum distillation at 4 mm Hg up to a maximum temperature of 125°C.

Phosgenation of Polyamines

The polyamine was dissolved in 11 times its weight of dry 1, 2-dichlorobenzene. Amine content was estimated based on two assumptions: 1) complete conversion of formaldehyde to methylene groups in the polyamine structure, and 2) complete conversion of secondary amine to primary amine.[29] Moles of formaldehyde used is, therefore, assumed to be equal to the moles of methylene groups (0.0194 mol) formed in the product. The weight of the polyamine, minus the theoretical weight of methylene groups, is assumed to be that of dehydroaniline from which the amine content can be estimated. 1.14 times the theoretical amount of triphosgene required for complete conversion of polyamine to polyisocyanate was dissolved in 10 times its weight of dry 1,2-dichlorobenzene. A 100 ml, 3-neck, round-bottom flask was equipped with a large magnetic stir bar, septum, thermometer, condenser, and dry N_2 gas. The entire apparatus was thoroughly flamed under a slow N_2 gas purge before adding reagents. The reaction flask was immersed into a cold water bath and the triphosgene solution was added to the flask, followed by the polyamine solution added as a continuous stream through a 19-gauge cannula. After the polyamine solution was added, the cold water bath was replaced with a silicone oil heating bath and heating was started. The maintenance of an inert atmosphere and extremely vigorous stirring are critical throughout the reaction. The reaction mixture was heated rapidly to 175°C where it was held for 30 minutes. The temperature was reduced to 150°C and the solution degassed for 15 minutes by blowing N_2 gas directly into the solution through a 19-gauge syringe needle. After transferring the solution to a 100 ml round-bottom flask, the 1,2-dichlorobenzene was removed by vacuum distillation at roughly 10 mm Hg and 90°C. In order to remove chlorine-containing impurities and to break down uretedione linkages formed by the dimerization of isocyanate,[28,29] the product was heat treated at 195°C for 5 minutes followed by degassing at 195°C for an additional 5 minutes. The isocyanate was quench-cooled by spraying the reaction flask with acetone and then submerging the flask in a cold water bath. The isocyanate content was measured using a modified version of ASTM Standard D 5155–91, Test Method C, where the standard procedure was scaled down to 10% of the stated volumes. This technique was practiced on a commercial resin with good precision and less than a 3% degree of error from the manufacturer's stated isocyanate content. Two tests were performed on the ^{15}N-pMDI resin synthesized in our lab. The two tests produced very similar results with an average isocyanate content of 25.60%.

Preparation of Cellulose Composites

Fisher brand cellulose filter papers, Type P8, were conditioned to various equilibrium moisture contents by storing over saturated salt solutions. Composites were made of the ^{15}N-labeled pMDI sandwiched between two filter papers. Resin was applied in the open atmosphere, using a Teflon-coated spatula, at a loading of 25% of the total composite weight. This resin loading was determined to be the lowest amount possible while still achieving equal distribution over the entire surface area of one side of one of the filter papers. No resin was applied directly to the second filter paper. Composites were pressed between thin Teflon sheets using a Micromet Instruments MP-2000 Minipress at 120°C and 50 psi platen pressure for 60 minutes. Samples were then placed in individual sealed containers under N_2 gas and stored over desiccant in a freezer to prevent postcure reactions.

NMR Measurements

All solution-state NMR measurements were obtained on a Varian Unity-400 MHz spectrometer. ^{1}H and ^{13}C spectra were referenced to tetramethylsilane at 0 ppm.

^{15}N CP/MAS 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 composite using a paper hole puncher, loaded 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 10 μsec in duration. 200 scans were collected for each contact time with a repetition time of 6 seconds. Samples were spun at 4.1 kHz and all spectra were referenced externally to ^{15}N-glycine at 31 ppm. Three separate experiments were performed using a variable spin-lock period prior to fixed contact times of 1.5, 3.0, and 5.0 msec. In these experiments the proton 90° pulse was 8 μsec in duration and all other parameters were as stated above.

RESULTS AND DISCUSSION

Synthesis of pMDI Resin

The formation of a suitable polyamine is critical for the synthesis of a fluid pMDI resin. As the literature has shown,[29] polyamine molecular weight is influenced primarily by three variables: 1) aniline: formaldehyde ratio, 2) aniline: HCl ratio, and 3) reaction time. Without tight control of these three variables, the resin may either be too viscous or even completely solid at room temperature.

