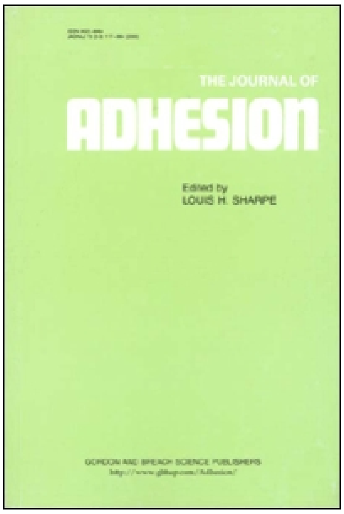

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^{15}N CP/MAS NMR Study of the Isocyanate/Wood Adhesive Bondline. Effects of Structural Isomerism

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^{15}N CP/MAS NMR Study of the Isocyanate/Wood Adhesive Bondline. Effects of Structural Isomerism

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Structurally isomeric ^{15}N-labeled polymeric methylenebis(phenylisocyanate), pMDI, adhesives were synthesized. One resin had a high content of 4,4′-MDI, and another was prepared with a high content of 2,4′-MDI. Both resins were cured with wood (*Liriodendron tulipifera*) for various times and temperatures and then analyzed using ^{15}N CP/MAS NMR. It was found that resin polymerization occurs *via* the reaction of isocyanate with wood moisture to form polyurea. Biuret formation and isocyanate dimerization were detected. Urethane formation probably also occurs; however, signal overlap of urea and urethane signals prevents a definitive conclusion. These findings are similar to previous ones; however, subtle differences are noted. The structurally isomeric resins displayed similar chemistries. Of the two resins, the resin prepared with a high content of 2,4′-MDI cured more slowly, and resulted in a network that was more mobile in the midkilohertz frequency range. This leads to the prediction that resins high in 2,4′-MDI may have a superior performance in impact loading.

Keywords: Wood; isocyanate; nitrogen-NMR; bondline chemistry; reaction with moisture; wood/adhesive interphase; particulate wood-based composites

INTRODUCTION

Because of the declining availability of mature timber, the increased production of adhesively bonded wood composite materials has been

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*Corresponding author.

strongly demanded. Wood adhesives are critical for the performance of these materials. Consequently, a better understanding of the wood/adhesive interphase is required to assist the evolution of wood composite technologies.

Polymeric methylenebis (phenylisocyanate), pMDI, has become an important wood binder, primarily for bonding oriented strand board (OSB) and similar particulate wood-based composites. It offers several unique features including:

1) Cure tolerance of high moisture environments,
2) Enhanced panel mechanical performance,
3) Weather durability and
4) No formaldehyde emission [1 – 5].

Also, pMDI has a broad range of chemical reactivity which may prove to be useful for bonding wood to a variety of non-wood surfaces.

pMDI used as a wood binder is a mixture of monomers and oligomers. The monomer fraction accounts for about 45 – 50% of the resin; higher order oligomeric polyisocyanates make up the remainder [6]. The monomer fraction is comprised mostly of 4,4′-MDI with a small amout of 2,4′-MDI (2 – 7% of the monomer fraction), and a trace of the 2,2′-isomer (Fig. 1). The performance of pMDI resin depends upon its composition, which is affected by molecular weight and structural isomerism, especially the 4,4′-/2,4′-isomer ratio. Structural isomerism refers to the positioning of the isocyanate group on the benzene ring and is controlled by synthetic manipulations. pMDI synthesis involves two steps. The first is normally an HCl-catalyzed formaldehyde/aniline condensation; the second step is the phosgenation of the resulting polyamine to polyisocyanate. Structural isomerism is controlled during the condensation reaction, which is typically conducted under homogeneous acid catalysis. These conditions favor production of the 4,4′-MDI isomer and lesser amounts of 2,4′-MDI and 2,2′-MDI [6]. The condensation is typically conducted such that the weight-average molecular weight of commercial pMDI is low, about 500 g/mol. The formaldehyde/aniline condensation can be manipulated to produce much higher quantities of 2,4′-MDI and 2,2′-MDI by employing heterogeneous catalysis and elevated reaction pressures [7, 8]. The corresponding isomeric modifications are also introduced into the oligomeric polyisocyanates.

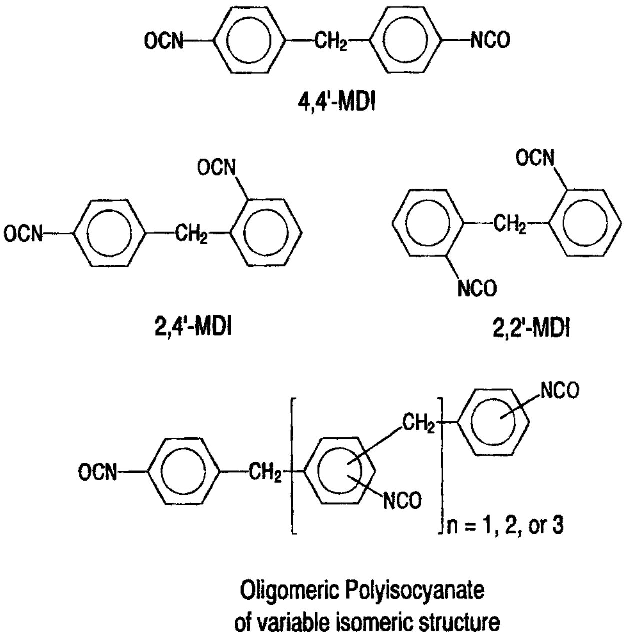

FIGURE 1 Molecular structure of the components of polymeric methylenebis (phenylisocyanate), pMDI, thermosetting adhesive.

The focus of this work is twofold. First, the objective is to learn more of the chemistry of the isocyanate/wood bondline, specifically using a low molecular weight pMDI which is high in 4,4′-MDI isomer. Such a resin is most typical of the forest products industry. This is a continuation of previous studies which used a higher molecular weight resin [9–11]. The second objective is to investigate the effects of structural isomerism in pMDI. Consequently, a second low molecular weight resin was synthesized, but with a higher concentration of the 2,4′- and 2,2′-MDI isomers. The cure chemistry of these isomeric resins is expected to be similar. However, the respective network architectures will have differing motional characteristics which should give rise to different physical properties. In fact, structural isomerism has been found to have considerable effects on the chemistry and physical properties of MDI-based flexible foams [12–15].

The pMDI resins studied here have been prepared with nitrogen-15 labeling in order to employ ^{15}N cross-polarization/magic angle spinning (CP/MAS) NMR. ^{15}N CP/MAS NMR is particularly suitable for the study of the pMDI/wood bondline. Overlapping wood signals are excluded so that resin chemistry can be directly observed [9, 10].

EXPERIMENTAL

Materials

Aniline-^{15}N (99 atom %) was purchased from Cambridge Isotope Laboratories and used as received. 95% paraformaldehyde, 37% aqueous hydrochloric acid, 10 N aqueous sodium hydroxide, as well as 98% triphosgene and anhydrous 1,2-dichlorobenzene (ODCB) were purchased from Aldrich Chemical and used as received. Montmorillonite K10 (a SiO_4-AlO_6 clay) was purchased from Aldrich and acid-activated before use; see below. Chloroform was distilled under dry nitrogen using anhydrous calcium chloride as desiccant.

