Solid state two-dimensional NMR studies of polymeric diphenylmethane diisocyanate (PMDI) reaction in wood

Shanci Bao
William A. Daunch
Yahong Sun
Peter L. Rinaldi
Joseph J. Marcinko
Chris Phanopoulos

Abstract

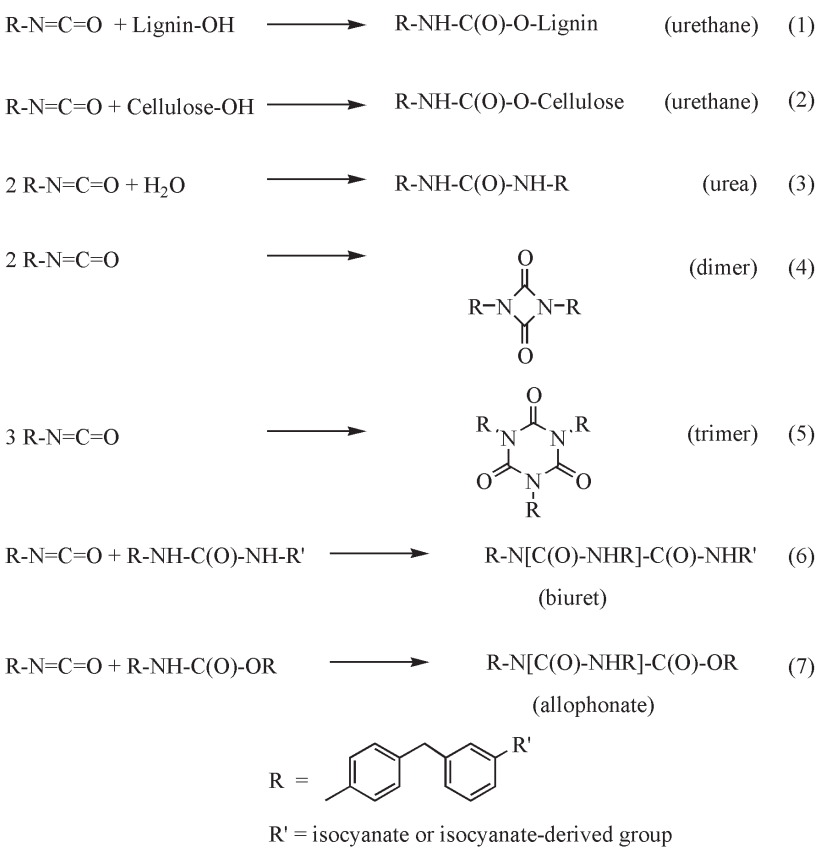
^{15}N-^{1}H heteronuclear correlation (HETCOR) NMR experiments were employed to study the products from the reaction of ^{15}N enriched polymeric diphenylmethane diisocyanate (PMDI) with cellulose, lignin, water, and aspen and southern yellow pine wood samples. Both urea and biuret structures can be clearly recognized in the wood/PMDI composites. Two peaks around 104 to 106 ppm result from different chemical environments of urea structures.

Polymeric diphenylmethane diisocyanate (PMDI) is a widely used adhesive in the forest products industry (Frink and Sachs 1981, Rowell and Ellis 1981, Skaar 1984, Johns 1989, Woods 1990). It has the advantage that it can be used at low concentration (about 2 to 5 wt%), and cures quickly (several minutes) at mild temperatures. All three major components of wood (cellulose, hemicellulose, and lignin) contain hydroxyl groups. The wood used in the manufacturing of wood composites usually has 6 to 12 percent moisture content (MC). Thus, there are two potential competing reactions with PMDI. One reaction is between water and PMDI to form urea structures. The second reaction is between PMDI and the sugar ring hydroxyl groups (or the lignin phenolic groups) to form urethane structures. Additional side reactions might be the addition of PMDI to urea to form biuret and the addition of PMDI with urethane to form allophonate. These possible reactions are shown in **Scheme 1.**

Previous studies of wood/isocyanate reactions have utilized Fourier transform infrared spectroscopy and differential scanning calorimetry (Rowell and Ellis 1979, 1981; Steiner et al. 1980; Owen et al. 1988; Galbraith and Newman 1992; Wendler and Frazier 1995). Conclusions drawn from some of that work are that dry wood can react with PMDI to form urethane structures, (Rowell and Ellis 1979, 1981) and that dry hemicellulose and lignin can react with PMDI to form urethane (Galbraith and Newman 1992, Owen et al. 1988), but dry cellulose cannot, under normal processing conditions (Owen et al. 1988). Other work has shown that the major products are urea/biuret structures if the MC is above 4.5 percent (Steiner et al. 1980). However, most of these studies were performed under laboratory conditions that were not necessarily representative of those employed during industrial manufacturing. Recently, Wendler and Frazier (1995, 1996a, 1996b) and Bao et al. (1999) have used ^{15}N cross polarization magic

The authors are, respectively, Graduate Research Assistants, Postdoctoral Research Associate, and Professor, Dept. of Chemistry, The University of Akron, Akron, OH 44325-3601; Senior Research Scientist, Huntsman Polyurethanes, 286 Mantua Grove Road, West Deptford, NJ 08066 (currently President, Polymer Synergies, LLC, P.O. Box 456, Mullica Hill, NJ 08062); and Senior Research Scientist, Huntsman Polyurethanes, Everslaan 45-B-3078 Everberg, Belgium. This paper was received for publication in September 2001. Article No. 9369.

Forest Prod. J. 53(6):63-71.



Scheme 1. — Possible reactions of MDI in wood.

angle spinning (CPMAS) NMR to study these complex reaction processes. Valuable information was obtained by using this powerful technique. The advantages of ^{15}N NMR are that: 1) all the signals come from the adhesive so that it offers a direct observation of the cure chemistry of the adhesive; 2) fewer resonances make interpretation of spectra easier (Wendler and Frazier 1995, 1996a, 1996b); and 3) the abundance of nitrogen-containing species in wood is low, so that there are no interfering signals from the wood. However, severe overlap of ^{15}N urea and urethane resonances in ^{15}N (CPMAS) NMR makes it difficult to resolve the signals of urethane from those of urea so that it is still not clear whether or not urethane structures exist.

