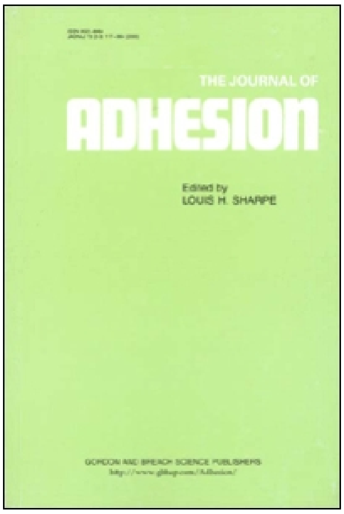

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Solid State NMR Studies of Polymeric Diphenylmethane Diisocyanate (PMDI) Derived Species in Wood

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^{15}N variable contact time (VCT) cross polarization magic angle spinning (CPMAS) NMR experiments were employed to investigate the reaction products formed in wood composites bonded with ^{15}N-enriched polymeric diphenylmethane diisocyanate (PMDI)-based adhesives. Two wood species were studied, Aspen (*Populus tremuloides*) and Southern Pine (*Pinus sylvestris*). The influence of temperature and wood moisture content on the distribution of PMDI-derived species are presented and discussed.

Keywords: Solid state NMR; wood; wood binder; PMDI; polyurethane

INTRODUCTION

Engineered wood composites are a major contributor to the North American economy. The increased growth of these industries that produce wood composites is directly attributable to three factors: the diminishing and controlled supply of old growth timber, the ease of manufacture, and the variety of structural applications developing for reconstituted wood and engineered lumber. The study of these

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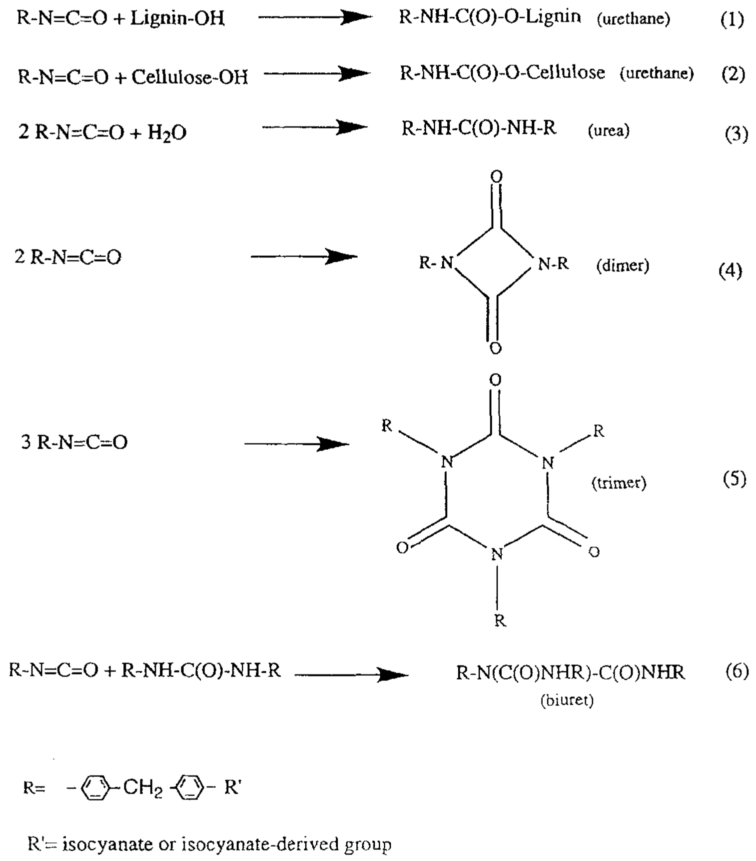
composites provides a challenge because of the natural diversity associated with any biological system and because the resin or adhesive phase is usually present in relatively low concentrations, typically 2 to 10 percent. The challenge thus present, is determining the relative contribution of the composite components and the adhesion mechanism(s) contributing to the performance of these composites.

