

CHARACTERIZATION OF THE WOOD/ISOCYANATE BONDLINE

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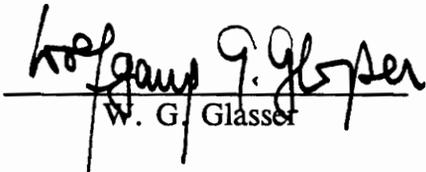
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Wood Science and Forest Products

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ABSTRACT

Polymeric diphenylmethane diisocyanate, pMDI, is a wood adhesive that provides excellent composite board properties. Much is unknown about the specific mechanism of pMDI/wood adhesion under conditions that are typical of wood gluing operations. The present research describes the use of ^{15}N cross-polarization, magic-angle spinning (CP/MAS) NMR as a technique for probing the cure chemistry and bondline morphology of pMDI-bonded wood composites.

A 99% ^{15}N -enriched pMDI resin with desirable adhesive properties was synthesized. A series of model cellulose/ ^{15}N -pMDI composites, cured as a function of cellulose precure moisture content, were tested prior to solid wood composites in order to test the feasibility of this technique. Solid wood/ ^{15}N -pMDI composites were then cured as a function of wood precure moisture content, cure temperature, and cure time.

The ^{15}N CP/MAS NMR spectra clearly show the dominance of the isocyanate/water reaction on the cure chemistry of all composites tested, both cellulose and solid wood. Four prominent resonances are observed in each spectrum: residual isocyanate, polyurea, and the amide and imide nitrogens of biuret type structures. Different trends

in the relative intensities of these resonances are observed as a function of the press variables. Significant amounts of urethane formation are not detected; however, low amounts could be obscured by signal overlap.

Relaxation studies using variable contact time experiments were complicated by excessively long cross-polarization rates for nonprotonated nitrogens. However, experiments using variable spin lock times prior to fixed contact periods indicate that the cured resin in these composites is probably a homogeneous continuum.

The utility of ^{15}N CP/MAS NMR for elucidating fine structural and morphological information from complex isocyanate-cured wood composites is clearly demonstrated.

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GLOSSARY

CP -	Cross-polarization.
DS -	Degree of substitution.
DSC -	Differential scanning calorimetry.
EMC -	Equilibrium moisture content.
FTIR -	Fourier transform infrared spectroscopy.
MAS -	Magic angle spinning.
MC -	Moisture content.
MDF -	Medium density fiberboard.
MDI -	Diphenylmethane diisocyanate, typically the 4,4'-isomer.
NMR -	Nuclear magnetic resonance spectroscopy.
PF -	Phenol formaldehyde resin.
pMDI -	Polymeric diphenylmethane diisocyanate. An undistilled mixture of the 4,4'-diisocyanate together with other isomers and higher functionality polyisocyanates.
OSB -	Oriented strand board.
RH -	Relative humidity.
$T_{1\rho\text{H}}$ -	Proton rotating-frame relaxation time.
T_{NH} -	^1H - ^{15}N cross-polarization rate.
VOC -	Volatile organic compounds.
WPG -	Weight percent gain.

CHAPTER 1

INTRODUCTION-----

Polymeric diphenylmethane diisocyanate, pMDI, is an important starting material in the production of polyurethane foams and binders. Roughly 1 billion pounds of pMDI were commercially produced for these applications in 1991 [1]. In general, most polyurethanes are formed by the catalyzed reaction of a polyisocyanate with a polyol. Since wood is by nature a polyhydroxylic material, researchers in the late 1960's began to theorize about the use of pMDI as a wood adhesive. It was not until the introduction of OSB in the mid to late 1980's, however, before the use of pMDI as a wood binder became widespread.

Since that time pMDI resins have been widely accepted because of their outstanding adhesion to wood. The specific mechanism by which isocyanates derive their superior adhesive properties remains the object of some controversy. The formation of covalent urethane linkages via the wood/isocyanate reaction must compete with the reaction of isocyanate and water. The polyhydroxylic nature of wood ensures that adsorbed moisture is always present. The extent and nature to which the isocyanate/water reaction takes place will affect the cure chemistry, and as a result, the adhesive mechanism of pMDI-bonded wood composites.