In order to overcome these limitations from insufficient signal dispersion, two-dimensional (2D-) NMR can be used (Schmidt-Rohr and Spiess 1994). Solid state two-dimensional heteronuclear ^{13}C-^{1}H correlation (HETCOR) NMR methods have been used successfully to assign spectra of macromolecules (Bielecki et al. 1991). The advantages of this technique include: 1) the resolution in the 2D spectrum is better than that in either ^{15}N or ^{1}H spectra alone; overlapped signals in the one dimensional spectra are spread into two dimensions to provide higher dispersion; and 2) it provides a map of the individual I-S dipolar coupling information, which is not available in the one dimensional spectra. This paper illustrates the use of ^{15}N-^{1}H HETCOR as a technique to study the complex wood-PMDI adhesive composite system.

Experimental

sample preparation

^{15}N labeled PMDI for ^{15}N NMR studies was synthesized in the laboratory by Huntsman Polyurethanes from 95 percent ^{15}N enriched aniline (Bao et al. 1999). Cellulose and REPAP lignin samples were obtained from the Aldrich Chemical Company. The samples were dried at 110°C in a forced air oven for 1 hour and stored over a desiccant prior to use. Two samples, one of cellulose and a second of lignin powder were each mixed with ^{15}N PMDI 1:1 by weight, spread on aluminum plates, and pressed at 220°C for 60 seconds. A third sample of PMDI mixed with an excess of water was allowed to react for 1 minute at 110°C until a solid was obtained. These samples from the reaction of PMDI with lignin, cellulose, and water were used as references.

Harvested logs of aspen (*Populus tremuloides*) and southern pine were obtained from two forest product structural panel manufacturers. A representative log was cross sectioned. The cross sections were further cut in a tangential plane into veneers of approximately 100 mm by 100 mm by 1 mm. The veneers were conditioned in a forced air oven at 110°C for 1 hour. After ovendrying, the veneers were equilibrated to either 7 or 14 percent wood MC in environmental chambers. MCs were determined using a Wagner moisture meter Model-L606. The measurements were obtained from stacked veneers to ensure proper sampling depth.

After equilibration, the veneers were further cut into samples approximately 50 mm by 50 mm by 1 mm. The samples were coated with 10 percent of ^{15}N-enriched PMDI based on total mass of wood, and cured via hot-pressing. A pressing force of 150 psi was applied to the samples for 60 seconds at temperatures ranging from 120° to 220°C. The final thicknesses of the samples were approximately 50 percent of their original thicknesses prior to hot-pressing. The hot-pressed, PMDI-coated samples were then cut into 3-mm disks with a cork borer and stacked in a ceramic rotor for solid state NMR analysis. The incompletely cured sample (sample without heat treatment) was painted with 10 percent PMDI and then kept at room temperature for 5 hours.

NMR spectroscopy

The NMR spectra were collected on a Varian Unityplus 200 MHz NMR spectrometer at room temperature. The spectral window was 20 kHz. Heteronuclear two-dimensional NMR spectroscopy employed ^{15}N and ^{1}H $\pi/2$ pulses of 6 μs and averaging of 1536 transients per free induction decay. The proton evolution period consisted of 0-16 BLEW-12 (Caravatti et al. 1982, 1983, Kaplan 1993) cycles of 72 μs (12 × 6 μs) each, to suppress ^{1}H-^{1}H dipolar interactions. Simultaneously, BB-12 (Caravatti et al. 1982,1983; Bielecki et al. 1991; Kaplan 1993; Schmidt-Rohr and Spiess 1994) pulses were applied to ^{15}N in order to suppress ^{15}N-^{1}H heteronuclear dipolar interactions. A 63° pulse (orthogonal to

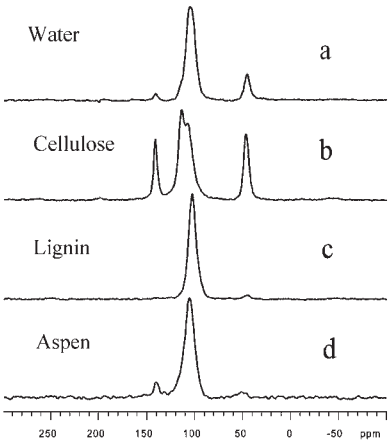


Figure 1. — The ^{15}N CPMAS spectra of PMDI reaction products from exposure to a) water at 110°; b) cellulose at 220°; c) lignin at 220°; and d) aspen at 220°.

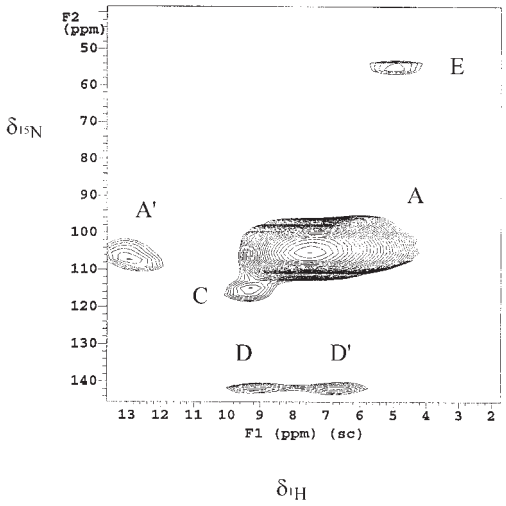
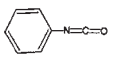
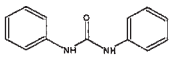
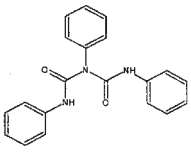
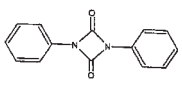
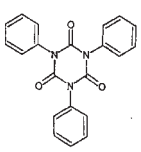


Figure 2. — ^{15}N(F2)-^{1}H(F1) HETCOR spectrum of PMDI/water reaction products.