As mentioned in the literature,[28,29] we found that an aniline: formaldehyde ratio of 2.2:1.0 yields favorable resin properties so this variable was not studied further. Table I displays the results of three sets of experiments performed to study the effects of aniline: HCl ratio and raction time. The number average molecular weight can be obtained from the ratio of the integrals of the aromatic protons (6.9–7.6 ppm) to the benzylic protons (3.5–4.1 ppm) obtained from solution state ^{1}H NMR. From the characteristic polyamine structure in Scheme III, we can define an upper theoretical limit for this ratio of 4.0 for pure methylenedianiline ($n = 0$) and a lower limit of 1.5 for infinite molecular weight material ($n = \infty$). The ratios in Table I indicate that the polyamines synthesized are primarily $n = 0$, with lesser amounts of $n > 0$ material.

Table I indicates that increasing the aniline: HCl ratio favors the production of methylenedianiline. Note that at an aniline: HCl ratio of 3.0:1.0 the dimer was essentially produced at all reaction times. The effect of reaction time can be seen to be dependent on the aniline: HCl ratio. At a ratio of 1.0:1.5, molecular weight increases with reaction time from 2 to 17 hours and then for unknown reasons decreases after 24 hours of reaction. When the ratio is reversed to 1.5:1.0, molecular weight decreases with reaction time over the same range. After 17 hours the polyamine becomes essentially dimer, but then increases in molecular weight after 24 hours of reaction. While no error anlaysis is given for the integral ratios in Table I, we believe that the minor molecular weight differences shown are indeed significant. It should be mentioned that the

TABLE I
Molecular Weight Characteristics of Polyamines by Solution State ^{1}H NMR

Aniline: HCl Ratio	Reaction Time (hrs)	Aromatic: Benzylic Proton Ratio[a]	Number Average Molecular Wt.
1.0:1.5	2	3.6	232
	12	3.4	248
	17	3.3	257
	24	3.4	248
1.5:1.0	2	3.6	232
	12	3.7	223
	17	4.0	198
	24	3.7	223
3.0:1.0	2	4.0	198
	12	4.0	198
	17	4.0	198
	24	4.0	198

[a] Determined from integration of the corresponding regions in solution state ^{1}H NMR spectra.

conditions of the aniline: formaldehyde condensation control the substitution pattern of the resulting methylenedianiline as well as that of the higher polyamines.[29] There are three possible diamine isomers, namely 4,4'-, 2,4'-, or 2,2'-methylenedianiline (Their relative occurrence decreases from left to right due to the steric hindrance of substitution ortho to the primary amine.). The precise methylenedianiline isomer ratio was not determined in this study, however ^{1}H NMR suggests that an excess of 90% of the isomers are 4,4'-methylenedianiline. We will return to this point later in the discussion of the structure of the ^{15}N-labeled pMDI.

Using the optimum conditions for the polyamine condensation reaction as determined from the previous experiments, a ^{15}N-labeled polyamine was synthesized. The reaction was scaled up from previous experiments, starting with 10g ^{15}N-aniline. Aniline: HCl was chosen to be 1.0:1.5 because this provided a suitable polyamine for the synthesis of a fluid pMDI resin. A reaction time of 6 hours was chosen because the product viscosity was favorable and the concentration of residual secondary amine is minimized. (This secondary amine is an intermediate formed during the condensation.[29] If present during the subsequent phosgenation, the secondary amine forms secondary carbamoyl chlorides which remain as impurities in the resin.) As in the previous experiments, triphosgene was used to carry out the phosgenation. Triphosgene is a crystalline solid which has been shown to be an effective substitute for the highly toxic phosgene gas.[30] The resulting ^{15}N-pMDI resin was produced in high yield ($>$ 90%); it was fluid with an isocyanate content of 25.60%. Commercial isocyanate resins used in the wood industry normally have isocyanate contents on the order of 30%. We suspect that the reduced isocyanate content obtained here is due to the presence of impurities resulting from the phosgenation of the residual secondary amine mentioned above. Evidence for this is shown in Figure 2 where the ^{1}H NMR of the ^{15}N-pMDI is compared with a commercial pMDI resin. The labeled resin exhibits a minor peak near 4.88 ppm which may correspond to the benzyl protons of an N-benzylcarbamoyl chloride. Otherwise, the ^{15}N-pMDI resin appears very similar in structure to the commercial resin. Figure 2 also shows that both resins are primarily composed of the 4,4'-isomer. This is qualitatively judged by the appearance of the *para* substitution pattern which appears as two strong and symmetrical doublets in the aromatic region. Smaller signals which deviate from the two doublets are primarily from 2,4'-isomer as well as higher polyisocyanates. The 2,2'-isomer is likely negligible, if present at all. Careful inspection of the aromatic region indicates that the commercial resin displays a slightly higher concentration of 4,4'-isomer. Figure 3 compares the ^{13}C solution NMR of the same samples. Here again the structural similarity of the ^{15}N-labeled resin to the commercial resin is apparent. In summary, the ^{15}N-labeled resin has an isocyanate content of about 26% (slightly less than commercial preparations), a number average molecular weight of approximately 240 g/mole which means that most of the resin consists of monomeric MDI, and the monomer is predominately the 4,4'-isomer.