It is likely that the cure behavior of pMDI resins will therefore depend on the precure moisture content of the wood furnish as well as other important press variables.

The present research utilizes ^{15}N CP/MAS NMR as a technique for probing the cure chemistry and bondline morphology of pMDI-bonded wood composites. CP/MAS NMR allows the study of molecular phenomena within these complex composite systems without disrupting the solid state. These molecular phenomena ultimately give rise to the macroscopic performance of the material, and as such makes study of the intact solid so interesting.

^{13}C CP/MAS is the most common nuclear magnetic resonance technique for the study of polymeric solids. However, the ^{15}N nucleus offers several advantages over ^{13}C for the study of pMDI-bonded wood composites. ^{15}N CP/MAS eliminates additional resonances from the adhesive backbone and wood substrates, allowing direct observation of the resin chemistry. Fewer resonances combined with a broad spectral width makes interpretation of ^{15}N spectra straightforward for these systems. The major disadvantage of ^{15}N NMR is the need to isotopically enrich the resin because of the inherently low sensitivity of the ^{15}N nucleus to magnetic resonance techniques. As a result, a 99% ^{15}N -enriched pMDI resin was first synthesized to facilitate the use of ^{15}N CP/MAS.

In the forthcoming Chapter 2, Literature Review, a detailed discussion is given on the history of pMDI as a wood adhesive, previous studies of the wood/isocyanate reaction, and CP/MAS NMR as a technique for studying cured resin systems. A brief statement of objectives is made in Chapter 3 followed by an outline of the experimental and analytical techniques used during this study in Chapter 4. Experimental results leading to the synthesis of a ^{15}N -pMDI resin are discussed in Chapter 5. Model

cellulose/¹⁵N-pMDI composites were studied prior to solid wood composites in order to test the feasibility of this technique. Chapter 6 describes the effect of cellulose precure moisture content on the cure chemistry and bondline morphology of these composites. Lastly, the technique was applied to solid wood/¹⁵N-pMDI composites to determine the effects of wood precure moisture content (Chapter 7), cure temperature (Chapter 8), and cure time (Chapter 9).

CHAPTER 2

LITERATURE REVIEW-----

2.1. POLYMERIC MDI AS A WOOD ADHESIVE

2.1.1. Historical Sketch

Polymeric MDI was first produced commercially in the early 1960's as a key ingredient for polyurethane foams and binders. Since its introduction, it has achieved widespread use in the production of rigid and flexible foams, elastomers, coatings, and adhesives. Roughly 1 billion pounds of pMDI were produced in North America in 1991 for these applications [1].

The same chemical reactions which form the basis of polyurethane foam production led researchers to theorize about the use of pMDI as a wood adhesive. Development of this new wood binder for particleboards began in Europe in the late 1960's [2]. Deppe and Ernst [3] were among the first to report a pMDI-bonded particleboard which met the German standards for exterior structural grade. Shortly thereafter the first commercial production of an isocyanate-bonded board was achieved by Deutsche Novopan of West Germany. They manufactured a product with a pMDI-bonded core and phenolic-bonded face layers.

The first commercial particleboard made with pMDI in the United States was produced by Ellingson Lumber Company. They made a product called Elcoboard which consisted of an isocyanate-bound saw mill waste core, including some bark and needles,

and two surface veneers of varying grades. However, the use of pMDI as a wood binder did not become widespread until the largescale introduction of waferboard/OSB around 1982. A vast amount of research was committed to improving these emerging products of the time, including the search for new and better adhesive systems. The first conversion of a waferboard plant to pMDI was in 1985 [1]. Since that time there has been significant penetration into the industry. In fact, Galbraith and Wells [4] estimate that pMDI had captured 15-20% of the OSB/waferboard resin market by 1990.