Table 1. — Structures and ^{15}N chemical shifts of MDI-derived species (based on data presented by Duff and Maciel 1990a, 1990b, 1991a, 1991b).

Name	Structure	δ_{15N}
isocyanate		46 ppm
urea		104 ppm
biuret		114 ppm (NH) 141 ppm (N)
uretidione (dimer)		145 ppm
isocyanurate (trimer)		149 ppm

the initial π/2 preparation pulse) was applied to tilt the proton magnetization into the xy plane. Following the evolution period, ^{1}H polarization was selectively transferred to ^{15}N with *n*-cycle(s) (*n* = 1 and 16) of the WIM-24 multiple-pulse sequence (Caravatti et al. 1982, 1983; Bielecki et al. 1991; Kaplan 1993; Schmidt-Rohr and Spiess 1994), which caused cross polarization while effectively suppressing ^{1}H-^{1}H dipolar interactions. The magic angle spinning rate was 1.7 to 3.5 kHz, which is equal to half of a WIM-24 frequency or *m* times half of a WIM-24 frequency (where *m* is an odd integer), with the specific value chosen for each sample to optimize the overall performance. Selective cross polarization was followed by ^{15}N detection with continuous wave ^{1}H decoupling using a field strength of 50 kHz. The acquisition time was 12.8 ms and the relaxation delay was 1.2 second. The ^{1}H chemical shift scaling factor (0.44) during the evolution period was determined experimentally from the ^{1}H chemical shifts of ^{15}N enriched succinimide.

Results and discussion

Figure 1 shows ^{15}N CPMAS NMR spectra obtained from the reaction of ^{15}N enriched PMDI with water, cellulose, lignin, and aspen wood. The resonances near 142 ppm could be attributed to the nonprotonated ^{15}N of biuret or dimer structures (**Figs. 1a, 1b, and 1d**) (Duff and Maciel 1990a, 1990b, 1991a, 1991b; Bronnimann et al. 1992). The chemical shifts of the resonances in this spectrum can be compared with those of model compounds presented in **Table 1**. While the shifts of these ^{15}N's are different, the resolution in the 1D spectra is not sufficient to distinguish between these species. The resonances in the region of 110 to 120 ppm can be attributed to CO-NH-R of biuret structures. This peak can be clearly observed in **Figure 1b**, and appears as a shoulder in **Figures 1a** and **1d**. The fact that the peaks at 110 to 120 and ca. 142 ppm increase together when comparing the spectra in **Figures 1a**, **1b**, and **1d** is consistent with the hypothesis that they arise from the same (biuret) structure.

In the 100- to 110-ppm region, signals from urea structures are observed (Bielecki et al. 1991, Kaplan 1993, Schmidt-Rohr and Spiess 1994, Bao et al. 1999). The signal at 48 ppm is from the nitrogens of unreacted isocyanate

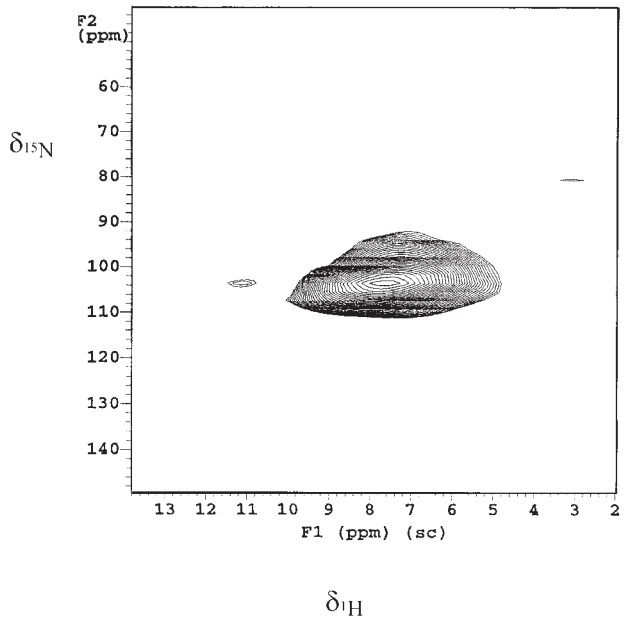


Figure 3.—^{15}N(F2)-^{1}H(F1) HETCOR spectrum of PMDI/lignin reaction products.

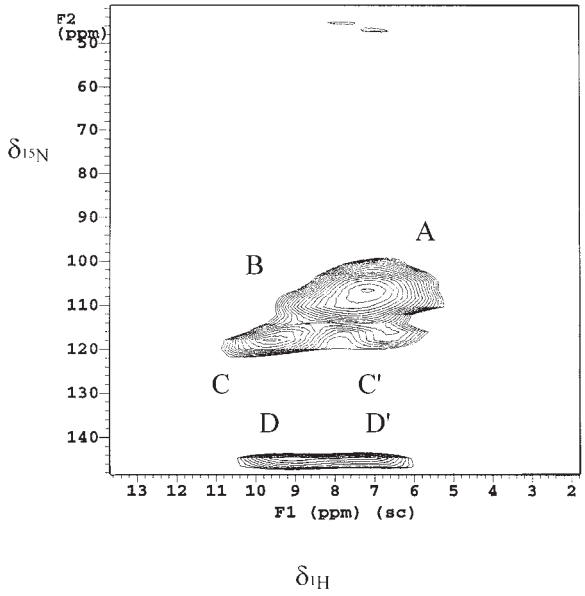


Figure 4.—^{15}N(F2)-^{1}H(F1) HETCOR spectrum of PMDI/cellulose reaction products.

groups in PMDI (Duff and Maciel 1990a, 1990b, 1991a, 1991b; Bronnimann et al. 1992). The ^{15}N CPMAS spectrum of PMDI-treated southern pine (not shown) is very similar to that of aspen (shown in **Fig. 1d**).