PMDI-based adhesives have been increasingly utilized in the manufacture of engineered wood composites because of advantages in composite performance and processing imparted by these adhesive systems. Wood consists of five major chemical components; cellulose, hemicellulose, lignin, extractives and water. Cellulose constitutes about



SCHEME 1

40–50% of dry wood, hemicellulose 25–35%, and lignin 18–35% [1]. The equilibrium moisture content in dry wood ranges from approximately 5–15%. Each of these components has the potential to react with the isocyanate functionality of PMDI adhesives. Several possible reactions are presented Scheme 1. The extractives constitute about 4–10% of dry wood, part of which are removed from the wood during the drying process [1]. Extractives also affect wood bonding through their pH effects and penetration effects. The adhesion process is greatly influenced by the pH value of the wood when acid-catalyzed UF adhesives are applied [1]. The influence of extractives on the adhesion process is not as noticeable in alkaline-catalyzed PF adhesives and non-catalyzed isocyanate adhesives as in acid-catalyzed adhesives. In this study we will discuss the differences observed between two wood species, Aspen and Southern Pine, in the presence of PMDI adhesive. ^{15}N and ^{13}C variable contact time (VCT) cross polarization magic angle spinning (CPMAS) NMR experiments were applied to investigate the influence of cure temperature and moisture content on the reaction of PMDI in Aspen and Pine. Recently, Ni and Frazier have used ^{15}N cross polarization magic angle spinning (CPMAS) NMR to study the complex reaction process and valuable information was obtained by this powerful technique [2]. The intent of this work is to determine the physicochemical properties contributing to the high performance observed for wood composites manufactured with PMDI adhesives.

EXPERIMENTAL

Sample Preparation

The PMDI used in the ^{13}C studies was Rubinate® Binder-1840. The PMDI resin had an isocyanate equivalent weight of 135, NCO content of 31.2%, and the viscosity at 25°C was 250 cps. ^{15}N-labeled PMDI for ^{15}N NMR studies was synthesized in the laboratory by ICI Polyurethanes from 95% ^{15}N-enriched aniline.

Harvested logs of Aspen 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 direction into veneers of approximate size 100 mm × 100 mm × 1 mm. The veneers were conditioned in a 110°C forced air oven for one hour. After oven drying, the veneers were equilibrated to 7% and 14% wood moisture contents in environmental chambers. Moisture contents 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 × 50 mm × 1 mm. The samples were coated with 10% (by weight of the wood sample) of ^{15}N-enriched PMDI and cured *via* hot pressing. A pressure of 150 psi was applied to the samples for sixty seconds at temperatures ranging from 120°C to 220°C. The final thicknesses of the samples were approximately 50 percent of their original thickness 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.

Cellulose and REPAP lignin samples were obtained from Aldrich Chemical. The samples were dried in a 110°C forced air oven for one hour and stored over desiccant prior to use. The cellulose and lignin powder were mixed with ^{15}N PMDI 1 : 1 by weight, spread on aluminum plates and pressed at 220°C for sixty seconds. The PMDI was also mixed with a large excess of water and allowed to react for 1 min at 110°C. The lignin, cellulose and water samples were used as references.

NMR Studies

The NMR spectra were collected on a Varian Unityplus 200 MHz NMR spectrometer and on a home-built 200 MHz NMR spectrometer, at room temperature.

Hexamethylbenzene (HMB) was used as an external reference for ^{13}C chemical shifts ($\delta^{13}C_{\text{methyl}} = 17.3$ ppm); double-labeled $^{15}NH_4{}^{15}NO_3$ was used as a reference for ^{15}N chemical shifts ($\delta^{15}N_{NH_4^+} =$ 0 ppm, $\delta^{15}N_{NO_3^-} = 352$ ppm).

^{15}N CPMAS spectra were obtained at 20 MHz using a 57 kHz proton decoupling field strength and a 50 kHz spin locking field strength. The contact-time in the VCT experiment was arrayed from 20 μs to 12 ms. The acquisition time was 12.8 ms, and a spectral window of 20 kHz was used. The magic angle spinning (MAS) rate was

5 kHz. A total of 2048 accumulations were sampled using a relaxation delay of 1 second between each acquisition.

^{13}C CPMAS spectra were obtained at 50 MHz using a 57 kHz proton decoupling field strength and a 50 kHz spin locking field strength. The data acquisition and spectral window were the same as given above. A total of 1024 accumulations were obtained using a relaxation delay of 1 second between each acquisition.

RESULTS AND DISCUSSION

The ^{13}C CPMAS spectra of wood with and without PMDI can be seen in Figure 1. The resonance assignments for the structure seen