Methods

1a. Synthesis of pMDI-^{15}N with a High Content of 4,4′-MDI(4,4′-pMDI)

Step 1: Aniline-^{15}N was degassed with N_2 bubbling for 3 minutes before use. The aniline-^{15}N: HCl molar ratio was chosen as 1 : 1.5, and the aniline-^{15}N: formaldehyde molar ratio was 4 : 1. 6N HCl (39.6 ml, 0.238 mole) was first added into a 100 ml triple neck round-bottom flask, which was submerged in a cold-water bath. Aniline-^{15}N (14.4 ml, 0.16 mole) was added slowly with stirring followed by 95% paraformaldehyde (1.25 g, 0.04 mole). The mixture was heated at 105°C for 8 hours. The contents were allowed to cool to room temperature, and added to a 250 ml separatory funnel containing freshly distilled chloroform (25 ml). The aqueous phase was neutralized with 10 N NaOH, and then extracted with chloroform (3 × 25 ml). The chloroform fractions were combined and washed with double-distilled water (3 × 25 ml), dried over excess Na_2SO_4, and concentrated on a rotational evaporator. Residual aniline-^{15}N was removed by vaccum distillation at 4 mm Hg and 120°C. The polyamine product (6.78 g) was stored under dry N_2 (86% yield, assuming the conversion of all formaldehyde to methylenedianiline).

Step 2: All reagents were degassed by N_2 bubbling, and all glassware was flamed under a slow N_2 purge before use. Immediately before use, the polyamine was vacuum dried overnight at 10 mm Hg and 50°C. The polyamine (6.78 g) was dissolved in 11 times its weight of dry ODCB (74.6 g). The amine content was calculated assuming a complete conversion of paraformaldehyde to methylenedianiline, in which case 6.78 g of the polyamine would contain 0.068 mole of amine. Triphosgene (7.62 g, 0.026 mole) was dissolved in dry ODCB (76.2 g). The triphosgene solution was added to a 100 ml round-bottom flask, followed by addition of polyamine solution. When adding polyamine to the triphosgene, vigorous stirring is critical to prevent particle agglomeration. After addition of the polyamine solution, the reaction mixture was heated to 175°C for 30 mins. under dry N_2 gas. The flask was then cooled to 150°C and degassed with N_2 bubbling for 15 mins. The resulting mixture was vaccum distilled (10 mm Hg and 90°C) to remove ODCB. The polyisocyanate was heat treated with an oil bath at 205°C for 10 minutes under N_2 purge. Immediately after heating, the flask was quench-cooled by spraying with acetone and submerging the flask into a cold-water bath. This heat treatment was performed to remove chlorine-containing impurities and to break down isocyanate dimers.

1b. Synthesis of pMDI-^{15}N with a High Content of 2,4′-MDI (2,4′pMDI)

Montmorillonite clay (5 g) was first acid activated by mixing with 6 N HCl (50 ml) in an Erlenmeyer flask. The mixture was stirred for 30 mins. and then filtered and vacuum dried at 10 mm Hg vacuum and at room temperature, overnight.

Step 1: Aniline-^{15}N was degassed by N_2 bubbling for 3 mins. before use. The aniline-^{15}N: formaldehyde molar ratio was chosen as 8 : 1, and the aniline-^{15}N: clay weight ratio was 10 : 1. The acid-activated clay (2.95 g) was weighed into a high pressure Parr reactor (250 ml), which was equipped with mechanical stirrer. Aniline-^{15}N (28.6 ml, 0.317 mole) was transferred into the reactor, followed by 95% paraformaldehyde (1.25 g, 0.040 mole). The reactor was flushed with N_2 gas, sealed, and then heated to 200°C for 2 hours. The reactor was cooled to room temperature, and the clay was removed by filtration.

Distillation of the filtrate at 4 mm Hg and 120°C gave 20.28 g of unreacted aniline-^{15}N and 7.38 g of polyamine (93% yield, assuming the conversion of all formaldehyde to methylenedianiline).

Step 2: The polyamine was phosgenated with triphosgene as described above.

2. Adhesive Analysis

The isocyanate content was measured according to ASTM Standard D 5155–91, Test Method C; however, the procedure was scaled down to one-tenth of the ASTM standard size. The isocyanate content of the 4,4′-pMDI was measured twice, yielding isocyanate contents of 27.8% and 27.9%. The isocyanate content of the 2,4′-pMDI was measured twice, yielding isocyanate contents of 28.9% and 29.3%.

Molecular weight was determined by using gel permeation chromatography (GPC) at 40°C. Solvent was HPLC-grade tetrahydrofuran. Columns were Waters Ultrastyragel with pore diameters of 10^3 A, 10^2 A, and 10 A. Other GPC equipment included Waters Model 510 HPLC pump, Waters Model 410 Differential Refractometer, and Viscotek Model 100 Differential Viscometer. A urea derivative of pMDI was made for GPC analysis as follows. ^{15}N-pMDI (0.1 g) was dissolved in freshly-distilled chloroform (1 ml), and then slowly added into diethylamine (0.8 ml). After a 30-minute reaction, the chloroform and residual diethylamine were removed on a rotational evaporator. The resulting urea derivative was used for GPC. Number average molecular weight (M_n) of the 4,4-pMDI was determined as 340 g/mole, and weight-average molecular weight (M_w) was 514 g/mole. M_n and M_w for the 2,4′-pMDI were 352 g/mole and 413 g/mole, respectively. These values are corrected for urea derivatization.

The diisocyanate isomer ratio was measured using gas chromatography. A Hewlett Packard HP6890 GC System was used with a capillary column (Hewlett Packard, HP-5), and the solvent for pMDI was chloroform. Gas chromatography analysis showed that the diisocyanate fraction of the 4,4′-pMDI was composed of 95% 4,4′-isomer, 5% 2,4′-isomer, and a trace of 2,2′-isomer. The diisocyanate fraction of the 2,4′-pMDI was comprised of 64% 2,4′-MDI, 27% 4,4′-MDI, and 9% of 2,2′-MDI.

3. Preparation of Wood Composites

A block of yellow poplar (*Liriodendron tulipifera*), clear of visible defects, with cross-sectional dimensions of 50 mm by 50 mm, was immersed in tap water for three days. The block was then sliced with a CAE disk flaker. All flakes were cut from the radial face of the block to a thickness of 0.3–0.4 mm, and with length and width of 50 mm. The flakes were vacuum dried at 10 mm Hg and room temperature for 24 hours to obtain their dry weight. They were then conditioned in a sealed container over saturated $CaCl_2$ solution for three days. The equilibrium precure moisture content of the flakes was 4.5–5.0% based on the dry weight of wood. To minimize the effects of wood surface deactivation, flakes were stored in the dark and used within 1–3 days after conditioning.

Two-ply flake composites were prepared. pMDI-^{15}N resin was sprayed onto two pieces of wood flake in the open atmosphere of the fume hood using an airbrush at a loading of 12% of the total composite weight. The resin was uniformly distributed over the entire surface area of one side of both flakes. The two wood flakes were pressed into a two-ply composite between thin Teflon sheets using a Carver Laboratory Press at at different cure conditions (temperature and time) and 500 psi (3.45 MPa) pressure. The post cure resin content was approximately 10% based on the dry weight of the wood. Samples were stored in individual sealed containers under N_2 and over desiccant in a freezer to prevent postcure reactions.

4. NMR Measurements

^{15}N CP/MAS spectra were obtained at 30.4 MHZ on a Bruker MSL-300 MHZ spectrometer using a 7 mm Probenkopf MAS.07.D8 probe. Small disks 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. The ^{1}H channel was tuned using adamantane, while glycine-^{15}N used to set the Hartmann-Hahn Condition. Standard phase cycling was used during acquisition. $T^{H}{}_{1\rho}$ measurements were made using a standard CP acquisition with a variable spin-lock delay (0.5 ms to 12 ms) prior to a fixed contact time (5 ms). The proton 90° pulse was 8 μs in duration. 800 scans were collected for each contact time with a repetition time of 6 s. Samples were spun at 6 KHz. Spectra were referenced externally to glycine-^{15}N at 31 ppm. In addition, a single CP/MAS interrupted-decoupling experiment was performed with interrupt times of 10 μs to 70 μs inserted between the contact period and signal acquisition.