2.1.2. Properties of Wood/pMDI Composites

Over the past 20 years, extensive research has been performed to compare the properties of wood composites bonded with pMDI to those bonded with PF resins. PF has historically been the resin of choice for exterior structural applications. The introduction of pMDI as a viable alternative for these applications, however, created direct competition between the two resins. This section provides a brief examination of the literature regarding the cure characteristics of pMDI resin and the properties of wood/pMDI composites.

The literature has shown that isocyanate adhesives possess superior adhesion to wood when compared to PF resins [2,5-10] under otherwise similar bonding conditions. However, the bonding conditions which are used for these two resins are seldom similar due to differences in their cure behaviors. pMDI resins have been demonstrated to cure at significantly higher moisture contents than are possible with PF resins [2,5-14]. In

general, sufficient cure of PF resins limits the wood precure moisture content to about 8% [13,15]. On the other hand, pMDI-bonded OSB/waferboards [2,10,13,14], hardboards [6,7], and medium density fiberboards [11,12] have shown excellent adhesion when cured at 10-12% moisture. In fact, Johns et al. [11] concluded from internal bond strengths that MDF does not achieve sufficient cure when bonded below 10% moisture. The upper limit at which good adhesion is achieved with pMDI appears to be about 18% moisture for all types of boards [2,13,14].

Other cure characteristics of pMDI compared to PF resins include faster press times [2,10,13], lower press temperatures [2,10,12,16], and lower resin loadings [2,6,8-10,12]. Reported plant trials have shown excellent board properties for 7/16" OSB pressed at 9% moisture, 1.75% pMDI, 360°F, and a 200 second press cycle [10]. Dry bending properties and internal bond strengths were higher than for control boards that were bonded with 4.5-5% liquid PF resin at 4% moisture, 400°F, and a 270 second press cycle. Wet properties could not be compared since wax had not been added to pMDI-bonded boards. In studies of other wood composites, McLaughlin et al. [12] concluded that MDF consolidated at 10% mat moisture content, 3% resin, and a press temperature as low as 290°F may be suitable for exterior purposes. In addition, Hawke et al. found that MDF bonded with 3% pMDI had much better strength [6] and physical [7] properties compared to 3% PF, and comparable or superior properties to 10% PF. Lastly, Johns et al. [11,14] have demonstrated that pMDI-bonded boards can be made with a more uniform density profile, eliminating the low density surface layers which are

characteristic of PF-bonded boards due to precure in those areas.

2.1.3. Proposed Mechanisms for Wood/pMDI Adhesion

These numerous studies which report the excellent strength and physical properties of pMDI-bonded wood composites [2,5-16] have led researchers to theorize about wood/pMDI adhesion. Although some controversy exists [5,11,17], it is generally believed that isocyanates derive their superior adhesion by forming direct covalent linkages to wood while the PF resins do not [2,13,18,30]. However, a cursory examination of isocyanate chemistry indicates that multiple, competing pathways exist for isocyanate cure in wood-based systems (Scheme I). The polyhydroxylic nature of wood certainly provides ample opportunity for covalent reactions with the isocyanate, forming urethane linkages. However, these same hydroxyl groups ensure the presence of adsorbed moisture at all times. Isocyanates react rapidly with water to form primary amines and carbon dioxide. These primary amines are also very reactive toward isocyanate and are rapidly converted to ureas. Furthermore, if an excess of isocyanate is present, the ureas may undergo further crosslinking reactions to form biuret type structures. The analogous reaction between a urethane and an isocyanate to form an allophanate structure is also possible, although it is not expected to be important in wood/isocyanate composites [2]. The extent and nature of the isocyanate/water reaction will affect the cure chemistry, and as a result, the adhesive mechanism of isocyanate-bonded wood composites. The controversy over the exact mechanism of wood/pMDI

adhesion likely stems from the fact that relatively little characterization of the isocyanate cure chemistry has been performed compared to their PF counterparts.

2.1.4. Previous Studies of the Wood/Isocyanate Reaction

Many of the studies directed toward the wood/isocyanate reaction have focused on the use of isocyanates as dimensional stabilizers rather than as adhesives [19-27]. As a result, specialized conditions have been used which are not analogous to typical wood gluing operations (i.e., the production of OSB). These conditions have included the use of small, monofunctional isocyanates [22-25], vapor phase isocyanates [20,26-27], catalysts which promote the isocyanate/hydroxyl reaction [19-21], and solvents which swell the wood microstructure [19-21,25-27].