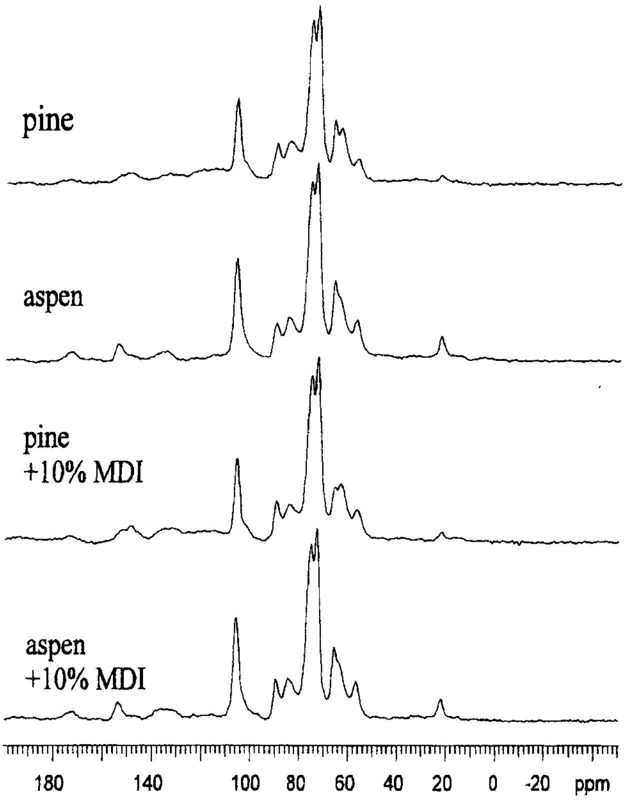
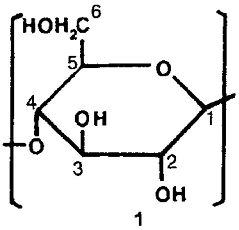


FIGURE 1 The ^{13}C CPMAS spectra of wood with and without PMDI.

below have been previously defined as follows [3], the C1 carbohydrate (**1**) carbon appears at approximately 105 ppm; C2, C3, and C5 at 73–78 ppm, C4 at 83–89 ppm, and C6 at 63–66 ppm. The peaks at 21 and 173 ppm can be attributed to CH_3 and C=O of acetate in hemicellulose. Resonances associated with lignin are the methoxyl groups appearing at 54 ppm and the aromatic carbons between 130 and 160 ppm. The aromatic peaks of PMDI also fall in the range of 130–160 ppm.



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The ^{15}N spectra are far less complicated when compared with the ^{13}C spectra. This can be attributed to the natural abundance of ^{15}N being low (0.37%) and the concentration of nitrogen-containing moieties within wood being small. Therefore, the ^{15}N resonances observed primarily arise from the ^{15}N-enriched PMDI and its reaction products. Figure 2 shows ^{15}N NMR spectra obtained from the reaction of ^{15}N-enriched PMDI with water, cellulose, REPAP lignin and aspen wood. The contact time is 3 ms in these CPMAS experiments. The NMR spectra of related model chemicals can also be found in the literature [4–8]. The resonances near 140 ppm can be attributed to nonprotonated ^{15}N of biuret (143 ppm) and dimer (145 ppm) structures. In the 100–120 ppm region, signals from CO-NH-R of biuret imide (116 ppm), urea (106 ppm) and urethane (104 ppm) structures are observed. The signal at 48 ppm is the nitrogen from the isocyanate group of MDI.

Figure 2a shows the reaction products of PMDI with water. The primary reaction products observed are polyurea and biuret. Unreacted isocyanate is also observed due to the high concentration of PMDI used to prepare this sample as well as from not allowing sufficient time and conditions for the isocyanate to react fully. The reaction of PMDI with dry cellulose (1–2% H_2O) yields urea, biuret, and possibly urethane (Fig. 2b). Cellulose is a highly-crystalline, polar