5. Preparation of Wood-Urethane Model

A model wood-urethane was synthesized by reacting the labeled 4,4′-pMDI with yellow poplar wood powder under extremely anhydrous conditions, using phenyl mercuric acetate as catalyst. Details of the procedure are reported elsewhere [9].

6. Dielectric Analysis

Dielectric analysis of resin cure within the wood bondline was performed using a Micromet Eumetric System III Micro-Dielectric Analyzer equipped with a Micromet Instruments MP-2000 Minipress. Unlabeled resins were synthesized in the same fashion as mentioned above, with the same molecular characteristics. Measurements were performed using a Micromet inter-digitized electrode (IDEX) sensor with a high-conductivity signal interface. All scans were performed at frequencies of 1 Hz, 100 Hz, and 1 KHz. The composite specimens were prepared as described above. Before bonding, an IDEX sensor was placed between the two wood flakes. Composites were pressed between thin Teflon sheets using the minipress at 120°C and 185°C under 500 psi (3.45 MPa) for 20 mins. Cure was monitored during hotpressing.

RESULTS AND DISCUSSION

Sample, 2-ply, composites were prepared by spraying yellow poplar flakes with pMDI-^{15}N, whereafter the specimens were hotpressed between thin Teflon sheets under 500 psi (3.45 MPa) pressure at various times and temperatures as described above. While the cure temperatures used are representative of industrial practices, it is clear that the curing environment for these specimens has little in common with the conditions found in a flake mat during industrial composite manufacture. The sample specimens will dry very rapidly during this curing process. Consequently, these conditions may approximate those found adjacent to the hotpress platens during commercial operations, but the comparison ends there. Inner layers of an industrial flake mat will experience higher moisture and steam conditions. In previous studies using similar experimental conditions, it was found that the chemistry of the wood-pMDI bondline was insensitive to changes in precure wood moisture content above 4.5%. At fixed temperatures, the bondline chemistry exhibited little or no change over a precure wood moisture content ranging from 4.5 to 31% [9]. It was only when the specimens were oven dry that a significant difference in bondline chemistry was detected, again at a constant cure time. Given these findings, a precure moisture content of 4.5–5% was selected for this study. This amount of moisture is more than a two-fold stoichiometric excess over the isocyanate that is present in the samples. The reader will also note that these specimens were cured with 12 weight % of pMDI-^{15}N, which resulted in a postcure resin content of 10%. This content is approximately two to three times that which is applied during commercial processes. Such a high loading was required to enhance NMR signal intensity in order to reduce NMR acquisition times. Lower resin loadings are easily achievable, but at great expense. Also, these specimens have continuous bondlines whereas the bondlines are discontinuous in particulate wood-based composites. We submit that the *localized* resin loadings are likely comparable between the respective conditions. Finally, it is evident that these specimens are a poor approximation of industrial composites. However, this is an effective method which will be easily transferred to the core of an actual flake mat in future studies.

For simplicity, the isomeric resins made for this study will be referred to as 4,4′-pMDI and 2,4′-pMDI, in reference to the predominate MDI isomer.

Part One: 4,4′-pMDI

It is generally accepted that there are multiple pathways for pMDI/wood reactions, Figure 2 [1–4, 16–18]. The isocyanate group reacts with hydroxyl groups to form urethane linkages. Therefore, wood

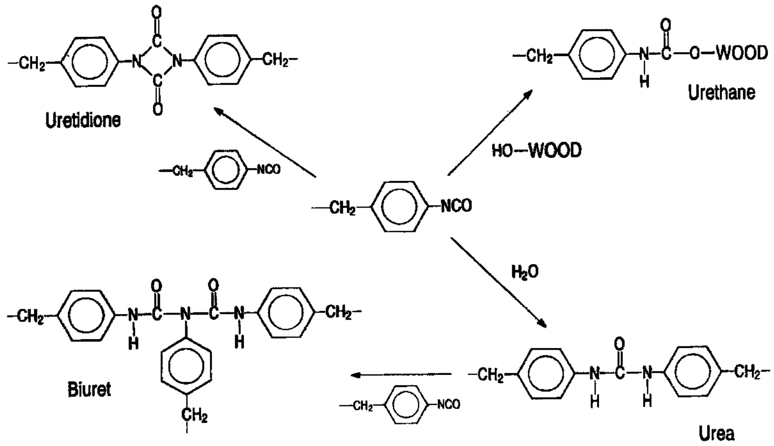

FIGURE 2 Examples of some of the reactions that isocyanates may undergo when cured with wood.

components (cellulose, hemicellulose, lignin, and wood extractives) will offer ample opportunity for covalent bonding with pMDI. However, the hydrophilicity of wood always ensures a high degree of hydration, thus promoting urea formation from the addition of water to isocyanate. Ureas may add additional isocyanate to form biurets, and isocyanate may dimerize to form uretidione. We can expect that there will be competition among these different reaction pathways when pMDI is cured with wood.

Two series of wood/4,4′-pMDI composites were cured as a function of time using 4.5–5.0% wood precure moisture content, 12 wt. % resin, and 500 psi (3.45 MPa) pressure. Two different cure temperatures, 120°C and 180°C, were chosen as respective approximations of mat core and platen. temperatures which occur during industrial manufacturing processes. Figure 3 shows two spectra which display some of the characteristic chemical shifts for this study. Chemical shifts are referenced to glycine-^{15}N at 31 ppm and are similar to literature reports [19]. The peak at 44 ppm corresponds to residual isocyanate. Urea appears at 104 ppm. The biuret imide nitrogen is located at 138 ppm, and the corresponding biuret amide nitrogen occurs as a shoulder at 111 ppm. Previous studies showed that the wood/pMDI urethane and the methanol/pMDI urethane signals both

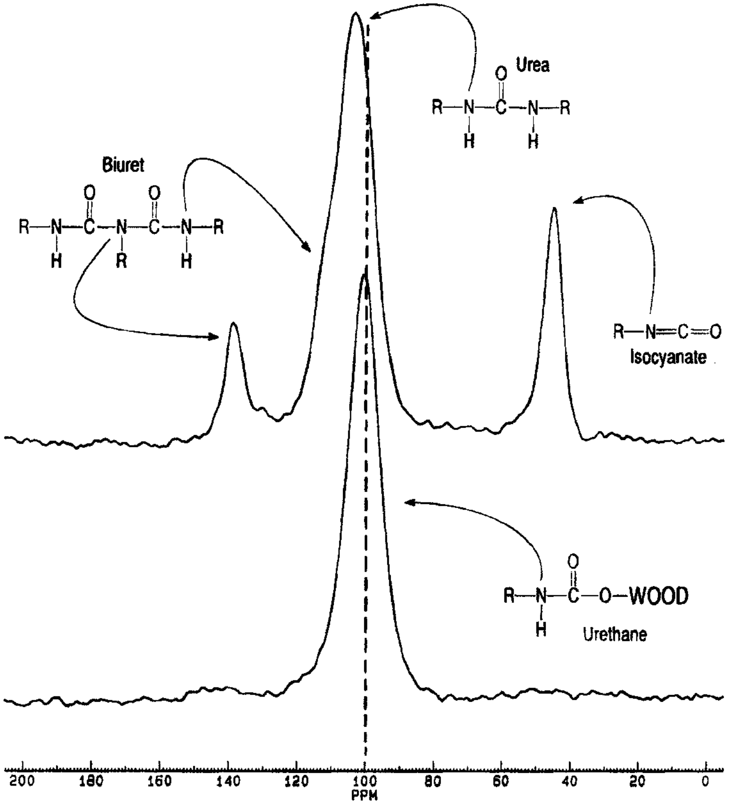

FIGURE 3 Representative CP/MAS NMR chemical shifts for ^{15}N-labeled species in this study. Top: ^{15}N-labeled 4,4′-pMDI/wood composite specimen. Bottom: Model urethane made with ^{15}N-labeled 4,4′-pMDI.

appear with maximum at 101 ppm [9, 11]. The bottom spectrum in Figure 3 shows the product formed when reacting the ^{15}N-labeled 4,4′-pMDI with yellow poplar wood powder under extremely anhydrous conditions. The maximum of the lone peak occurs at 101 ppm, corresponding to the wood/pMDI urethane.