^{15}N CP/MAS NMR

Model cellulose/^{15}N-pMDI composites were examined in this study to test the feasibility of this method for solid wood composites. A series of composites using

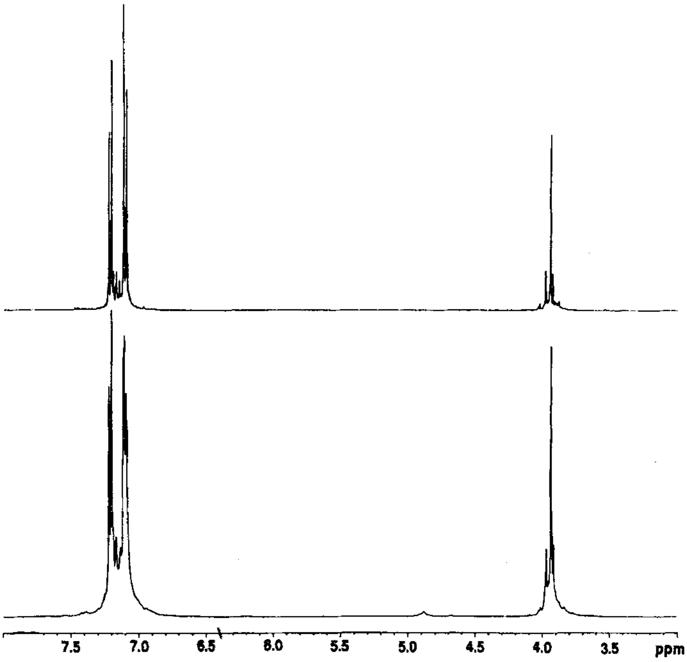


FIGURE 2 Solution state ^1H NMR spectra of ^{15}N-enriched pMDI (bottom) compared with a commercial pMDI resin (top). Samples were run in acetone-d_6 and referenced to tetramethylsilane at 0 ppm.

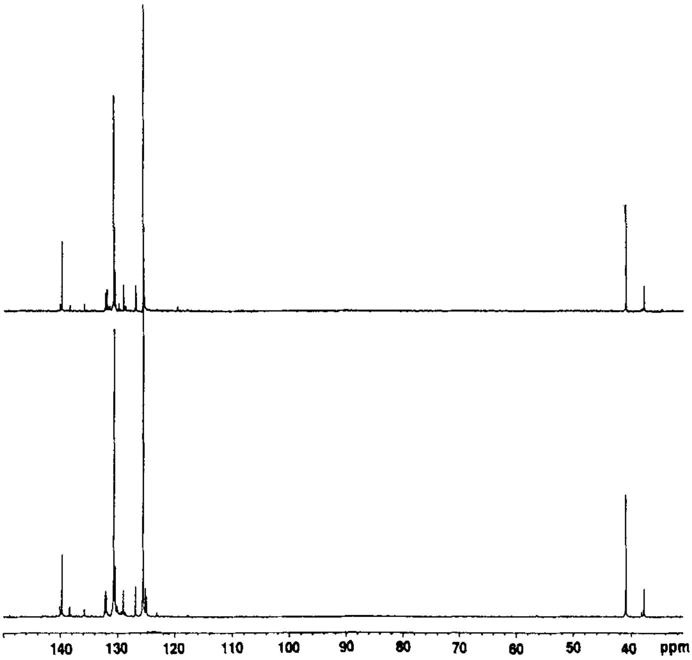


FIGURE 3 Solution state ^{13}C NMR spectra of ^{15}N-enriched pMDI (bottom) compared with a commercial pMDI resin (top). Samples were run in acetone-d_6 and referenced to tetramethylsilane at 0 ppm.

different cellulose precure moisture contents were cured at 25 wt.% resin, 50 psi, and 120°C for 60 minutes. While this may seem to be a very high resin loading, it must be emphasized that these composites have continuous bondlines. 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 4 displays the effect of moisture on the cure chemistry. Four distinct resonances are present in the spectra. The resonance at 44 ppm is due to residual isocyanate. The resonance at 104 ppm corresponds to urea nitrogens formed by the reaction of isocyanate with amines, the amines being produced by the reaction of isocyanate with water. Further reaction of urea with isocyanate is shown by the presence of amide (111 ppm) and imide (138 ppm) nitrogens of a biuret network. Note that a small shoulder appears on the isocyanate peak at 52 ppm for the composite cured at 23% moisture content. The chemical shift of this shoulder corresponds to nitrogens of an amine functional group. Identification of resonances is based upon ^{15}N chemical shifts previously reported in the literature for isocyanate-based resins.[21] Note that there is also a small resonance at 130 ppm. This resonance is particularly noticeable for the composite cured at 2% moisture, but visibly decreases at the higher moisture levels. The exact identity of this resonance is currently unknown, but it displays a slow cross-polarization rate characteristic of a nonprotonated species. Based solely on the