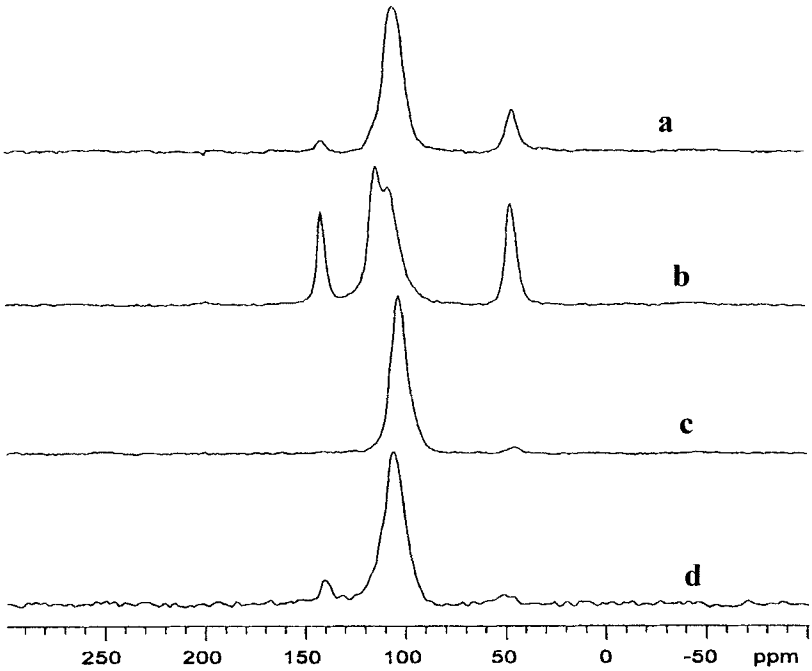


FIGURE 2 The ^{15}N CPMAS spectra of MDI-derived species from the reaction of PMDI in different media (a) Water at 110°C, (b) Cellulose at 220°C, (c) REPAP lignin at 220°C, (d) Aspen (7% moisture) at 220°C. All spectra were obtained with 3 ms contact times.

material with a strong affinity for water. In addition to the adsorbed water, the highly crystalline nature of the cellulose would surely limit the absorption of PMDI into the structure. As a result of these factors the observation of urethane formation is limited. The peak at 110 ppm is consistent with urea NH groups. The signals at 117 and 140 most likely arise from the NH and the tertiary nitrogens of biuret structures. We further observe unreacted isocyanate as indicated by the peak at 48 ppm in Figure 2b. This again we attribute to the high crystallinity of cellulose, the dry nature of the sample and the high concentration of PMDI used to prepare this sample.

The reaction of PMDI with lignin may produce urea and/or urethane products (Fig. 2c). Although the sample was dry (1–2% H_2O), just as was observed with cellulose we expect adsorbed moisture to be present since lignin also contains polar hydroxyl groups. Because the severe overlap of urea and urethane signals in this area, it is very hard to prove clearly or to disprove whether urethane structure exists. Our further two-dimensional NMR work proves that the only species detected in Figure 2c is from urea NH's of PMDI (to be published).

The products observed from the reaction of PMDI with Aspen wood (7% moisture) are similar to those observed in the PMDI/water sample (Fig. 2d). This is not surprising since water is the most favorable reactant in the wood samples.

Quantitative Analysis

In the CPMAS experiment, the relative peak intensities of two components, B and C, (at contact time = A) depend on their cross polarization rates (T_{CH}), their relaxation times in the rotating frame ($T_{1\rho}$) [9, 10] and the relative fraction of the components. In homogeneous materials a single $T_{1\rho}$ ensures that the relative intensities of two components are the same as the relative fractions of the components for different contact times once cross polarization is completed (see Fig. 3). Beyond CT = 5000 μs the curves for components 1 and 2 parallel each other. Quantitation can be obtained from any single spectrum with CT greater then 5000 ms. However, in heterogeneous materials spin diffusion between regions containing dissimilar structures may not be sufficiently fast to give a single $T_{1\rho}$, so the relative intensities of signals from components in different domains vary with the contact time. T_{CH} is proportional to the sixth power of the distance between ^{13}C or ^{15}N nuclei and the nearest protons. Thus, the T_{CH} of ^{15}N nuclei with ^{1}H directly attached will be much shorter than those of ^{15}N nuclei without directly-attached protons.

Wood is a heterogeneous system in which there are a number of phases, cellulose/hemicellulose and lignin. The $T_{1\rho}$ and T_{CH} are different for species in different phases. The ^{15}N-^{1}H distances in the raw material are different from those in the MDI-derived species, as are the mobilities. Therefore, it is not possible to compare directly the relative signal strengths from a single spectrum in Figure 2 to extract relative quantities of material.

Plots of peak intensity *vs.* CT for the signals at 110 and 48 ppm in a series VCT CPMAS are shown in Figure 4. It is clear that the ratio of the peak intensities change over the entire range of contact times.