In the presence of a large excess of water, the predominant product is expected to be urea (106 ppm), as is observed in **Figure 1a**. When there is a deficiency of water, once all the available water is consumed, isocyanate will react with urea to form biuret. It is observed that the intensities of the peaks at 142, 115, and 48 ppm are much higher in cellulose (**Fig. 1b**) than in any of the other samples. Because this sample contains very little water and cellulose is highly crystalline, the possibility of PMDI reacting with water is very low. Due to the inavailablity of H_2O, the amount of unreacted isocyanate is much higher in cellulose. For the same reason, the unreacted isocyanate reacts preferentially with NH of urea to form biuret, rather than with the OH of cellulose to form urethane, which is also expected to produce resonances in the 105- to 110-ppm region.

In the solid state, NMR cross polarization between nuclei is not through the chemical bonds. As long as the concerned nuclei are close in space, cross polarization can occur in the absence of chemical bonding. The crosspeaks in the HETCOR spectrum will primarily arise from interactions between ^{15}N atoms and directly attached protons. However, additional crosspeaks will be observed between ^{15}N and other protons on the same molecule, and protons on neighboring molecules.

In order to understand the reaction of the different components of wood with PMDI, model samples were obtained from the reactions of each component with PMDI separately. The NMR spectra of related model chemicals can be found in references (Okuto 1966; Purgett et al. 1982; Duff and Maciel 1990a, 1990b, 1991a, 1991b; Bronnimann et al. 1992; Kricheldorf and Meier-Haack 1992; Pouchert and Behnke 1993a, 1993b, 1993c).

The 2D HETCOR NMR spectrum of the mixture from the reaction of PMDI in water (cured at 110°C for 1 min.) is shown in **Figure 2**. This spectrum clearly shows the crosspeak correlating the shifts of the urea ^{1}H and ^{15}N atoms (A) and a spinning sideband from this peak (A′). Crosspeaks C and D correlate the shifts of the biuret NH protons with the secondary and tertiary ^{15}N atoms of biuret structures, respectively. Because the ^{15}N that produces the signal at 142 ppm does not have directly attached protons, it is more likely to show correlations to the resonances of remote protons on the same and adjacent molecules. Crosspeak D′ is observed, relating these ^{15}N's with the aromatic protons of PMDI. It is observed that even when mixed with water, there is unreacted isocyanate remaining (crosspeak D). The resonance at 50 ppm (crosspeak E) is from interaction of the isocyanate nitrogen with protons having a chemical shift at 4 to 5 ppm (possibly from bulk H_2O or cellulose). The biuret ^{15}N resonance at 115 ppm is from the NH nitrogen that cross polarizes with the directly attached amide protons (9.4 ppm). The chemical shift of these amide protons in biuret is almost the same as those found in solution NMR spectra

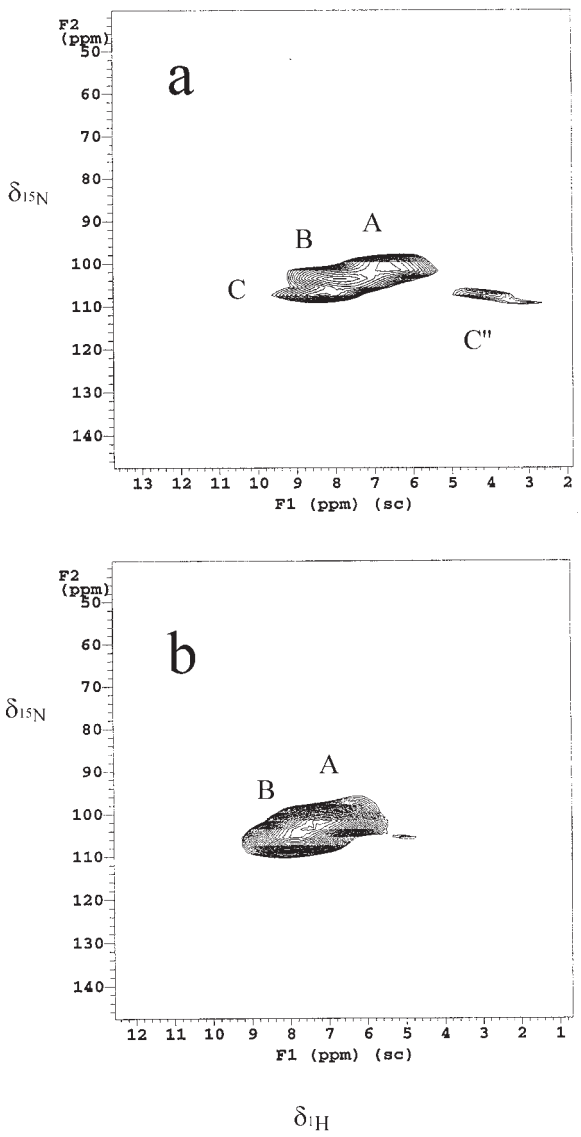


Figure 5. — $^{15}N(F2)$-$^{1}H(F1)$ HETCOR spectra of PMDI on aspen having 7 percent MC: a) uncured sample; and b) cured at 120°C for 1 minute.

(9.6 ppm). It is not as easy to form intermolecular hydrogen bonds with nitrogen nuclei in biuret as with those in urea. The resonance at 106 ppm contains contributions from the urea nitrogen that cross polarizes with protons whose chemical shifts are at 7.6 ppm.

The 2D HETCOR NMR spectrum of the mixture from the reaction of PMDI in lignin (cured at 200°C for 1 min.) is shown in **Figure 3**. The urea ^{15}N resonance is at 104 ppm compared with the 106-ppm shift of this resonance observed for the corresponding structure in **Figure 2**. A shoulder on the aromatic area is observed when compared to the spectrum of the sample from the reaction of PMDI in water. This indicates that aromatic protons in lignin are in proximity to the PMDI nitrogens. The fact that there is no signal from unreacted isocyanate or from biuret implies that there are more hydroxyl groups (from water or from wood components) or that the hydroxyl groups are more available for reaction. It is noticed that urea structures in an aromatic ring-rich environment have ^{15}N atoms with a chemical shift of 104 ppm, which cross polarize with the amide protons whose chemical shift is 7.7 ppm.