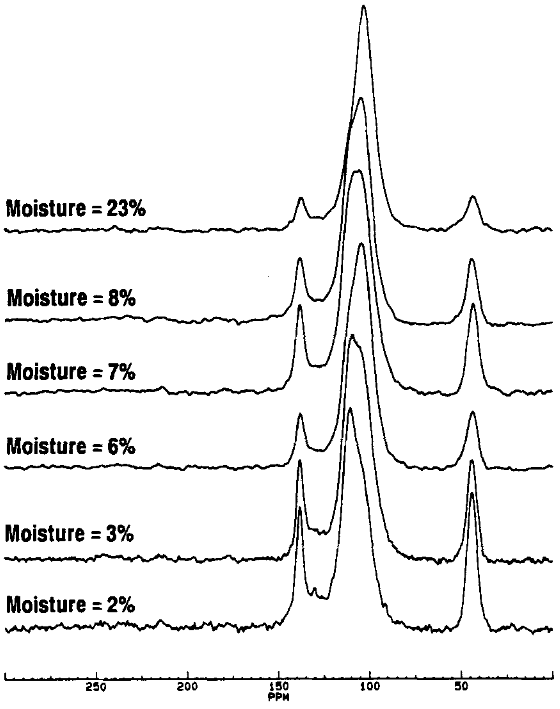


FIGURE 4 ^{15}N CP/MAS NMR spectra of cellulose/^{15}N-enriched pMDI composites as a function of cellulose precure moisture content. Contact time is 2 ms and spectra are referenced to ^{15}N-glycine at 31 ppm.

chemical shift, it is unlikely that this resonance is from uretedione (δ 145 ppm[21]) or isocyanurate (δ 149 ppm[21]) linkages, which are formed by the dimerization and trimerization of isocyanates, respectively.

The spectra clearly show the dominance of water on the cure chemistry. At low moisture contents ($< 3.3\%$) the isocyanate reacts first with water to form primary amines, which, in turn, react with isocyanate to form polyureas. Much of the polyurea also reacts with residual isocyanate to form biuret structures. Some residual polyurea remains as revealed by the shoulder at 104 ppm on the amide nitrogen resonance (Figure 4, 2% MC). As the moisture is increased to 6%, the cure chemistry shifts to primarily polyurea type structures. The high concentration of water molecules, combined with their greater mobility, results in less biuret formation. The amide nitrogen is reduced to a shoulder at 111 ppm on the urea nitrogen resonance and a significant decrease in imide nitrogen (138 ppm) intensity can also be noted. When the cellulose is saturated at 23% moisture, an overwhelming dominance of urea formation is noted.

Urethane formation is not detected in any of the samples. In fact, on three separate attempts dry cellulose papers did not bond under the curing conditions described earlier. In each instance of bonding dry papers, the composites were easily peeled apart by hand after pressing and most of the resin remained as a liquid. (This is in contrast to yellow poplar, *Liriodendren tulipifera*, wood flakes which did cure after being rigorously dried. The discussion of these wood composites will be saved for a future publication). Only upon addition of a suitable catalyst, stannous octoate, was adhesion of the dry papers, achieved. The cure chemistry of this catalyzed composite shows a prominent peak at 103 ppm which corresponds to the urethane nitrogen formed by reaction between isocyanate and cellulose hydroxyls (Figure 5). Note also the difficulty of achieving complete dryness with cellulosics as some biuret formation still occurs. Also shown in Figure 5 are the urethane product from the reaction of ^{15}N-pMDI with dry methanol and, for comparison, a cellulose composite cured at 2% moisture. There does not appear to be a significant amount of urethane formation, if any, in the composite even when cured at such a low moisture content. The long press time of 60 minutes was chosen to establish a reference point of "complete cure". This will serve for comparison in future studies employing cure times more representative of industrial practice. It is evident that amide, urea, and urethane nitrogens are not well resolved in ^{15}N solid-state spectra. Therefore, it is conceivable that low amounts of urethane formation are undetectable.