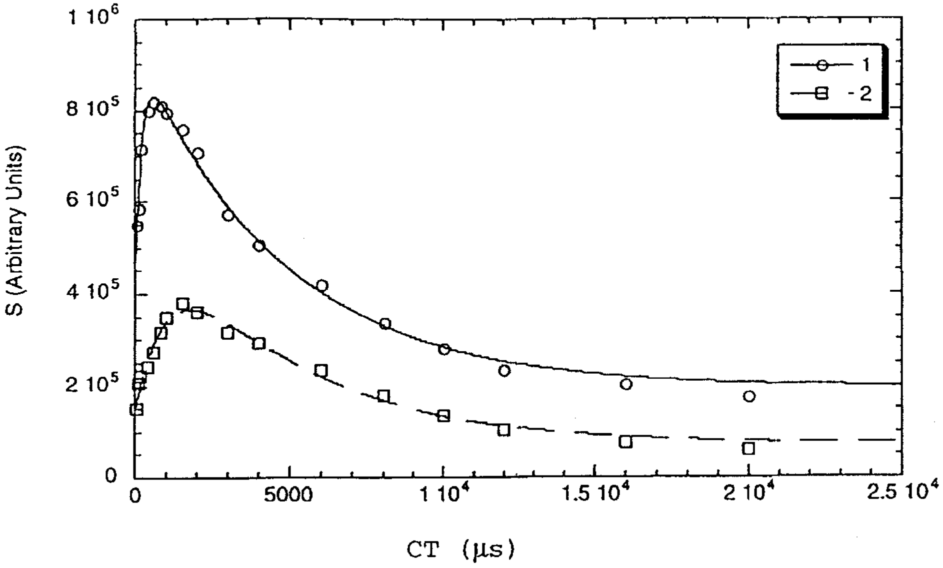


FIGURE 3 Plots of signal intensity *vs*. CT in a variable contact-time experiment of a homogeneous sample which contains two species with the same $T_{1\rho}$ (generalized plots).

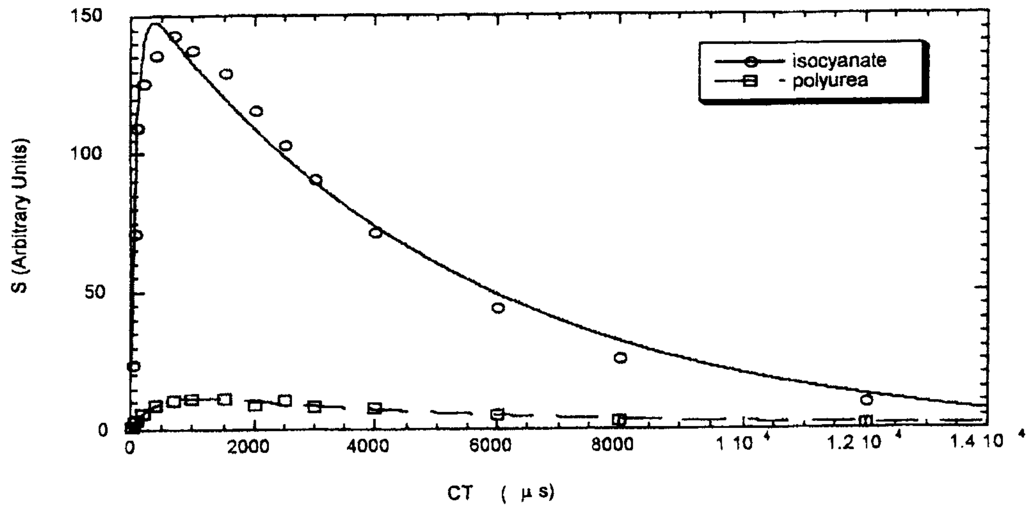


FIGURE 4 Plots of signal intensity *vs.* CT in a variable contact-time experiment of a heterogeneous sample which contains two species with different $T_{1\rho}$.

The intensity variation with contact time follows a biexponential curve described by

$$S = [S_0 - (S_0 - S_{\mathrm{inf}}) \times \exp(-A/T_{\mathrm{CH}})] \times \exp(-A/T_{1\rho}) \qquad (7)$$

The spectral intensity (S) of each peak at contact time $= A$ is a function of the product of a decreasing exponential function with a time constant $T_{1\rho}$, and an increasing exponential function with a time constant T_{CH}, S_0 is the signal intensity at CT $= 0$ if cross polarization were instantaneous, and is related to the absolute amount of a material in a sample. By fitting the intensity variation of each peak to Eq. (7), S_0 values can be obtained. The relative S_0 values for peaks is representative of the relative concentrations of species. The relative fraction (Fj) of MDI-derived species j was then calculated from their S_0 as follows:

$$Fj = S_{0j} / \sum_i S_{0i} \qquad (8)$$

where S_{0j} is the S_0 of component j and the denominator contains the sum of the S_0 values for all the detectable MDI-derived species in the sample.

Quantitative analyzes of all samples were performed by determining S_0 values for each component.