Some of the earliest work on wood/isocyanate adhesion was performed by Morak and coworkers [19-21]. They learned that diisocyanates readily bonded to cellulose fibers, thus increasing the strength and dimensional stability of paper products. The best results were obtained when the isocyanate was carried in a good swelling solvent such as pyridine and combined with a catalyst such as dibutyltin diacetate [19]. However, the formation of urea from the reaction of isocyanate with water cannot be discounted since the samples had been conditioned to 50% RH and 73°F prior to treatment. In fact, this possibility was acknowledged and no evidence was cited for the formation of urethane linkages except for the enhancement of properties [19].

Rowell et al. [22-24] extended this work by demonstrating the stability of urethane bonds formed by impregnating Southern pine with methyl isocyanate at elevated temperature and pressure. Samples were treated to various retention levels up to a maximum of 47.2 weight percent gain (WPG). FTIR spectra show a clear increase in the carbonyl stretching absorption at 1730 cm^{-1} (attributed to the urethane carbonyl) with increasing WPG [23]. A corresponding decrease in the hydroxyl stretching region ($3000\text{-}3400\text{ cm}^{-1}$) is not visually apparent. Further evidence of urethane formation is presented as the unextractable nitrogen content of the treated samples after extraction with benzene/ethanol (2/1, v/v) followed by water. This technique is stated to remove any residual isocyanate which is not chemically attached to the wood structure, and indeed, this is confirmed by the absence of an isocyanate absorption (2250 cm^{-1}) in the FTIR spectra. The unextractable nitrogen contents were converted to degree of substitution (DS) values for both holocellulose and lignin [23]. Lignin DS was reported as high as 0.89 and holocellulose DS as high as 0.209 at 47.2 WPG. Together with the FTIR spectra, these results imply that a tremendous amount of reaction took place between the isocyanate and the wood cell wall components.

Owen et al. [25] have presented similar results for wood, lignin, and holocellulose reacted with a n-butyl isocyanate/pyridine mixture (1/2 v/v) at elevated temperature. FTIR "difference" spectra between treated and untreated samples show a prominent absorbance at 1710 cm^{-1} which they attribute to the carbonyl stretching vibrations of a urethane. When excess n-butyl isocyanate was used, the hydroxyl stretching band in the

normal FTIR spectrum was replaced by a weaker and sharper absorbance at 3360 cm^{-1} . The authors attributed this to the replacement of all hydroxyl groups, with the new absorbance resulting from the urethane N-H stretches. In addition, the carbonyl region was split into two absorbances (1726 and 1692 cm^{-1}) analogous to the twin carbonyl vibrations of an allophanate. Lastly, they found that the reaction of isocyanate was faster with lignin than with holocellulose. Weaver and Owen [17] presented similar results for the triethylamine-catalyzed reaction of phenyl isocyanate with lignin, cellulose, and wood. FTIR spectra show the reaction of phenyl isocyanate with dry wood, having two strong carbonyl absorbances at 1712 and 1694 cm^{-1} . However, water dominated the reaction when it was present (carbonyl absorption at 1651 cm^{-1}). Very little urethane formation, if any, was noted at 7% moisture. It should also be noted that experiments were performed using a large excess of isocyanate (wood/isocyanate of 1/1, 1/2, and 1/4) and cured for lengths of up to several days at room temperature.