The peak intensities shown in Figure 4 can be used to approximate the relative concentrations, of the various species present in the bondline. However, for a given contact time, cross-polarization and proton rotating-frame relaxation rates are not the same for all types of nitrogen. Direct comparisons of intensities at a given contact time are, therefore, inaccurate. A useful equation exists for converting intensities at a given contact time to a standardized value corrected for variations in rotating-frame and cross-polarization relaxation rates.[21,31]

$$I(\tau) = I^*(T_{1\rho H}/T_{1\rho H} - T_{NH})(\exp^{-\tau/T1\rho H} - \exp^{-\tau/TNH}) \qquad (1)$$

$I(\tau)$ is the nitrogen magnetization at a given CP contact time, τ, and I^* is the nitrogen magnetization one would obtain if cross-polarization were instantaneous and rotating-

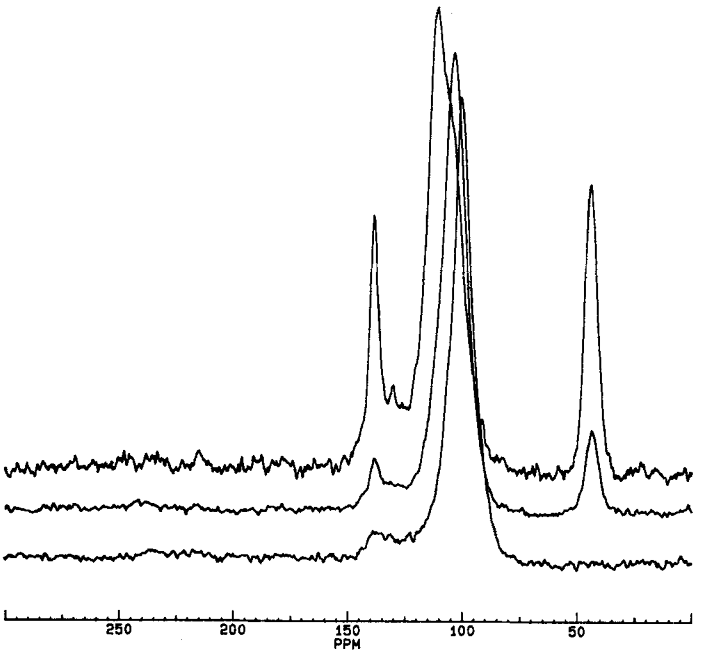


FIGURE 5 ^{15}N CP/MAS NMR spectra of cellulose/^{15}N-pMDI composite cured at 2% moisture (top), cellulose/^{15}N-pMDI composite cured dry with 1% stannous octoate (middle), and the urethane product from reaction of ^{15}N-pMDI with dry methanol (bottom).

frame relaxation were infinitely slow. I^*, then, is the corrected intensity in which we are interested. $T_{1\rho H}$ is the spin-lattice relaxation time in the rotating frame and T_{NH} is the ^1H-^{15}N cross-polarization time constant.

Table II provides the relaxation parameters and corrected relative intensities for the major peaks of each composite. The relaxation parameters, T_{NH} and $T_{1\rho H}$, are obtained by fitting the signal intensity *versus* contact time data to Equation (1). The corrected relative intensity is simply the corrected intensity for a desired peak divided by the sum of all corrected intensities. It is, in essence, the percent composition of each chemical moiety present at the bondline. (We have found that the signal-correction technique employed here is complicated by the unique cross-polarization character of these samples. The resulting corrected intensities are, therefore, still only approximate and the following concentration data should be considered as qualitative. The discussion of this issue is saved until later). Note that only the major peak of the overlapping urea and amide nitrogen resonances was assessed. The overlap in this area made it impossible to evaluate signal intensities for both resonances correctly, and deconvolution was not attempted. The corrected relative intensity values confirm the trends discussed (Figure 6). A trend of increasing urea content is observed as well as a general decline in imide nitrogen concentration. A severe discontinuity is present in the plot of amide/urea intensity for the composite cured at 7.3% moisture. The source of the discontinuity is not clear but it may be attributable to random error. A gradual

TABLE II
Relaxation Parameters and Relative Intensities Obtained from ^{15}N CP/MAS NMR as a Function of Precure Cellulose Moisture[a]

Moisture (%)	Peak[b] (ppm)	T^c_{NH} (ms)	$T^c_{1\rho\mathrm{H}}$ (ms)	Corrected Rel. Intensity (%)[d]
2.1[e]	44	2.5(0.13)	12.9(0.97)	32.2(4.00)
	104	—	—	—
	111	0.07(~0)	4.9(0.05)	39.9(4.53)
	138	2.5(0.20)	8.3(0.16)	27.9(0.78)
3.3	44	2.5	12.1	23.3
	104	—	—	—
	111	0.07	4.5	56.7
	138	2.4	8.7	20.0
6.3	44	3.5	14.2	23.8
	104	0.07	5.5	52.0
	111	—	—	—
	138	3.6	7.9	24.2
7.3	44	3.0	12.3	27.2
	104	0.07	4.9	41.9
	111	—	—	—
	138	3.4	6.7	30.9
8.1	44	2.3	26.4	20.8
	104	0.07	5.4	56.7
	111	—	—	—
	138	2.5	12.5	22.4
23	44	3.5	13.1	15.7
	104	0.07	5.2	68.1
	111	—	—	—
	138	3.9	7.4	16.2