^{15}N NMR Data

Figure 5 shows a plot of the variation in the fraction of MDI-derived species in a series of samples of Aspen equilibrated to a 7% moisture content, coated with 10% ^{15}N-labeled PMDI, and cured at different temperatures. These temperatures are representative of those which might be reached through the thickness of a composite board going from the surface to the center of the board. The influence of temperature on the reaction is apparent. The relative fraction of unreacted isocyanate decreases rapidly with increasing temperature. Very little isocyanate functionality remains unreacted after 1 min reaction time at 200°C. At 120°C, under the conditions of our experiments, over 40% of the isocyanate remains unreacted and the only other component detected is polyurea. Increasing the reaction temperature results

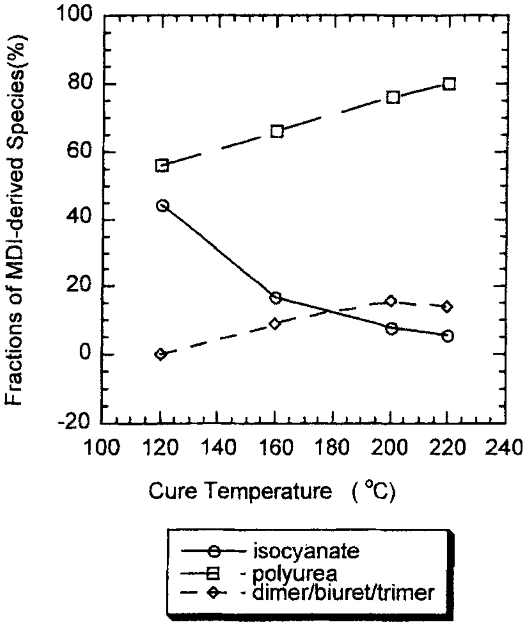


FIGURE 5 Relative fraction of MDI-derived species in Aspen with 7% moisture + 10% PMDI cured 1 min.

in modest increases (30%) in the fraction of polyurea structures, but a substantial increase (from 0% to 15%) in the amount of branching structures (biuret). This change in the number of cross-linking structures can have a dramatic influence on the mechanical properties of the wood composite.

Figure 6 illustrates data obtained for Aspen wood conditioned to have a 14% moisture content. Comparing these data with the data in Figure 5 we observe little difference in the percentage of reaction products at 120°C and 220°C, the low and high temperature extremes. However, the higher moisture content wood appears to produce the final fractional distribution of PMDI reaction products at a lower temperature; *i.e.*, there is little difference in the fractional percentage of products in the samples cured at 160°C and 220°C.

For Southern Pine, the influence of temperature appears to be less pronounced (Fig. 7). It appears that the conversion of PMDI to reaction products is quicker in Southern Pine as compared with Aspen. As can be observed, approximately 80% of the isocyanate is converted

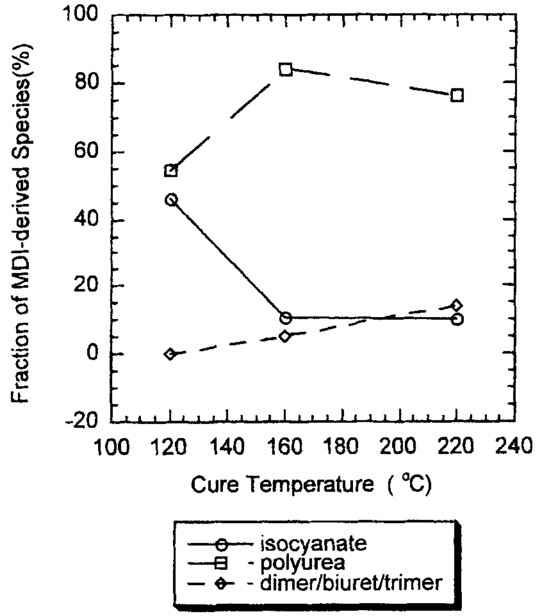


FIGURE 6 Relative fraction of MDI-derived species in Aspen with 14% moisture + 10% PMDI cured 1 min.

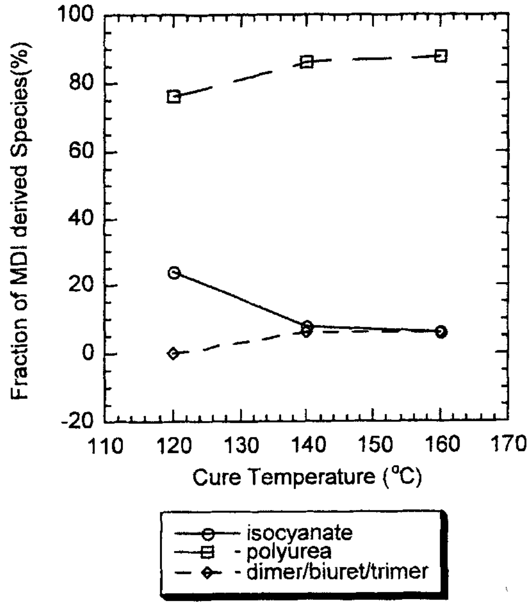


FIGURE 7 Relative fraction of MDI-derived species in Pine with 7% moisture + 10% PMDI cured 1 min.