Without doubt the previous studies have provided evidence that isocyanates can react with wood under certain conditions. However, Johns [5] has noted a lack of published literature regarding the wood/isocyanate reaction under conditions common to the processing of wood composites. The primary, if not the sole, isocyanate that is used as a binder in wood composites is pMDI which is a much larger, less mobile molecule than those used in the preceding studies. Furthermore, it is used at lower dosages, without solvent or catalyst, and is cured for much shorter times. There is also a significant amount of water present when curing wood composites, introducing the competitive

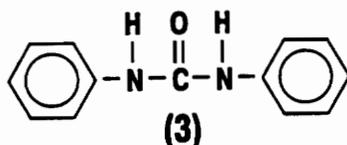
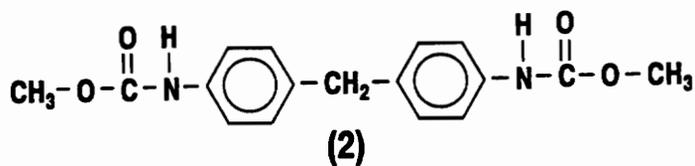
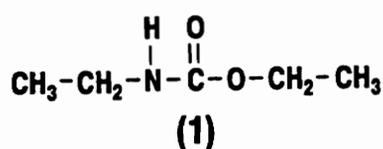
isocyanate/water reaction which forms ureas and various biuret type structures. Johns [5] cites one unpublished study by McLaughlin [29] which noted copious amounts of polyurea formation when waferboard at 5% moisture was pressed with pMDI. The study used subtractive difference FTIR between the cured pMDI/wood composite and untreated waferboard flakes. Only when a large amount of catalyst was used to specifically enhance the probability of urethane formation were a trivially small amount of urethane linkages detected. On the other hand, Chelak and Newman [13] have made reference to an unpublished FTIR study in which they show the presence of urethane linkages in pMDI-bonded waferboard. Similar published reports on waferboards are curiously lacking.

Steiner et al. [28] have reported specifically on the wood/pMDI reaction in the presence of moisture and without the use of solvent or catalyst to aid urethane formation. They used differential scanning calorimetry (DSC) to show the domination of urea formation when an excess of moisture is present. Ground wood samples were conditioned to 5% and 28% moisture, mixed with various amounts of pMDI, and then heated in a DSC sample pan. Samples with 5% moisture that were mixed with more than 9 wt.% pMDI showed an exothermic reaction in the DSC thermogram at 40° to 50°C. Since this exotherm was not present in the thermograms of pMDI/water reactions, the authors attributed it to a rapid reaction between pMDI and wood. Its absence from the thermogram when only 9 wt.% pMDI was added indicates that the reaction does not take place at low resin loadings. Increasing the wood MC to 28% also greatly reduces

the size of this exotherm, and instead, shows a very broad endotherm centered at about 90°C. This endotherm is similar to those from the pMDI/water reaction. The authors concluded from the DSC results that pMDI reacts rapidly with wood at relatively low MC (5%), but that urea formation from the pMDI/water reaction dominates at high MC (28%). The authors also used FTIR to characterize the pMDI/wood reaction at 5% moisture. They noted a rapid decline in the isocyanate absorbance (2000-2500 cm⁻¹) when cured at 80°C. However, water was present in the system so this observation alone cannot distinguish between the competing cure reactions. Particular attention was paid to two absorbances in the carbonyl region, 1635 cm⁻¹ and 1670 cm⁻¹. Cure at 25°C or 60°C for 17 hours showed a significant increase in the 1635 cm⁻¹ absorbance. When the cure temperature was increased to 160°C, however, this absorbance decreases and a new band at 1670 cm⁻¹ appears. It was hypothesized that this spectral change could indicate different stages of urethane formation or the initial formation of polyureas by reaction with water. However, the authors also acknowledged the difficulty in making definitive assignments from FTIR for pMDI/wood systems because of the multitude of possible reactions and the overlapping absorbances from wood.

This complexity of the FTIR spectrum for wood/isocyanate systems appears to be one of the reasons for the continuing controversy over the exact mechanism of adhesion for pMDI-bonded wood composites. The sheer number of absorbances present in the spectrum, many of them overlapping, simply makes interpretation difficult. In the preceding literature review, evidence for urethane formation was given as a carbonyl

absorbance at 1730 cm^{-1} [23], 1710 cm^{-1} [25], and either 1635 or 1670 cm^{-1} [28]. Model urethane compounds display a carbonyl absorbance at 1700 cm^{-1} for both N-ethylurethane (1) [31] and the dimethylurethane of MDI (2) [32]. A model urea compound, diphenylurea (3), has a carbonyl absorbance at 1649 cm^{-1} [32]. These are the model compounds closest in structure to the pMDI/wood and pMDI/water reaction products for which spectral data could be found in the literature. However, absorption frequencies for all urethanes and for all ureas should be quite similar since the nature of infrared absorbances is based on atomic motions rather than molecular structure.