The 2D HETCOR NMR spectrum of the mixture from the reaction of PMDI in cellulose (cured at 200°C for 1 min.) is shown in **Figure 4**. It is obvious that the content of biuret structures is much higher (crosspeaks C and C′, and D and D′) in this sample than in the PMDI/water sample cured at the lower temperature, and the PMDI/lignin and PMDI/aspen samples cured at the same temperature. The resonance at 142 ppm primarily contains contributions from the tertiary nitrogen of the biuret structure. The resonance at 116 ppm contains contributions from the secondary amide nitrogen of the biuret structure, which cross polarize with protons at 9.3 ppm (amide protons) and 7.2 ppm (aromatic protons). The cellulose is highly crystalline so that only a limited amount of moisture can be absorbed on the surface of crystals. The lack of moisture results in the formation of a high percentage of biuret structures. One urea peak is observed around 106 ppm, which cross polarizes with amide protons at a chemical shift of 7.3 ppm (crosspeak A).

The different chemical shifts of the amide protons of PMDI in lignin and in cellulose environments may be due to the different shielding effects of the aromatic rings of lignin compared to the saturated sugar rings. They may also be due to chemical shifts averaging from chemical exchange with the phenolic hydroxyl protons of lignin or the alcoholic hydroxyl protons of the sugar ring. The observed relative shifts of the amide-type protons in PMDI are certainly consistent with the former explanation.

In the spectrum of uncured PMDI in aspen wood having a 7 percent MC (**Fig. 5a**), the nitrogen nuclei with chemical shifts between 100 to 110 ppm cross polarize with four types of protons: the aromatic proton (6.7 ppm, A), two types of amide protons (8 and 8.3 ppm, B and C) of urea structure and the protons from the sugar rings in cellulose and hemicellulose (3 to 5 ppm, C′). The aromatic protons (6.8 ppm, A) can arise from both PMDI- and/or lignin-rich environments (Lundquist 1980, Jin et al. 1997). It can be assumed that the signals of aromatic protons are mainly from PMDI because all of the ^{15}N's are near PMDI aromatic protons on the same molecule, although the relative intensity of lignin resonances in the ^{13}C NMR spectrum (not shown) is low. Both the hydroxyl protons and aliphatic sugar ring protons can contribute to the signals at 3 to 5 ppm. If the signals in this region arise primarily from the aliphatic protons, there should be no change after the

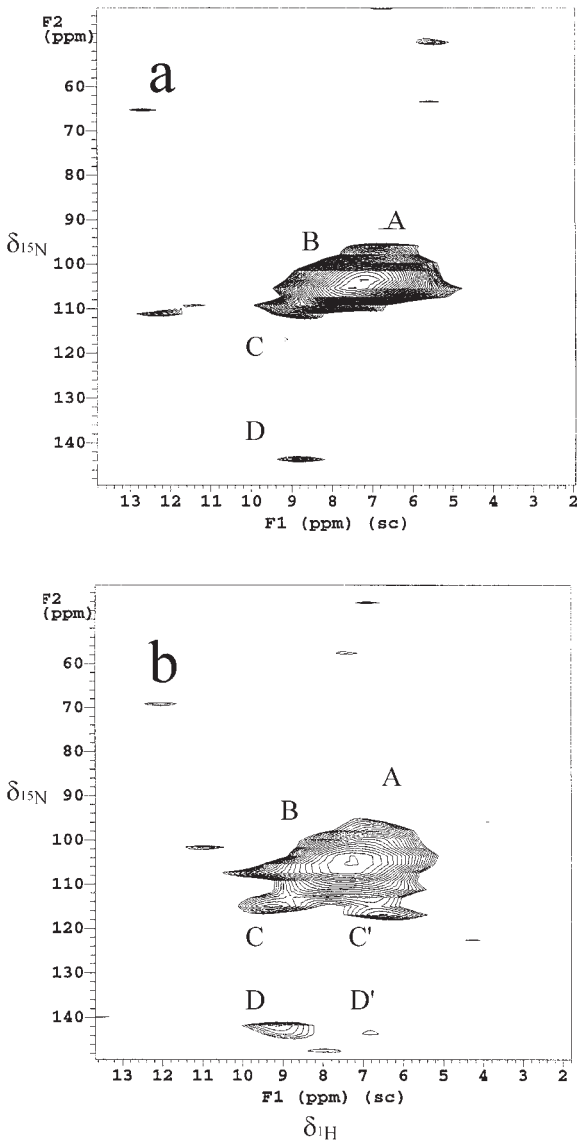


Figure 6. — ^{15}N(F2)-^{1}H(F1) HETCOR spectra of PMDI: a) in aspen having 7 percent MC and cured 1 minute at 160°C; and b) in southern pine having 7 percent MC and cured 1 minute at 220°C.

wood is cured. If the signals in the 3- to 5-ppm region are mainly from water and the hydroxyl groups of cellulose, some change must occur because during the curing period the water is consumed and the hydroxyl groups are incorporated into amide-type structures. It is noticed that the cured samples do not have proton signals in this area (**Figs. 5b** to **7b**), indicating that the signals come mainly from water.

Of particular interest is the fact that there are two kinds of amide protons at 8 ppm and 8.3 ppm. The corresponding ^{15}N chemical shifts are about 1 to 2 ppm apart. Those resolved resonances could suggest the presence of both urea and urethane structures. However, it is well known that the reaction rate of water with isocyanate is much more rapid than the reaction of secondary alcohols with isocyanate (Pirkle and Hauske 1977). The presence of water will further minimize the formation of urethane. Furthermore, rotational echo double resonance (REDOR) (Gullion and Schaefer 1989) experiments performed in our laboratory failed to reveal signals from dipolar interactions between ^{15}N of PMDI-derived species and the ^{13}C resonances of cellulose; this is consistent with the absence of urethane structures. The only REDOR signals observed were those indicating the proximity of PMDI-derived ^{15}N and aromatic ^{13}C resonances of aromatic groups from PMDI-derived species and/or lignin. The limit of detection for the REDOR experiments performed is several percent. Therefore, it is not likely that the reaction between wood (with about 7% to 14% moisture) and PMDI can result in a high percentage of urethane structures at room temperature in 5 hours. The two kinds of amide protons might also arise from urea structures in different chemical environments such as the aromatic ring-enriched environment of polyurea in voids between cells, and the cellulose-hydroxyl proton-enriched environment within the cell structure.