The complexity of the wood-based model shown in Figure 3 makes it impossible to prove unequivocally that this is urethane. (For example, infrared analysis is not helpful due to the presence of overlapping carbonyl signals in wood). Nevertheless, the identification as urethane is a reasonable conclusion given previous findings, and the fact that this model was prepared under meticulously dry conditions. It is evident that clear identification of urethane is prevented by the overlap of the urea signal. Making matters worse is the known sensitivity of ^{15}N chemical shifts to secondary interactions occurring in the local environment [20, 21]. We must conclude that the unambiguous indentification of urea and urethane signals requires a complimentary technique. It has been shown that ^{13}C NMR provides resolution between urethane and urea carbonyl carbons [22, 23]. The extent of resolution is specific to the system being examined. Making use of the carbonyl carbon involves the insertion of ^{13}C label into the isocyanate group, which requires the synthesis of ^{13}C-labeled triphosgene. Labeling with ^{13}C is, therefore, much more difficult than with ^{15}N. However, this approach is feasible and will be the subject of future work. Unfortunately, we must rely solely on the ^{15}N method at present. For this discussion, we will tentatively assign the urea and urethane nitrogens the respective chemical shifts of 104 and 101 ppm. This degree of uncertainty is clearly undesirable, so any distinctions between urea and urethane must be considered cautiously. Nevertheless, evidence in support of these assignments will be presented.

Figure 4 shows the ^{15}N CP/MAS spectra for the samples cured at 120°C as a function of cure time. At 140 sec. the three prominent resonances are seen. Careful inspection reveals two shoulders on the biuret imide peak, which is seen at 138 ppm. The high-field or right-hand shoulder at 130 ppm was noticed previously; however, the identity of this species is still unknown [11]. The low-field or left-hand shoulder at 143 ppm corresponds to the uretidione nitrogen, which is the isocyanate dimer [19]. The central broad band appears to contain possibly three peaks at 111, 104, and 101 ppm. A line has been drawn at 100 ppm in order to accent signal intensity in that region. The maxima at 101 ppm may represent the urethane. The breadth of the central peak also indicates that a significant amount of urea is present. Biuret amide is seen as a shoulder on the left side of the central peak at 111 ppm. If the signal intensity at 101 ppm indicates the presence of urethane, this would be in contrast to previous findings [10]. Previously, using a higher molecular weight and lower isocyanate content resin, urethane (signal maxima at 101 ppm) was detected only under high temperatures and long cure times [10]. The resin used here has a much lower molecular weight ($M_w = 514$ g/mole vs. 4500 g/mole)

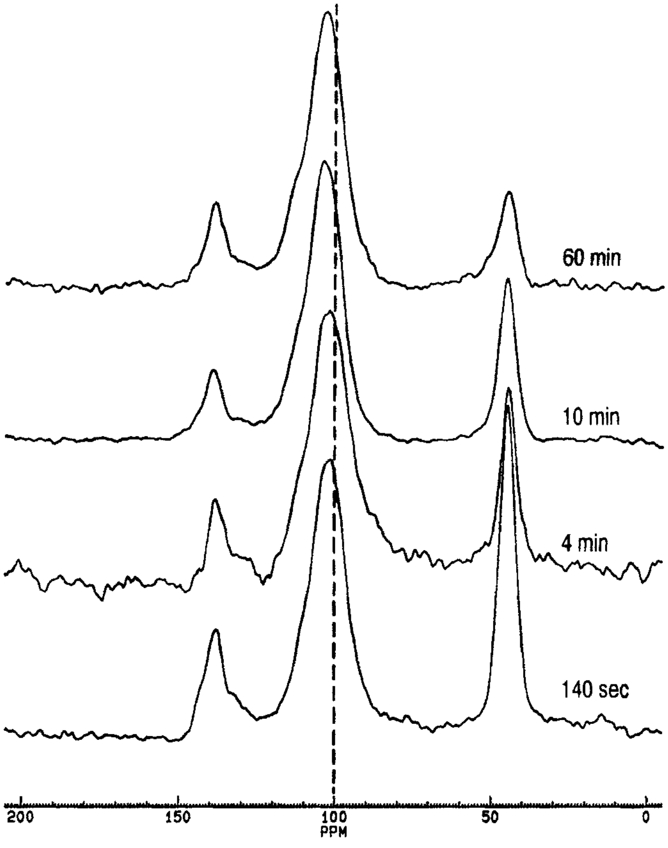

FIGURE 4 ^{15}N CP/MAS NMR spectra of wood (*Liriodendron tulipifera*) flake composites cured with ^{15}N-labeled 4,4′-pMDI at 120°C, and 500 psi (3.45 MPa) for various times.

and higher isocyanate content (27.9% vs. 25.6%) than the previously studied resin. It appears that bondline chemistry may be affected by these pMDI variables. While the effects of isocyanate content are not yet clear, lower molecular weight preparations of pMDI will be more reactive. Furthermore, the enhanced mobility of the lower molar mass pMDI will allow for better access to wood reactive sites. Consequently, urethane formation should occur more readily with a lower molecular weight resin as might be the case here. Aside from urethane formation, the chemistry of this specimen is very similar to previous findings. In other words, urea and subsequent biuret formation appear to be dominant. Notable differences between the systems will be discussed below.

As cure time increases to 4 min., there appears to be little difference in cure chemistry (Fig. 4). However, as cure time increases to 10 and 60 min., the central peak maximum shifts slightly from 101 ppm to 103 – 104 ppm. If signal intensity at 101 ppm is from urethane, this shift in the peak maximum would suggest that urethanes are thermally decomposing under extended cure times. The thermal cleavage of biuret linkages in the wood/pMDI bondline was reported previously [10], and the thermal instability of urethane is well known. Thermal dissociation of urethane is reported to occur in the following order [24]:

Aryl – NHCOO – Aryl (Aryl urethane) 120°C
Aryl – NHCOO – Alkyl (Alkyl urethane) 200°C

Wood macromolecules contain aliphatic and phenolic hydroxyl groups which will form the corresponding alkyl and aryl urethanes. Wood polysaccharides possess aliphatic hydroxyls, and phenolics occur as: 1) components of the lignin structure in approximately 10 – 30% of the lignin C_6C_3 repeat units, and 2) as low molecular weight phenolic metabolites which are referred to as phenolic extractives. Consequently, it is possible that both alkyl and aryl urethanes may form. If the time-dependent shift from 101 to 104 ppm (Fig. 4) corresponds to urethane decomposition, we should expect that this represents the thermal cleavage of aryl urethanes.

A qualitative observation reveals that the amount of residual isocyanate appears to decline with cure time as expected. Signal intensities were not corrected for differential relaxation rates, consequently a quantitative evaluation is not possible here [25, 26]. Figure 4 demonstrates that ^{15}N CP/MAS NMR is effective for detecting residual isocyanate, which should be of some practical interest to the industry.