[a] Cured at 25 wt.% resin, 120°C, 50 psi, for 60 minutes.
[b] Chemical shifts of ^{15}N resonances referenced to glycine at 31 ppm.
[c] Calculated from CP variable contact time experiments. Mean error is ± 10% for T_{NH} and ± 12% for $T_{1\rho\mathrm{H}}$.
[d] Calculated from corrected peak intensities at a contact time of 4 msec.
[e] Average of three repetitions at this condition. Standard deviations shown in parentheses.

decrease in residual isocyanate content is also noted, but it is interesting that some is still present even after curing for 60 minutes at 23% precure moisture.

The variability of this NMR procedure was tested by making three identical composites at 2% moisture content. This moisture content was chosen because it was the easiest to replicate since the composites were simply equilibrated to room conditions. Mean values are given in Table II with standard deviations shown in parentheses. The results indicate good reproducibility of both T_{NH} and $T_{1\rho\mathrm{H}}$ relaxation values and the corrected relative intensities.

Morphological information about the bondline can be obtained from evaluation of the $T_{1\rho\mathrm{H}}$. The $T_{1\rho\mathrm{H}}$ relaxation parameter is generally influenced by molecular mobility and spin diffusion.[32,33] In the case of some highly crosslinked networks, molecular mobility is restricted and the $T_{1\rho\mathrm{H}}$ becomes the average over all protons in the sample due to spin diffusion. Such homogeneous systems display efficient "communication" among all protons in the sample and, therefore, exhibit the same $T_{1\rho\mathrm{H}}$ value for all chemical moieties present.[32,33] On the other hand, heterogeneous systems consisting of

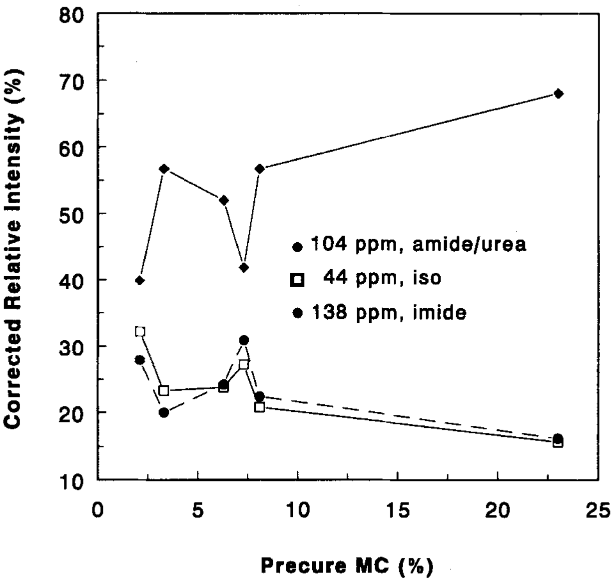


FIGURE 6 The corrected relative intensity, or percent composition, of the major chemical moieties present in the bondline of cellulose/^{15}N-enriched pMDI composites as a function of cellulose precure moisture content.

distinct chemical domains have been noted to exhibit different $T_{1\rho H}$ values when probed through chemically-distinct carbons.[21,34-36] This results from discontinuities which inhibit energy transfer across phase boundaries. Distinct phases then exhibit relaxation rates which are a local average and which often differ from one phase to the next.

Figure 7 displays the $T_{1\rho H}$ values from Table II for each nitrogen moiety as a function of cellulose precure moisture content. Again, due to signal overlap, the composite relaxation of the amide and urea signals is shown. Table II and Figure 7 indicate that each of the major peaks has a distinct $T_{1\rho H}$ relaxation rate. Note that the amide/urea relaxation rate is very fast and unchanging as a function of precure moisture. The relaxation rates of the isocyanate and imide nitrogens are also unchanging with the exception of the sample cured at 8.1% moisture. Ordinarily, this would be evidence for phase-separated bondline in which the isocyanate, urea, biuret structures exist in separate phases which possess distinct relaxation rates. However, notice that at precure moisture contents below 6% the biuret amide peak is the major component in the amide/urea composite signal. Given this, the relaxation rates in Table II seem to suggest that the amide and imide nitrogens of biuret structures have significantly different relaxation rates while only being separated by one carbon atom.

This irregularity indicates that these $T_{1\rho H}$ values are being affected by something other than spin diffusion and molecular mobility. Keep in mind that these data have come from variable contact time experiments in which signal intensity is monitored as a function of the period of Hartman-Hahn contact. In other words, the processes of cross-polarization and proton rotating-frame relaxation are effectively in competition.