The spectrum from the sample of 7 percent MC aspen with 10 percent PMDI cured at 120°C for 1 minute is shown in **Figure 5b**. When comparing this spectrum with the spectrum in **Figure 5a**, one can observe common peaks A and B are present. However, peak C′ is absent as a result of the reaction of PMDI with moisture. Without heating, unreacted PMDI has time to diffuse into the cellulose-rich environment of the wood cell wall. Crosspeak C″ in **Figure 5a** indicates the PMDI urea nitrogens are in the proximity of cellulose sugar rings. The presence of unreacted isocyanate in this environment is consistent with the low probability of finding urethane linkages.

The spectrum of 7 percent MC aspen with 10 percent PMDI (cured at 160°C for 1 min.) is shown in **Figure 6a**. The peaks at 112 ppm (C) and 141 ppm (D) are biuret NH and the tertiary nitrogens, respectively. Isocyanate reacts more rapidly at 160°C than at room temperature, so the available water near the isocyanate was exhausted and urea NH groups are the only other readily available reactive group. Therefore, the isocyanate can react with urea to form biuret. However, the NH group of urea is less reactive than water, so the content of biuret is low. Another explanation for the formation of biuret is that the reactivities of isocyanate with water and NH groups of urea become less selective as the reaction temperature increases. There are two peaks (104 and 106 ppm, A and B) in the center of **Figure 6a**. The chemical shifts along the F1 axis are at 7.4 ppm and 7.8 ppm, consistent with the shifts of amide protons in the aromatic ring enriched environment. The shift of the aromatic protons cannot be resolved because of extensive peak overlap.

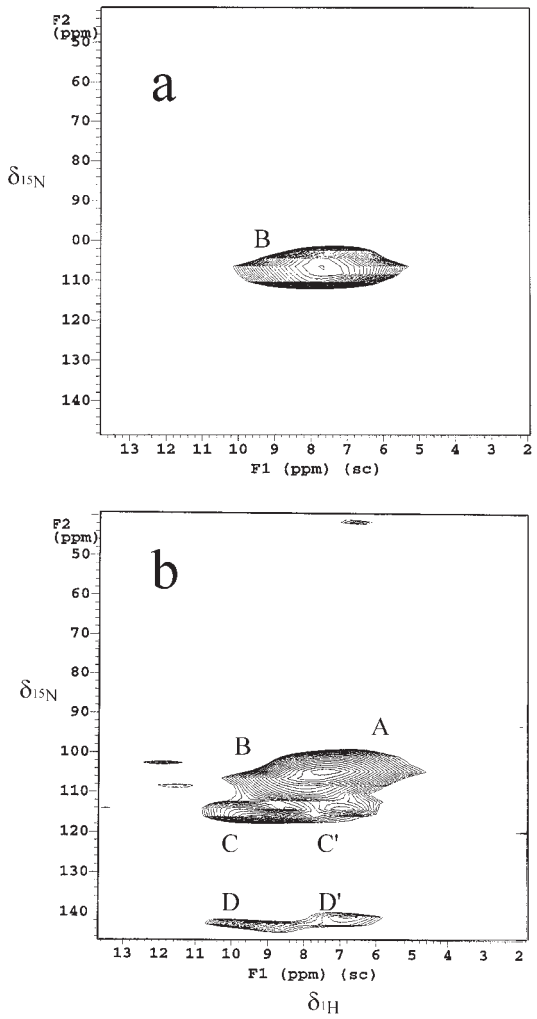


Figure 7. — $^{15}N(F2)$-$^{1}H(F1)$ HETCOR spectra of PMDI: a) in aspen having 14 percent MC and cured 1 minute at 160°C; and b) in southern pine having 7 percent MC and cured 1 minute at 220°C.

The 2D HETCOR NMR spectrum of the 7 percent MC southern pine with 10 percent PMDI (cured at 220°C for 1 min.) is shown in **Figure 6b**. The peak intensities for biuret structure (C, C′, D, and D′) are less intense than the corresponding peaks in **Figure 4** but stronger than the corresponding peaks in **Figure 6a**. This may be because the reaction rates for formation of both urea and biuret increase with the temperature. When there is a low water content in the wood and more urea NH groups are present in proximity to the isocyanate, more biuret structure will be produced.

For 14 percent MC aspen (**Fig. 7a**), only one urea peak is observed when the wood composite is cured at or below 160°C. This indicates that when wood has a high MC, the PMDI is mainly in one type of environment. Because there is a high content of water available at the beginning of the reaction, the PMDI formation rate is too rapid to permit a significant amount of PMDI to penetrate into the wood cells. In the case of low MC (such as 7% MC), some of the PMDI can react with moisture to form urea, and some of the PMDI can penetrate into wood cells and then form urea. Consequently, PMDI can exist in two different environments.

The spectrum of 14 percent MC southern pine cured with 10 percent PMDI at 220°C for 1 minute is shown in **Figure 7b**. A high percentage of biuret structures are apparent. This phenomenon was not observed for the wood samples with 7 percent MC or when the cure temperature was lower. This may be because: 1) PMDI can initially penetrate into the wood cell quickly but as the PMDI reacts, higher molecular weight PMDI cannot; 2) the diffusion rate of water is slower than the reaction rate of the PMDI with water at high temperature; 3) the reaction rate for urea formation depends both on the availability of water and the temperature. When southern pine with 14 percent MC was cured at 220°C, a large amount of water is available at the very beginning of the reaction and isocyanate reacts too rapidly to diffuse into the wood cell. When the available water is exhausted and urea NH groups are readily available, the isocyanate will react with the urea to form the biuret structure. For aspen with 14 percent MC, a similar phenomenon was observed. However, the percentage of biuret structure is much lower (Bao et al. 1999), possibly because the structures of wood cells of aspen are different from those of southern pine.