Figure 5 shows the ^{15}N spectra for the series of composites cured at 185°C. The major and minor peaks are similar to those noted in Figure 4. Unlike the series cured at 120°C, the central maxima now occur at 103 – 104 ppm for all specimens cured at 185°C. The lack of signal maximum at 101 ppm may indicate that urethane formation is

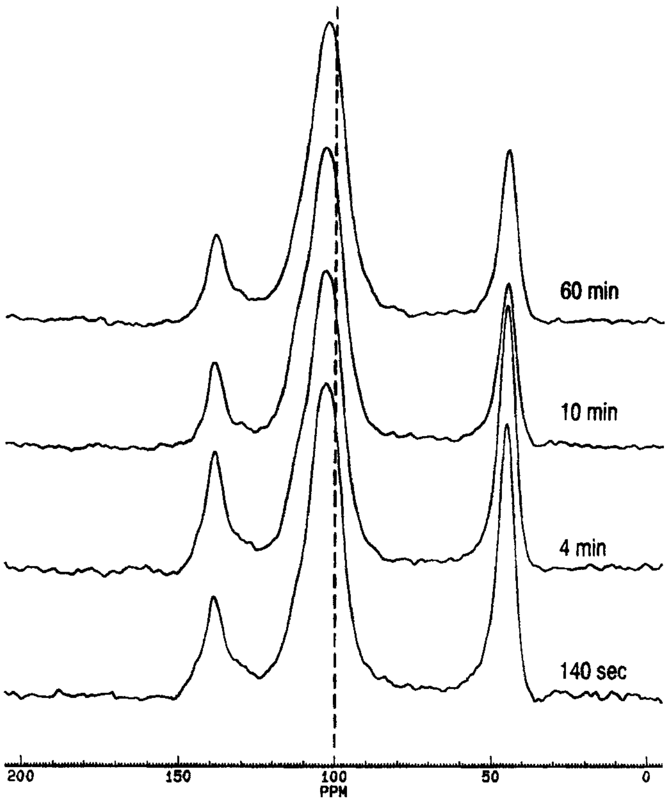

FIGURE 5 ^{15}N CP/MAS NMR spectra of wood (*Liriodendron tulipifera*) flake composites cured with ^{15}N-labeled 4,4′-pMDI at 185°C, and 500 psi (3.45 MPa) for various times.

less common at higher cure temperatures for this system. Again, this is in contrast to previous findings where signal mamixum at 101 ppm (possible urethane) was found only after curing at 185°C for 60 minutes with a much higher molecular weight pMDI [10]. Another distinctive difference is in the occurrence of biuret linkages. In former studies, the high molar mass pMDI produced significantly higher concentrations of biuret in which the biuret amide appeared as the largest peak in the spectrum [10]. In this study the biuret amide is never more than a shoulder on the central peak. It is apparent that pMDI resins with differing molecular weight (and possibly differing isocyanate content) produce similar cure chemistries, but that the balance of competing reactions results in subtle differences.

Midkilohertz frequency molecular motions were probed with measurements of proton longitudinal relaxation in the rotating-frame, $T^{H}_{1\rho}$. $T^{H}_{1\rho}$ relaxation times are presented in Tables I and II. Each value was replicated one or two times by preparing separate samples. At 120°C, the biuret imide and isocyanate $T^{H}_{1\rho}$ increase with cure time, which is probably due to reduced mobility as cure advances. For the central peak at 101/104 ppm, relaxations initially rise with cure time, but then drop after 4 minutes of cure. This discontinuity in relaxation behaviour coincides with the postulated occurrence, and then decomposition, of urethane. Ureas and urethanes could be expected to exist in different motional regimes given their different capacities for hydrogen bonding, and that the urethane may be an anchor to wood polymers. At 185°C, the biuret imide and isocyanate $T^{H}_{1\rho}$ increase with cure time. However, the central peak at 104 ppm shows no change in mobility over the entire range of cure times. Recall that samples cured

TABLE I $T^{H}_{1\rho}$ relaxation times[a] for 4,4′-pMDI/wood composites cured at 120°C[b]

Cure Time (min : s)	*Peak (ppm)*			
	138	*104*	*101*	*44*
2:20	4.3 (0.1)[c]	–	4.4 (0.1)	4.2 (0.1)
4:00	4.5 (0.1)	–	4.9 (0.1)	4.1 (0.3)
10:00	4.8 (0.1)	4.1 (0.1)	–	5.1 (0.2)
60:00	4.9 (0.1)	4.0 (0.1)	–	5.0 (0.1)

[a] $T_{1\rho H}$values are averages of at least two experiments using separate samples.
[b] Cured at 12 wt. % resin, 500 psi.
[c] Value in parentheses is standard error.

TABLE II $T^{H}_{1\rho}$ relaxation times[a] for 4,4′-pMDI/wood composites cured at 185°C[b]

Cure Time (min : s)	*Peak (ppm)*		
	138	*104*	*44*
2:20	4.4 (0.1)[c]	4.2 (0.1)	4.6 (0.1)
4:00	4.3 (0.1)	4.3 (0.1)	4.7 (0.2)
10:00	4.8 (0.1)	4.2 (0.1)	5.2 (0.1)
60:00	4.8 (0.1)	4.2 (0.1)	5.1 (0.1)

[a] $T^{H}_{1\rho}$values are averages of at least two experiments using separate samples.
[b] Cured at 12 wt. % resin, 500 psi.
[c] Value in parentheses is standard error.

at 185°C did not show a central peak maximum at 101 ppm, possibly suggesting that urethane did not form. Under this scenario it may be that when ureas predominate the relaxations of the central peak are unchanging, whereas, when urethane is prevalent, the relaxations of the central peak tend to change as cure advances.

If ureas and urethanes are present in different motional regimes, it may be possible to manipulate differential mobility as a means for resolving overlapping signals. An interrupted decoupling experiment was employed for this purpose. Delay periods of 10, 30, 50 and 70 μs were inserted after the CP contact period at the beginning of data acquisition. During that delay period, the ^{1}H decoupler is turned off and ^{15}N magnetization is attenuated by the ^{15}N—^{1}H dipolar interaction. ^{15}N nuclei with different relaxation rates will have different degrees of attenuation, which may allow some degree of resolution.

Figure 6 shows the results of the interrupted-decoupling experiment as performed for the sample cured at 120°C for 140 sec. The spectrum at 10 μs is similar to the one in Figure 4. At the interrupt time of 50 μs, the 104 ppm urea shoulder on the left side of the central band becomes clear. Also, a maximum is seen at 101–102 ppm, probably from the urethane. While the interrupted decoupling experiment does not provide baseline resolution, it does demonstrate that two overlapping peaks exist in the 100 to 104 ppm range. It is probable that these peaks are urea and urethane linkages.

Increases in $T_{1\rho}^H$ with cure time can indicate that the network becomes either more rigid or more mobile depending on the motional characteristics of the sample [27]. Variable temperature NMR acquisitions were performed to clarify mobility changes in these samples. $T_{1\rho}^H$ was measured for one sample at various temperatures. Table III shows that as NMR acquisition temperature is raised form 25°C to 50°C, the $T_{1\rho}^H$ values of all signals decline. This indicates that the network is relatively rigid in character. Therefore, increases in $T_{1\rho}^H$ as a function of cure time generally correlate with reduced molecular mobility, as would be expected.