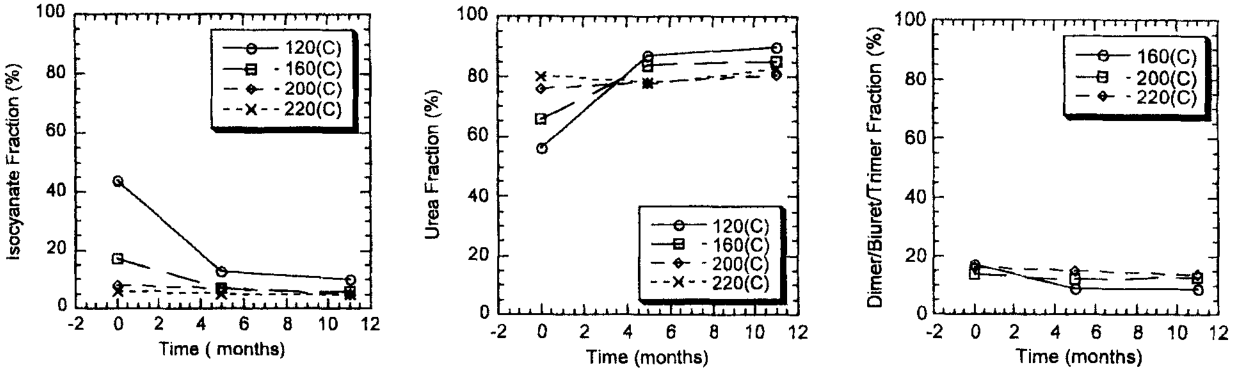
to polyurea at 120°C. Only modest increases in polyurea reaction products are obtained at higher reaction temperatures. The decrease in the amount of unreacted isocyanate at higher reaction temperatures appears to be associated with biuret formation, and a relatively modest increase in the amount of polyurea. Southern pine wood conditioned to 14% MC produced essentially complete reaction of MDI with quantitative conversion to polyurea even at 120°C. At higher temperature, the fractional percentage of biuret increased and polyurea decreased. Perhaps pine is much more porous, resulting in better dispersion of the isocyanate into the wood. Consequently, more of the moisture present in the wood is accessible to the isocyanate. At higher temperature, significant amounts of biuret were formed at the expense of urea.

Figure 8 shows the results from aging (under ambient conditions) samples of Aspen with 7% moisture and 10% PMDI that had been initially cured 1 minute at a variety of temperatures. Under the initial curing conditions a significant amount of isocyanate remains unreacted at the lower reaction temperatures (120°C and 160°C). With time, the sample absorbs moisture from the atmosphere, which promotes the formation of additional polyurea. Between 6 and 11 months, essentially all of the unreacted isocyanate is consumed by formation of urea-linkages. The fractions of dimer/trimer/urea remains unchanged within the error of the measurements.

^{15}N T_{CH} and $T_{1\rho}$ Studies

In addition to information about the relative fractions of MDI-derived species, VCT CPMAS experiments can also provide information about molecular motions as indicated by changes in $T_{1\rho}$ and T_{CH} relaxation rates. Increases in molecular motions in the kHz regime can shorten observed $T_{1\rho}$ values. T_{CH} relaxations are sensitive to the near static or low frequency motions. Therefore, rigid components in a heterogeneous system will have shorter T_{CH} times compared with mobile components [11–13]. In addition, since molecular motions are associated with changes in molecular structure and molecular packing arrangements, T_{CH} and $T_{1\rho}$ can provide indirect evidence of changes in molecular structure and/or molecular ordering.

The T_{CH} of polyurea appears to be independent of cure temperature, Figure 9. In contrast, biuret reaction products show a



(a) (b) (c)

FIGURE 8 Relative fraction of MDI-derived species in Aspen with 7% moisture + 10% PMDI and kept at room temperature for 11 months.