Because of the complexity of FTIR spectra for pMDI-bonded wood composites, it may be necessary to develop a new technique that is capable of providing concise information regarding the cure chemistry and morphology of these composite systems. One such technique which holds promise is solid state nuclear magnetic resonance (NMR) spectroscopy.

2.2. SOLID STATE NMR

2.2.1. Solid State NMR for Cured Resins

During the past 40 years or so, NMR has emerged as one of the most powerful techniques which provides information about the molecular structure of chemical substances [34]. However, it was not until more recently that the elucidation of fine structural information could be obtained from samples in the solid state. Prior to that time, high resolution NMR experiments had been constrained to samples that could be dissolved into solution because of the line broadening effects and insensitivity associated with solid samples [35]. These problems were alleviated by the development of superconducting magnets which greatly enhanced magnetic field strengths and by the emergence of techniques such as high power ^1H decoupling [36], magic angle spinning [37], and cross-polarization [36]. High power ^1H decoupling and magic angle spinning greatly reduce the line broadening effects of heteronuclear dipole-dipole interactions and chemical shift anisotropy in solids, respectively [35,38]. Greater magnetic field strengths and cross-polarization techniques have greatly reduced the time required to obtain high resolution NMR of solids [35]. Thus began the evolution of cross-polarization, magic angle spinning (CP/MAS) NMR for the structural and morphological study of solids. CP/MAS allows the study of molecular phenomena within the material without disrupting the solid state. Molecular events in the solid give rise to the macroscopic performance of materials and as such makes study of the intact solid most interesting. Dissolution of materials might remove the fundamental chemical, physical, or mechanical properties

associated with the solid.

CP/MAS NMR has proven very effective in the chemical characterization of highly cured network polymers [38-48]. In particular, the usefulness of this technique for studying wood adhesives has been noted in an excellent review article [49]. Not only is CP/MAS capable of elucidating fine structural information from the solid state, but relaxation phenomena can also provide information about the polymer morphology and molecular chain dynamics [39,50-53]. Of particular importance for the study of isocyanate resins is the recent emergence of ^{15}N CP/MAS NMR for the analysis of nitrogen-containing compounds [54-58].

2.2.2. ^{15}N CP/MAS for Isocyanate-Based Resins

^{13}C CP/MAS is the most common magnetic resonance technique used to probe polymeric solids. However, the ^{13}C spectrum of a pMDI-bonded wood composite is complicated by overlapping resonances from the resin and the substrate. Numerous additional resonances are present from carbons of the pMDI backbone structure and also from the chemical constituents of wood. These resonances often overlap with those from the resin cure chemistry, making interpretation of the spectrum difficult. ^{15}N CP/MAS offers the advantage of direct observation of the resin chemistry. No additional resonances are present from the wood structure, and each resonance from the resin provides concise information regarding cure chemistry. Fewer resonances combined with a broad spectral width makes interpretation of ^{15}N spectra straightforward for these

systems. Indeed, the advantages of ^{15}N NMR over ^{13}C experiments for isocyanate-based systems have been noted as early as 1981 [54]. More recently, Duff and Maciel [55-58] have demonstrated the usefulness of ^{15}N CP/MAS for elucidating fine structural and morphological information from cured isocyanate-based resin systems.