Rotating frame relaxation is influenced by the effects of molecular mobility and spin diffusion. Spin diffusion results from magnetization transfer between protons and is largely due to the abundance and close spatial proximity of protons in organic solids [28]. The spatial

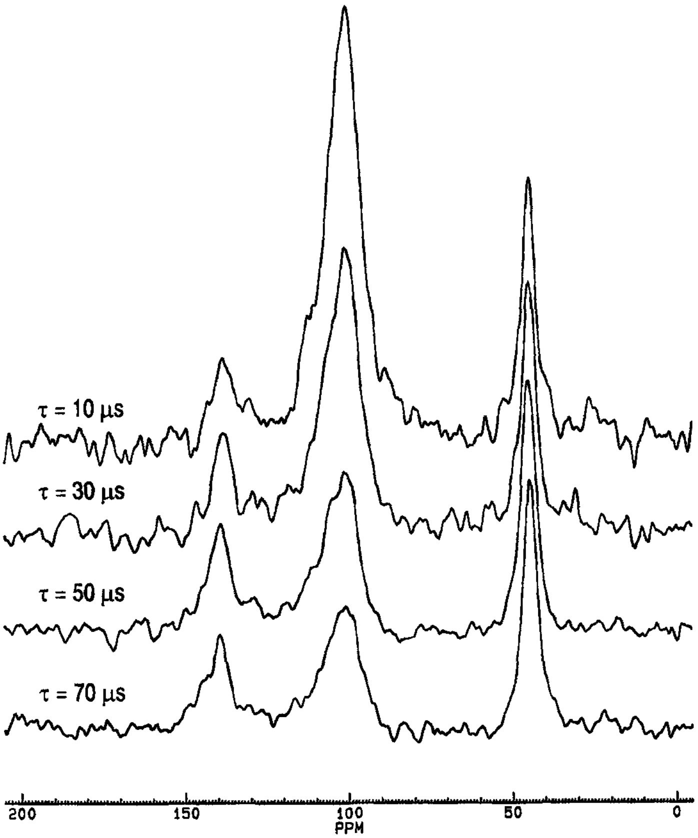

FIGURE 6 ^{15}N CP/MAS NMR spectral series from an interupted decoupling experiment on a ^{15}N-labeled 4,4′-pMDI/wood composite specimen cured at 120°C for 140 sec.

TABLE III $T^{H}_{1\rho}$ values of a 4,4′-pMDI/wood composite sample[a] as a function of NMR acquisition temperature

Temperature (°C)	*Peak (ppm)*		
	138	*104*	*44*
25	4.3 (0.2)[b]	3.7 (0.1)	4.6 (0.1)
40	3.9 (0.2)	3.5 (0.1)	4.1 (0.1)
40	3.7 (0.4)	3.3 (0.2)	3.8 (0.4)
50	3.0 (0.2)	3.0 (0.1)	3.9 (0.5)

[a] Cured at 12 wt. % resin, 500 psi, and 120°C for 60 minutes.

[b] Value in parentheses is standard error.

dependence of spin diffusion allows one to obtain some morphological information about the sample. For example, a one-phase homogeneous sample will display a single value of $T_{1\rho}^{H}$ regardless of which nucleus is sampled during the cross-polarization experiment. Conversely, phase boundaries will inhibit spin diffusion between domains in heterogeneous systems. Discrete phases relax independently, often with distinctive rates. Table I shows that samples cured at 120°C appear to develop phase heterogeneity as cure progresses. All signals display similar $T_{1\rho}^{H}$'s early in cure. However, as cure progresses the central polyurea signal relaxes more rapidly than the imide and isocyanate nuclei. The sample may or may not be homogeneous early in cure, but it is clearly heterogeneous later in cure. Table II shows that heterogeneity also develops in the samples cured at 185°C. However, in this case, the central signal (polyurea) retains a rapid relaxation regardless of cure time.

Summarizing the general findings with 4,4′-pMDI, many of the results of this study are in accord with previous findings [10, 11]. For example, residual isocyanate has always been observed, regardless of cure conditions. With or without urethane formation, urea and subsequent biuret formation appear to dominate in the isocyanate/wood bondline. The lower molecular weight and higher isocyanate content of this 4,4′-pMDI appear to have produced some new findings. For example, isocyanate dimerization is somewhat more common, but variable in occurrence. Also, it appears that biuret formation is much less common with the resin studied here. Finally, there are indications that urethane formation may be more common than in previous studies. The fact remains, however, that signal overlap prevents a definitive conclusion on this matter. Curiously, reproducible changes in molecular motions mirror the postulated change from urethane to urea predominance. This differential mobility was manipulated to reveal fine structure in the 101/104 ppm peak that is consistent with the presence of urethane and urea.

Part Two: 2,4′-pMDI

The aniline/formaldehyde condensation using heterogeneous catalysis provided a pMDI resin with a high 2,4′-MDI content. Gas chromatography revealed that the diisocyanate fraction was comprised of

64% 2,4′-MDI, 9% of 2,2′-MDI and 27% of 4,4%-MDI. Figure 7 shows partial ^{13}C solution NMR spectra of 2,4′-pMDI compared with 4,4′-pMDI (The 4,4′-pMDI has 95% 4,4′-MDI momomer). The peaks at 34.5 ppm, 37.8 ppm, and 41.0 ppm correspond to methylene carbons of the 2,2′-, 2,4′- and 4,4′-isomers, respectively. Unfortunately, solution NMR cannot be used to determine the isomer ratio in these materials because signals from the oligomeric polyisocyanates are overlapping. Figure 8 compares the same resins but with ^{15}N solution NMR. Assignment of the ^{15}N chemical shifts for the isomers was not attempted. Gel permeation chromatography showed that the 2,4′-pMDI has a weight-average molecular weight of 413 g/mole and molecular weight polydispersity of 1.17. The isocyanate content was measured and found to be approximately 29%. Besides being

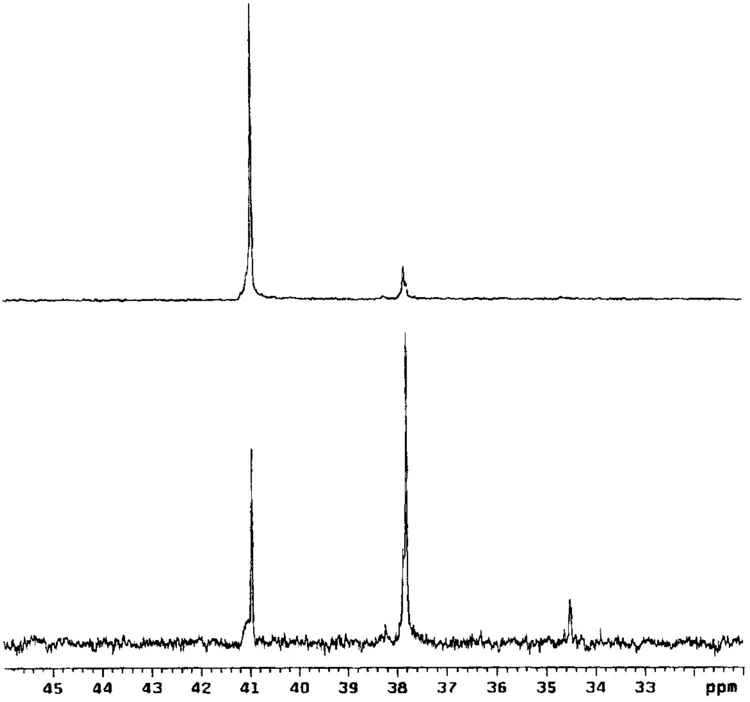

FIGURE 7 Partial ^{13}C solution NMR spectra of 4,4′-pMDI (top) and 2,4′-pMDI bottom in acetone-d_6, referenced to tetramethylsilane at 0 ppm.