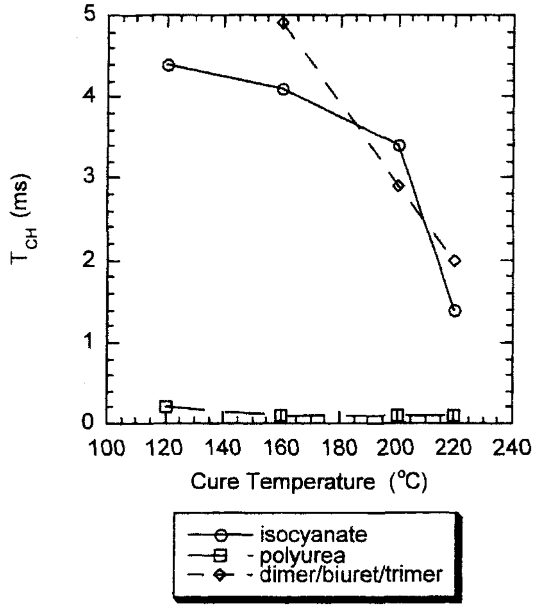


FIGURE 9 T_{CH} of MDI-derived species in Aspen with 7% moisture cured 1 min.

decrease in T_{CH} as a function of temperature. T_{CH} rates are sensitive to molecular distance, a $1/r^6$ internuclear dependence, and molecular motions; higher motion can make cross polarization less efficient and, thus, increase T_{CH}. Urea nitrogens have directly-bonded protons permitting efficient cross polarization between proton and nitrogen. One of the biuret nitrogens is nonprotonated. Thus, changes observed for nonprotonated biuret nitrogens as a function of temperature are probably due to decreases in molecular mobility as a result of a greater number of crosslinks at higher temperatures. The T_{CH} of remaining isocyanate decreased with an increase in cure temperature. This is explained by the fact that, at lower cure temperatures, a large fraction of remaining isocyanate is monomeric MDI, and/or is located in pools of unreacted MDI with high mobility. At higher cure temperatures the percentage of remaining isocyanate is much lower, and is probably located within a matrix of PMDI so that the molecular motion of the remaining isocyanate is greatly reduced. These factors result in the decrease of the T_{CH}. This explanation is consistent with the fractional percentage data discussed above.

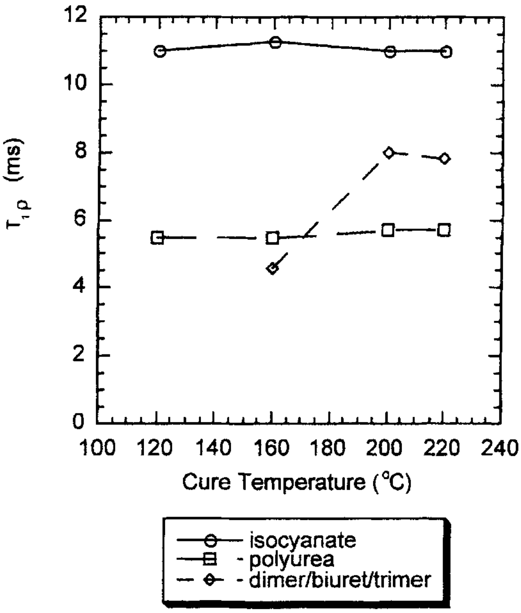


FIGURE 10 $T_{1\rho}$ of MDI-derived species in Aspen with 7% moisture cured 1 min.

Figure 10 illustrates the changes in proton $T_{1\rho}$ as a function of temperature. The trends observed are similar to those observed for T_{CH}. That is, $T_{1\rho}$ does not change for the polyurea reaction products as temperature increases. In contrast, $T_{1\rho}$ increases as a function of temperature for the biuret reaction products. Again, this trend is consistent with a system which is more highly crosslinked.

CONCLUSIONS

Experimental and theoretical data show that the major reaction products formed from the curing PMDI in wood are polyurea and biuret. Little evidence of urethane formation resulting from reaction with lignin or cellulose hydroxyls was observed. Temperatures above 140°C appear to promote the reaction of isocyanate functionality with urea to formed crosslinked biuret polymers. The different $T_{1\rho}$ values of ^{15}N between the different PMDI substructures (polyurea and biuret) indicate that the PMDI is a heterogeneous system. The changes of T_{CH} and $T_{1\rho}$ values of nonprotonated ^{15}N in isocyanate and biuret structures indicate that the more rigid PMDI structure was formed with the increase of the cure temperature. The rate of reaction as a function of temperature and moisture content appears to be greater in Southern Pine when compared with Aspen. While the primary MDI-derived species in cured samples are urea and biuret, the presence of small amounts of cyclic dimer and trimer can not be discounted.

Results from this study are consistent with those reported by earlier workers [2]. The primary differences between this and earlier work are that: (1) sample preparation in this study more accurately reflects conditions used in commercial processes; (2) the ^{15}N NMR signals were acquired under conditions that produce quantitative estimates of the relative fractions of components; and (3) earlier work notes the formation of urethane after much longer reaction times.

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