Model for PMDI bonding

Based on the previous discussion, a model for the PMDI bond can be proposed, which is illustrated with the aid of the diagram in **Figure 8**. PMDI can penetrate into the wood cells and into the middle lamellae between the wood cells. Once there, it reacts with the available moisture stored in the wood to form either linear urea structures (indicated by the linear segments in **Fig. 8**) and/or crosslinking biuret/dimer/trimer structures (indicated by ■ in **Fig. 8**). The chain length of each linear PMDI segment will probably be short compared to the dimensions of the wood cell. The crosslinking structures join chain segments to form a PMDI network. At high crosslink densities, this PMDI forms one network polymer. Because some chain segments are within wood cells and some chain segments are between wood cells, the PMDI network can mechanically and physically bind wood composites at the molecular level. Additionally, the PMDI may bond hydrogen with the chemical components of the wood (Chen et al. 1998) and can further contribute to adhesion. The crosslinking can also serve to increase the rigidity of the plywood, especially at high levels of crosslinking.

Conclusions

The major components formed from the curing of PMDI in wood are urea structures arising from the reaction with water. At higher temperatures and low MC, PMDI can react with urea NH's to form crosslinking biuret and/or dimer

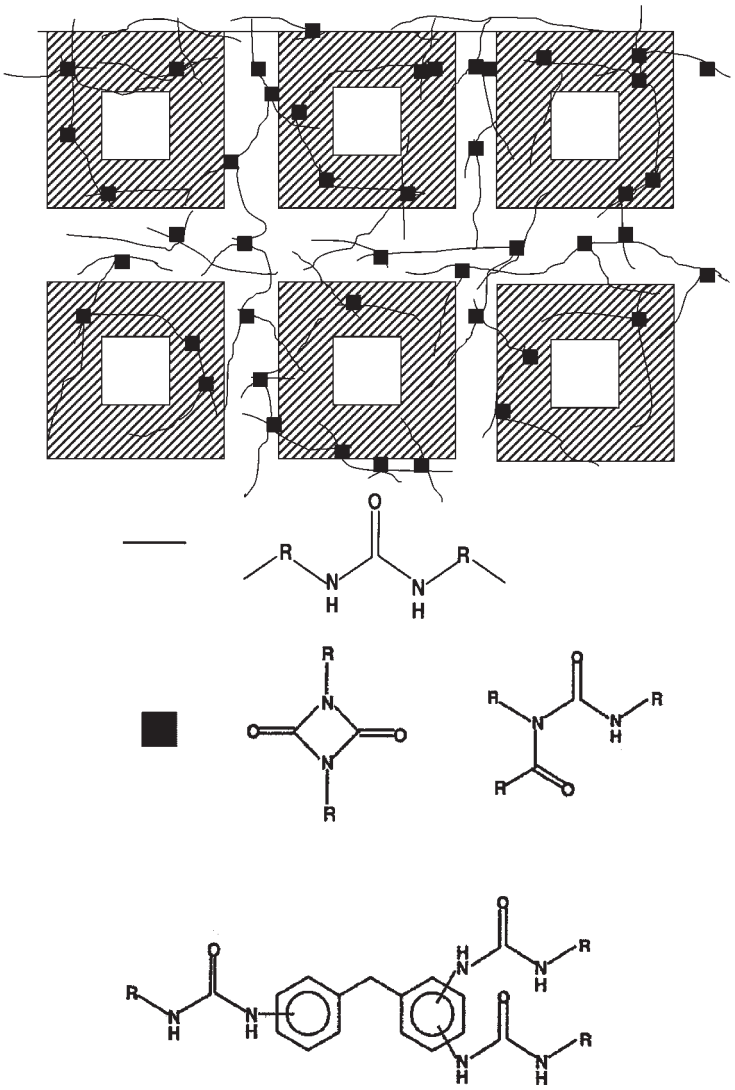


Figure 8. — Model for PMDI bonding.

and trimer structures. Two peaks around 104 to 106 ppm result from different chemical environments of urea structure. The excellent adhesion properties of PMDI might be linked to the good penetration ability of PMDI before reaction with moisture in the wood matrix, and the ability to use MC, isocyanate equivalent weight, and cure temperature to control the fraction of crosslinking structures formed in the final product.

Literature cited

Bao, S., W.A. Daunch, Y. Sun, P.L Rinaldi, J.J.Marcinko, and C. Phanopoulos. 1999. Solid state NMR studies of methylene diisocyanate (PMDI) derived species in wood. J. Adhesion 71:377-394.

Bielecki, A. ,D.P. Burum, D.M. Rice, and F.E. Karasz. 1991. Solid-state two-dimensional ^{13}C-^{1}H correlation (HETCOR) NMR spectrum of amothphous poly(2,6-dimethyl-p-phenylene oxide)(PPO). Macromolecules 24(17):4820-4822.

Bronnimann, C.E., C.F. Ridenour, D.R. Kinney, and G.E. Maciel. 1992. 2D ^{1}H-^{13}C heteronuclear correlation spectra of representative organic solids. J. Magn. Reson. 97(3):522-534.

Caravatti, P., G. Bodenhausen, and R.R. Ernst. 1982. Heteronuclear solid-state correlation spectroscopy. Chem. Phys. Letters. 89(5):363-367.

_____, L. Braunschweiler, and R.R. Ernst. 1983. Heteronuclear correlation spectroscopy in rotating solids. Chem. Phys. Letters 100(4):305-310.