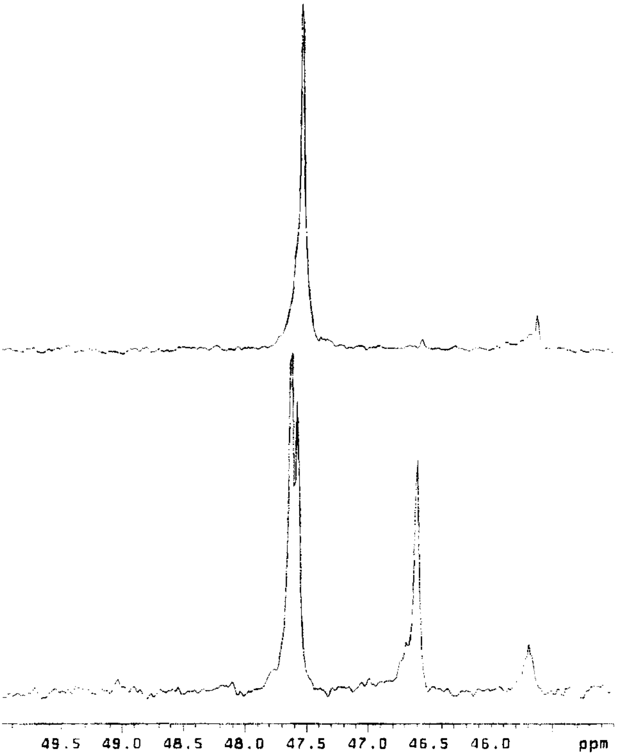

FIGURE 8 Partial ^{15}N solution NMR spectra of 4,4′-pMDI (top) and 2,4′-pMDI ′ bottom in acetone-d_6, referenced to glycine-^{15}N at 31 ppm.

structurally isomeric, this 2,4-pMDI resin is generally comparable with resins typically used in the forest products industry. In this discussion reference will only be made to differences in the isomeric composition of the diisocyanate fraction. The reader is reminded that isomerism in the monomers will create the corresponding isomerism in the oligomeric polyisocyanate fraction. No attempt was made to characterize the polyisocyanates.

Two series of wood/^{15}N-pMDI composites were prepared with the 2,4′-pMDI resin. They were cured at 120°C and 185°C, respectively. All specimens were cured with 4.5–5.0% wood precure moisture content, 12 wt.% resin, and were hot pressed under 500 psi (3.45 MPa) pressure for periods of either 140 sec., 4 min., or 10 min.

Figure 9 displays the ^{15}N CP/MAS NMR spectra for the samples cured with 2,4′-pMDI at 120°C as a function of cure time. At 140 sec., three major resonances are seen which were typical for the 4,4′-pMDI resin; see above. Most characteristics of these spectra are similar to those found using the resin high in 4,4′-MDI. For example, residual isocyanate is persistent, and urea and biuret formation appear to be dominant. One subtle difference is seen at a cure time of 140 sec. In this instance, the central peak appears to have some fine detail in the form of upfield (96–98 ppm) and downfield (118 ppm) shoulders. From 4 to 10 min. of cure it appears that the biuret imide and amide decline in intensity. This is indicative of biuret thermal decomposition,

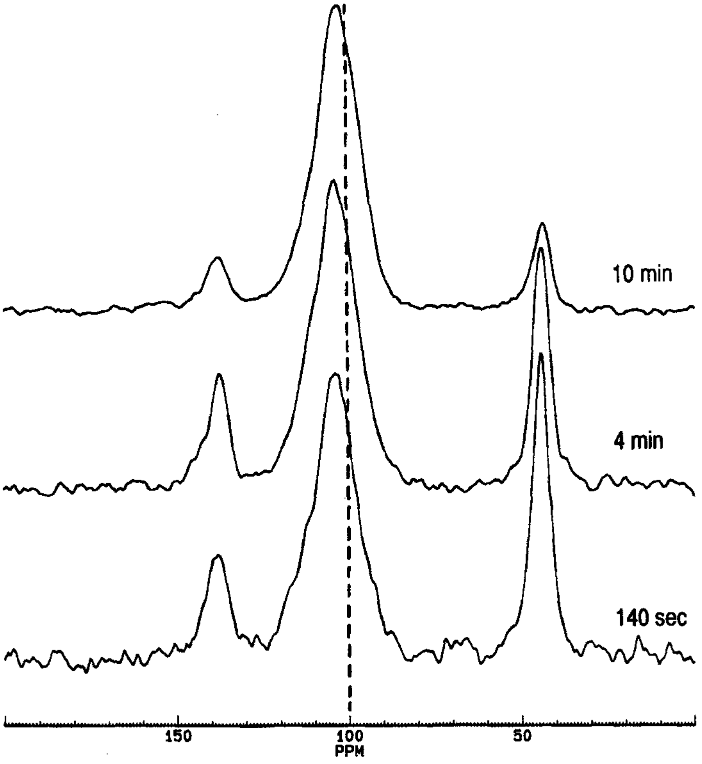

FIGURE 9 ^{15}N CP/MAS NMR spectra of wood (*Liriodendron tulipifera*) flake composites cured with ^{15}N-labeled 2,4′-pMDI at 120°C, and 500, psi (3.45 MPa) for various times.

which was detected previously [10]. Note that signal intensities in the CP/MAS spectra have not been corrected for differential relaxation, and that only qulitative conclusions regarding concentrations can be made.

Figure 10 shows the ^{15}N spectra for the samples cured with 2,4'-pMDI at 185°C. The sample cured for 140 sec. is similar to that seen when curing at 120°C. Here again the central maximum occurs at 104 ppm, suggesting that urea is predominate. As cure time increases to 4 min., the central band dramatically broadens. A strong biuret amide shoulder appears at 111 ppm, and two shoulders appear on the right at

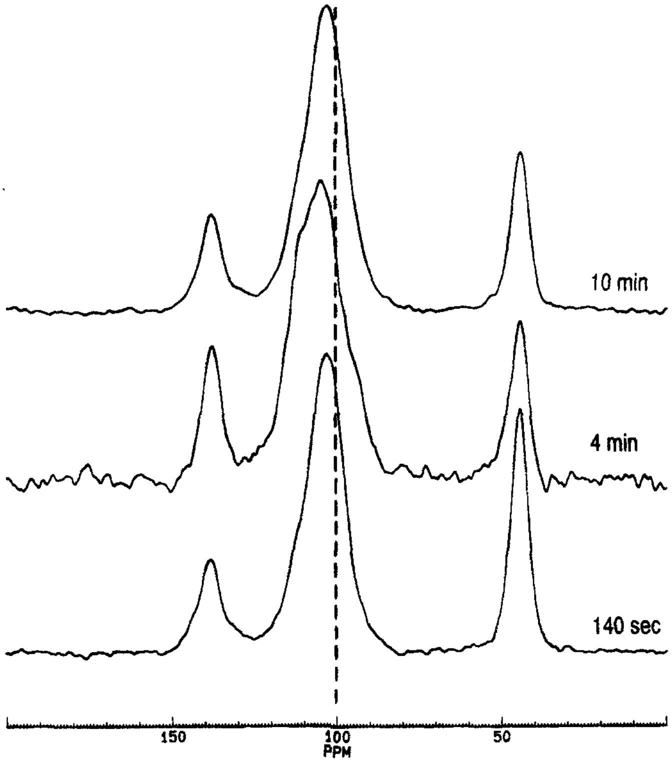

FIGURE 10 ^{15}N CP/MAS NMR spectra of wood (*Liriodendron tulipifera*) flake composites cured with ^{15}N-labeled 2,4'-pMDI at 185°C, and 500, psi (3.45 MPa) for various times.