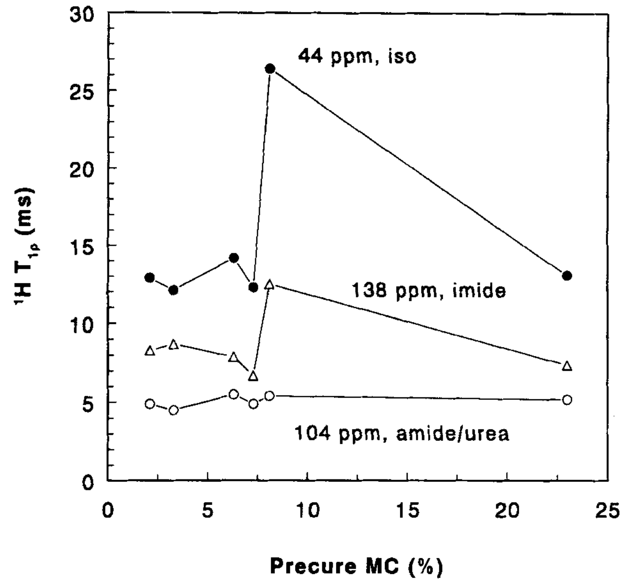


FIGURE 7 $T_{1\rho H}$ values obtained from cross-polarization variable contact time experiments for the major chemical moieties present in the bondline of cellulose/^{15}N-enriched pMDI composites *versus* precure moisture. Mean error for these values was ± 12%.

This is typically of little concern for protonated species which cross-polarize very rapidly. However, notice that the nonprotonated isocynate and imide nitrogens have excessively long cross-polarization rates which are of the same magnitude as the $T_{1\rho H}$. Inspection of Equation (1) demonstrates that excessively long cross-polarization rates could serve to inflate the value of $T_{1\rho H}$ artificially due to the latent effects of long range cross-polarization (Schaefer *et al.* report a similar phenomenon when performing variable contact time experiments on mixtures of polystyrene with perdeuteropolystyrene.[37] They show that buildup of carbon magnetization is slow in samples containing a significant amount of deuterons, or samples that are proton deficient.). The interaction of cross-polarization and proton rotating-frame processes can be avoided by spin-locking the proton reservoir for variable times prior to a fixed period of Hartmann-Hahn contact. Of the three composites cured at 2.1% moisture, one was reanalyzed using a variable spin-lock prior to a fixed contact period. Table III shows the resulting $T_{1\rho H}$ values where the effects of slow cross-polarization are excluded. Three separate experiments were performed using fixed contact times of 1.5, 3.0, and 5.0 ms. The data in Table III show that all nitrogen species in this composite are relaxing rapidly with a similar $T_{1\rho H}$ of about 4.5 ms. This is very similar to the $T_{1\rho H}$ of the protonated amide/urea peaks measured with the variable contact time experiment shown in Table II. Figure 8 graphically compares the relaxation of the biuret imide during a variable contact time experiment (curvilinear) and during an experiment using a variable spin-lock prior to a fixed contact period (linear). (The data in Figure 8 are all from the same sample, a cellulose composite cured at 2.1% moisture.) The linear portion of the variable contact time experiment has been extended to aid comparison

TABLE III
$T_{1\rho H}$ Values Measured Using a Variable Spin Lock Period Prior to a Fixed Contact Time for a Cellulose/^{15}N-pMDI composite[a]

Contact Time (msec)	^{15}N Resonance[b] 44 ppm	104 ppm	138 ppm
1.5	4.3	4.2	5.6
3.0	4.6	4.4	4.6
5.0	4.0	4.6	4.3

[a] Cured at 2% precure moisture content, 25 wt.% resin, 120°C, and 50 psi platen pressure for 60 minutes.

[b] Chemical shifts of ^{15}N resonances referenced to glycine at 31 ppm.