Chen, Q., G. Yang, Y. Wang, X. Wu, H. Kurosu, and I. Ando. 1998. Hydrogen bonding interactions in polyureas as studied by variable-temperature high-resolution ^{1}H NMR spectroscopy. J. Molecular Struct. 471:183-188.

Duff, D.W. and G.E. Maciel. 1990a. ^{13}C and ^{15}N CP/MAS NMR characterization of MDI-polyisocyanurate resin systems. Macromolecules 23(12):3069-3079.

_____ and _____. 1990b. ^{13}C and ^{15}N CP/MAS NMR characterization of biuret-rich 4,4'-methylenebis(phenyl isocyanate) based resins. Macromolecules 23(20):4367-4371.

_____ and _____. 1991a. Monitoring the thermal degradation of an isocyanurate- rich MDI-based resin by ^{15}N and ^{13}C CP/ MAS NMR. Macromolecules 24(3):651-658.

_____ and _____. 1991b. Monitoring postcure reaction chemistry of residual isocyanate in 4,4'-methylenebis(phenyl isocyanate) based isocyanurate resins by ^{15}N and ^{13}C CP/MAS NMR. Macromolecules 24(2):387-397.

Frink, J.W. and H.I. Sachs. 1981. Isocyanate binders for wood composite boards. *In*: Urethane Chemistry and Applications. K.N. Edwards, ed. Am. Chem. Soc., Washington, DC. pp. 285-309.

Galbraith, C.J. and W.H. Newman. 1992. Reaction mechanisms and effects with MDI isocyanate binders for wood composites. In: Proc. Pacific Rim Bio-Based Composites Symp., Rotorua, New Zealand. New Zealand Forest Research Institute, Rotorua, NZ. pp. 130-142.

Gullion, T. and J. Schaefer. 1989. Rotational-echo double-resonance NMR. J. Magn. Reson. 81(11):196-200.

Jin, S., P.M. Mungara, and K.E. Gonsalves. 1997. Synthesis of polyamides and polyureas containing leucine-tyrosine linkages. J. Polym. Sci. Polym. Chem. 35:499-507.

Johns, W.E. 1989. The chemical bonding in wood. *In*: Wood Adhesives: Chemistry and Technology. A. Pizzi, ed. Marcel Dekker, New York. pp. 75-96.

Kaplan, S. 1993. Compatibility of TPD/polycarbonate blends by ^{13}C-^{1}H HETCOR in the solids state. Macromolecules 26:1060-1064.

Kricheldorf, H.R. and J. Meier-Haack. 1992. Polymers of carbonic acid, 8. Makromol. Chem. 193:2631-2645.

Lundquist, K. 1980. NMR studies of lignins. 4. Investigation of spruce lignin by ^{1}H NMR spectroscopy. Acta Chem. Scan. Ser.B. 34:21-26.

Okuto, H. 1966. Studies on the structure of polyurethane elastomers II. High resolution NMR spectroscopic determination of allophanate and biuret linkages in the cured polyurethane elastomer: Degradation by amine. Makromol. Chem. 98:148-163.

Owen, N.L., W.B. Banks, and H. West. 1988. FTIR studies of the "wood"-isocyanate reaction. J. Molecular Struct. 175:389-394.

Pirkle, W.H. and J.R. Hauske. 1977. Broad spectrum methods for the resolution of optical isomers: A discussion of the reasons underlying the chromatographic separability of some diastereomeric carbamates. J. Org. Chem. 42:(11)1839-1844.

Pouchert, C.J. and J. Behnke. 1993a. The Aldrich library of ^{13}C and ^{1}H FT NMR Spectra. Aldrich Chemical Company, Milwaukee, WI. 1-300.

_____ and _____. 1993b. The Aldrich library of ^{13}C and ^{1}H FT NMR Spectra. Aldrich Chemical Company, Milwaukee, WI. 1-900.

_____ and _____. 1993c. The Aldrich library of ^{13}C and ^{1}H FT NMR Spec-

tra. Aldrich Chemical Company, Milwaukee, WI. 2-358.

Purgett, M.D. W. Deits, and O. Vogl. 1982. Functional polymers. XIX. Biuret oligomers and polymers of biologically active primary aliphatic amines. J. Polym. Sci. Polym. Chem. 20:2477-2499.

Rowell, R.M. and W.D. Ellis. 1979. Chemical modification of wood: Reaction of methyl isocyanate with southern pine. Wood Sci. 12(2):52-58.

_____ and _____. 1981. Bonding of isocyanates to wood. *In*: Urethane Chemistry and Applications. K.N. Edwards, ed. Am. Chem. Soc., Washington, DC. pp. 263-284.

_____, W.C. Feist, and W.D. Ellis. 1981. Weathering of chemically modified southern yellow pine. Wood Sci. 13(4):202-208.

Schmidt-Rohr, K. and H.W. Spiess. 1994. Multidimensional Solid-State NMR and Polymers. Academic Press, San Diego, CA.

Skaar, C. 1984. Wood-water relationships. *In*: The Chemistry of Solid Wood. Advances in Chemistry Series. R. Rowell, ed. 207:127-172. Am. Chem. Soc., Washington, DC. .

Steiner, P.R., S. Chow, and S. Vadja. 1980. Interaction of polyisocyanate adhesive with wood. Forest Prod. J. 30(7):21-27.

Wendler, S.L. and C.E. Frazier. 1995. The ^{15}N CP/MAS NMR characterization of the isocyanate adhesive bondline for cellulosic substrates. J. Adhesion 50:135-153.

_____ and _____. 1996a. Effect of moisture content on the isocyanate/wood adhesive bondline by ^{15}N CP/MAS NMR. J. Appl. Polym. Sci. 61:775-782.

_____ and _____. 1996b. The effects of cure temperature and time on the isocyanate-wood adhesive bondline by ^{15}N CP/MAS NMR. Int. J. Adhesion and Adhesive 16(3)179-186.

Woods, G. 1990. An introduction to polyurethanes. *In*: The ICI Polyurethane Book, 2nd ed. John Wiley & Sons, New York. pp. 1-30.