96 to 98 ppm. Similar but less obvious shoulders were noted above when curing at 120°C for 140 sec, Figure 9. These shoulders in the 96 ppm region have not been previously observed using 4,4′-pMDI and could be characteristic of reactions with 2,4′- and 2,2′-MDI. The 4,4′-pMDI urethane signal appears nearby at 101 ppm, so it may be that the 2,4′-pMDI urethane signal is shifted into the 96 to 98 ppm region. This is speculative since model urethanes were not synthesized using the 2,4′-pMDI. This unusual peak shape is reproducible and seems to be characteristic of these specific cure conditions; a similar peak shape was reproduced in two additional replicate samples cured at 185°C for 4 min. It seems likely that structural isomerism in the 2,4′-pMDI creates a dispersion in chemical shifts resulting from isomeric network conformations. The notable broadenings in the amide and (possibly) urethane shoulders disappear as cure time increases to 10 min, again indicative of thermal decomposition. Cure at 185°C produces a considerable amout of residual isocyanate. This may be related to the noted thermal decomposition of biuret and possibly urethane linkages. In both cases, thermal decomposition will produce isocyanate.

Although the chemistry of the isomeric resins appears similar, we can expect that some significant differences must exist. Figure 11

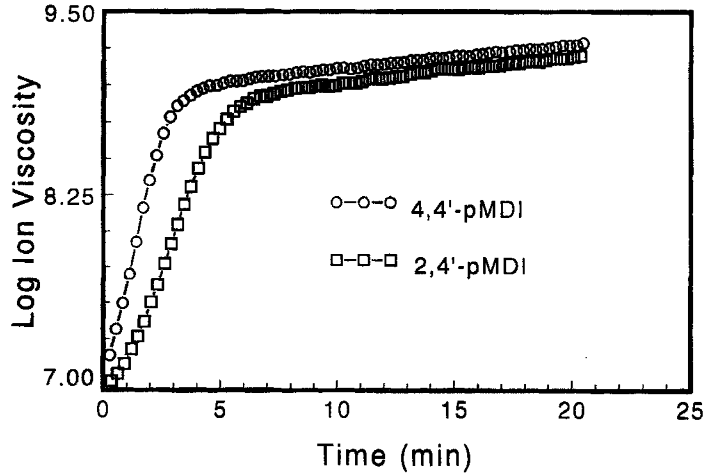

FIGURE 11 Comparison of cure rates for isomeric pMDI adhesives using microdielectric analysis in which the dielectric sensor is placed between bonded wood flakes during hotpressing. Ion viscosity is the reciprocal of conductivity.

compares the cure rates of the isomeric resins using dielectric analysis under 120°C isothermal cure. 4,4′-pMDI vitrifies about 2 min. faster than the 2,4′-pMDI resin. Dielectric analysis revealed no difference when the respective resins were cured isothermally at 185°C. This implies that 2,4′-pMDI resin in the outer or "face" layers of a wood-based composite would not reduce hotpress times. However, 2,4′-pMDI used in the core layer would apparently require longer hotpress times.

To this point, a comparison of isomeric pMDI resins shows that bondline chemistries are generally similar, and that cure rates are slightly different. We would expect the molecular architectures of the respective networks to be remarkably different. For example, urea chains from a 4,4′-pMDI resin may be crystalline or contain some degree of 2-dimensional order. In contrast, a polyurea network resulting from a 2,4′-pMDI resin may be more extensible because the coil-like chains could undergo a greater degree of torsional bond rotation. These differences should be revealed when probing molecular relaxations using CP/MAS NMR. $T_{1\rho}^{H}$ values for all 2,4′-pMDI samples are presented in Tables IV and V. At 120°C, $T_{1\rho}^{H}$ values for the three major peaks tend to decline with cure time. This opposes the trend seen for the 4,4′-pMDI resin, Table I. Samples cured at 185°C (with 2,4′-pMDI) show a trend of increasing $T_{1\rho}^{H}$ with cure time; however, a sharp discontinuity is seen at 4 min. Four min. cure at 185°C produces at network with relatively high vales of $T_{1\rho}^{H}$. Recall that these same cure conditions created the exceptionally broad central peak shown in Figure 5. As mentioned above, this atypical sample was replicated twice; relaxations shown in Table V for these cure

TABLE IV $T_{1\rho}^{H}$ relaxation times[a] for 2,4′-pMDI/wood composites cured at 120°C[b]

Cure Time (min : s)	*Peak (ppm)*		
	138	*104*	*44*
2:20	4.9 (0.2)[c]	7.4 (0.2)	4.5 (0.2)
4:00	3.8 (0.2)	6.7 (0.2)	4.3 (0.2)
10:00	3.8 (0.1)	5.3 (0.1)	4.0 (0.1)

[a] $T_{1\rho}^{H}$ values are averages of at least two experiments using separate samples.
[b] Cured at 12 wt. % resin, 500 psi.
[c] Values in parenthesis are standard errors of the $T_{1\rho}^{H}$.

TABLE V $T_{1\rho}^{H}$ relaxation times[a] for 2,4′-pMDI/wood composites cured at 185°C[b]

Cure Time (min : s)	Peak (ppm)		
	138	104	44
2:20	3.1 (0.1)	4.3 (0.1)	3.4 (0.2)
4:00	4.4 (0.2)	5.9 (0.1)	4.6 (0.1)
10:00	3.7 (0.1)	4.8 (0.1)	3.6 (0.1)

[a] $T_{1\rho}^{H}$ values are averages of at least two experiments using separate samples.
[b] Cured at 12 wt. % resin, 500 psi.
[c] Values in parenthesis are standard errors of the $T_{1\rho}^{H}$.

conditions are averaged from three separate samples. It is apparent that networks resulting from the two isomeric resins have different molecular mobilities, as expected. This point is further demonstrated by a variable temperature NMR acquisition performed on the 2,4′-pMDI sample which was cured at 120°C for 10 min. Table VI shows that $T_{1\rho}^{H}$ increases for the three major peaks as NMR acquisition temperature increases. This indicates that 2,4′-pMDI samples cured at 120°C are relaxing on the high-frequency side of the relaxation minimum, meaning that the 2,4′-pMDI resin produces a network which is relatively more mobile than the 4,4′-pMDI network, as expected. Furthermore, the differences shown here are in the mid-kilohertz frequency range, frequencies characteristic of impact loading. Consequently, we could expect that the wood adhesive bondlines of the respective isomeric networks would display dissimilar impact performance. It may be reasonable to predict that 2,4′-pMDI resins will have a higher resistance to impact loading.

TABLE VI $T_{1\rho}^{H}$ Values of a 2,4′-pMDI/wood composite sample[a] as a function of NMR acquisition temperature

Temperature (°C)	Peak (ppm)		
	138	104	44
5	3.0 (0.2)[b]	3.1 (0.1)	2.7 (0.3)
25	4.2 (0.2)	5.1 (0.1)	3.5 (0.2)
40	5.3 (0.2)	5.1 (0.1)	5.0 (0.1)

[a] Cured at 12 wt. % resin, 500 psi, and 120°C for 10 minutes.
[b] Values in parenthesis are standard errors of the $T_{1\rho}^{H}$.

CONCLUSIONS

The chemistry of the pMDI/wood adhesive bondline is complex and dynamic. Low molecular weight pMDI resins with a high content of the 4,4′-MDI isomer polymerize *via* the reaction with moisture in the wood bondline. Additional reactions involve isocyanate dimerization, biuret formation and probably urethane formation. The thermal decomposition of biurets is known to occur, and the thermal reversion of aryl urethanes may have been detected. Residual isocyanate is found under all curing conditions. These findings are similar to previous ones using a higher molecular weight resin; however, subtle differences exist. For example, it appears that urethane formation may be more common and biuret formation may be less common with a lower molecular weight resin. Low molecular weight pMDI resins with a high content of the 2,4′-MDI isomer generally exhibit the same cure chemistry as resins with high amounts of 4,4′-MDI, although minor dispersions in chemical shift are produced by the resin rich with 2,4′-MDI. Among the two resins, the one high in 2,4′-MDI cured more slowly and displayed a greater network mobility in the mid-kilohertz frequency range.

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