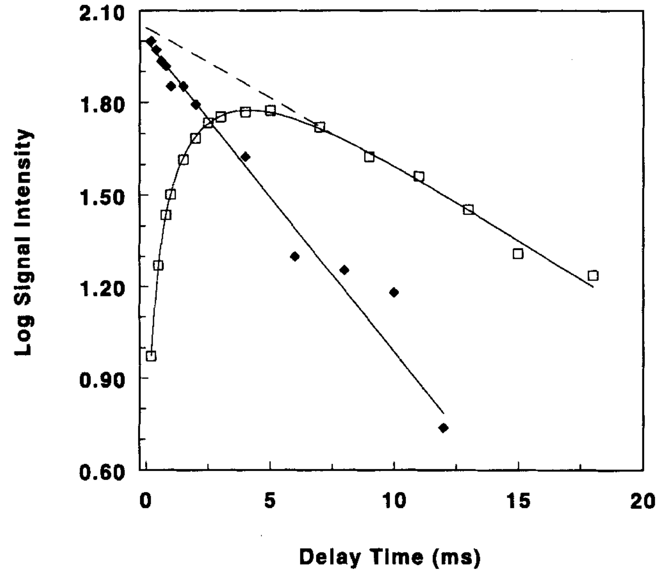


FIGURE 8 Relaxation data for the imide nitrogen (138 ppm) of a cellulose/^{15}N-enriched pMDI composite which was cured at 2.1% moisture. Both experiments shown here are from the same sample. Open squares: variable contact time experiment (Table II). Closed diamonds: variable spin lock prior to a fixed contact time experiment (Table III), contact time is 5 ms.

with the data from the variable spin-lock/fixed contact time experiment. If slow cross-polarization was not confounding the variable contact time experiment then the slopes of the two linear lines would be identical, but they are clearly not. This finding indicates that the cross-polarization and proton rotating-frame relaxation processes are interacting in the variable contact time experiment for nonprotonated nitrogens. In other words, variable contact time experiments produce artificially high values of $T_{1\rho H}$ for the imide and isocyanate peaks, while values for the amide/urea composite peak appear to be accurate. (This is precisely the reason why the corrected signal intensities and the trends shown in Figure 6 are only qualitative). The conclusion must, therefore, be drawn that the cured resin in these composites is probably not phase separated.

Relaxation studies such as these may also be used to probe the character of the residual isocyanate present in these model composities. Residual isocyanate may be present either in the form of free, unreacted pMDI molecules or as dangling ends from partially-reacted molecules which are, in turn, part of a polyurea or biuret structure. Chemical shift information cannot distinguish between these two isocyanate types. However, it is plausible that free isocyanate and dangling isocyanate would have substantially different mobilities. In this instance, each type might contribute to the total signal intensity of the isocyanate resonance and be manifested as biexponential signal decay. On the other hand, simple monoexponential decay would suggest that the isocyanate signal is derived solely from groups within one motional regime. Isocyanate groups within a single motional regime would be consistent with the presence of a single type of isocyanate, presumably those attached to the network as dangling ends rather than free molecules. This topic has been treated thoroughly by Duff and Maciel who have used ^{15}N CP/MAS variable contact time experiments on MDI-based isocyanurate resins.[23] Our findings with variable contact time and variable spin-lock (prior to fixed contact) experiments show simple monoexponential decay for the isocyanate signals. This is in agreement with the findings of Duff and Maciel, suggesting that residual isocyanate is present in one form, probably that which is anchored to the cured network. This conclusion should be supported by the observation of simple monoexponential decay of ^{15}N T_1 or $T_{1\rho}$, the latter of which will be the subject of future study. Interestingly, Duff and Maciel do show that the isocyanate ^{15}N T_1 exhibits single exponential decay, supporting the contention that residual isocyanate is present in one motional regime.

In summary, ^{15}N CP/MAS NMR appears to be a powerful technique for elucidating fine structural and morphological information from intact, pMDI-bonded cellulosic composites. It is expected that this technique will be equally useful when applied to solid wood substrates. Indeed, preliminary experiments on pMDI/solid wood composites have proven very promising, the results of which will be forthcoming in subsequent publications.

CONCLUSIONS

1. A 99% ^{15}N-labeled pMDI resin with favorable adhesive properties and structural similarity to commercial pMDI was successfully synthesized in high yield.
2. Model cellulose/^{15}N-pMDI composites were cured at various cellulose precure moisture contents. ^{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 biuret-type structures.
3. At low moisture conditions, the cure chemistry is primarily biuret-type structures with some residual polyurea and a significant amount of unreacted isocyanate. When the moisture is increased to 6%, the cure chemistry is primarily polyurea-type structures with less biuret formation and residual isocyanate.

4. Significant urethane formation was not detected at any moisture level; however, signal overlap could obscure low levels of urethane formation.
5. ^{15}N-pMDI bonded dry cellulose papers did not cure unless catalyzed, but dry yellow poplar flakes do cure without the use of catalyst.
6. Variable contact time experiments produce artificially-inflated $T_{1\rho H}$ values for nonprotonated nitrogens due to the interaction of cross-polarization and proton rotating-frame relaxation processes.
7. $T_{1\rho H}$ values obtained from experiments using a variable spin-lock prior to fixed contact time suggest that the cured resin is probably a homogeneous continuum.
8. The utility of ^{15}N CP/MAS NMR for elucidating fine structural and morphological information from these complex composite system has been demonstrated.

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