Duff and Maciel have used both ^{13}C and ^{15}N CP/MAS to study isocyanurate-rich [55] and biuret-rich [56] MDI-based resins. They noted that the ^{13}C spectra were complicated by the broadening influence of the ^{14}N nucleus [55]. The resonances of ^{13}C nuclei that are located near ^{14}N nuclei are broadened by the combination of ^{13}C - ^{14}N dipole-dipole interactions and the ^{14}N quadrupole effect. Use of a 99% ^{15}N -enriched resin eliminated the effects of ^{14}N quadrupolar broadening, but the reduction on the overall broadening of the ^{13}C resonances was minimal. Furthermore, the spectra were complicated by overlapping resonances which made interpretation difficult and quantitative treatment of the results impossible [55]. The isocyanate carbonyl resonance overlapped with various aromatic carbons and with other unresolvable resonances in the broad and relatively featureless region between 120 and 145 ppm. As a result, changes in chemistry due to variations in the curing conditions could only be assessed qualitatively by comparing the peak height of a particular resonance from one spectrum to the next.

On the other hand, ^{15}N CP/MAS proved to be a very effective technique for analyzing the ^{15}N -enriched resins. Specific identification of each resonance was possible since there were fewer overlapping resonances. In particular, they were able to identify

minor reaction products and to monitor the extent of cure through the isocyanate nitrogen resonance. The well resolved nature of the resonances also made it possible to accurately measure peak intensities. These peak intensities are only useful, however, if they can be quantitatively related to one another. For a given CP contact time, the cross-polarization efficiency is not the same for all types of nitrogen nuclei in different chemical environments. Direct comparisons of peak intensities at a given contact time are therefore inaccurate. A useful equation exists for converting intensities at a given contact time to a standardized value corrected for variations in cross-polarization efficiency [55,59]:

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

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

I^* , then, is the corrected peak intensity which is of interest. The corrected relative intensity is calculated by simply dividing the corrected intensity for a desired peak by the sum of all corrected intensities for that spectrum. It is in essence the percent composition of each chemical moiety that is present. Duff and Maciel have demonstrated the ability of this technique to quantitatively monitor the crosslink density [55] and the postcure reaction chemistry [57] of MDI-based resins.

CP/MAS is also capable of providing information regarding molecular motion and

polymer morphology [50-53,55-58]. Of particular interest is the $T_{1\rho H}$ relaxation parameter which is obtained from CP variable contact time experiments [55-58]. The $T_{1\rho H}$ time constant is generally influenced by molecular mobility and spin diffusion [39,50]. In the case of some highly crosslinked networks, molecular mobility is restricted and the $T_{1\rho H}$ becomes the average over all protons in the sample due to spin diffusion. This is not a diffusion process per se, but actually a dissipation of magnetization in the form of thermal energy. Homogeneous systems display an efficient "communication" among all protons in the sample and therefore exhibit the same $T_{1\rho H}$ value for all chemical moieties present [39,50]. On the other hand, heterogeneous systems consisting of distinct chemical domains have been noted to exhibit different $T_{1\rho H}$ values when probed through chemically distinct carbons [38,51,60]. This results from discontinuities which inhibit energy transfer across phase boundaries. Distinct phases then exhibit relaxation rates which are a local average and which often differ from one phase to the next. Monitoring the $T_{1\rho H}$ relaxation rate is not specific to ^{13}C experiments, but can also be employed using ^{15}N CP/MAS. In fact, Duff and Maciel [56] have used $T_{1\rho H}$ experiments to note the phase separation of MDI-based resins into an isocyanate-rich phase and a biuret-rich phase.

There are two disadvantages associated with using the ^{15}N nucleus. The first is a low natural abundance (0.37%) compared to the ^{13}C nucleus (1.1%) and the second is a small magnetogyric ratio, which is only 40% that of ^{13}C [34]. Since both of these factors are directly related to the sensitivity of the NMR technique, the ^{15}N nucleus has

an inherently low sensitivity. In order to obtain a high resolution ^{15}N CP/MAS spectrum at natural abundance, an extremely large number of scans (i.e., very long acquisition time) is required. As a result, isotopic enrichment is usually required to make acquisition times reasonable. Indeed, 99% ^{15}N -enriched MDI has been demonstrated to be superior to natural abundance MDI for ^{15}N CP/MAS studies [55].

2.3. SYNTHESIS OF POLYMERIC MDI

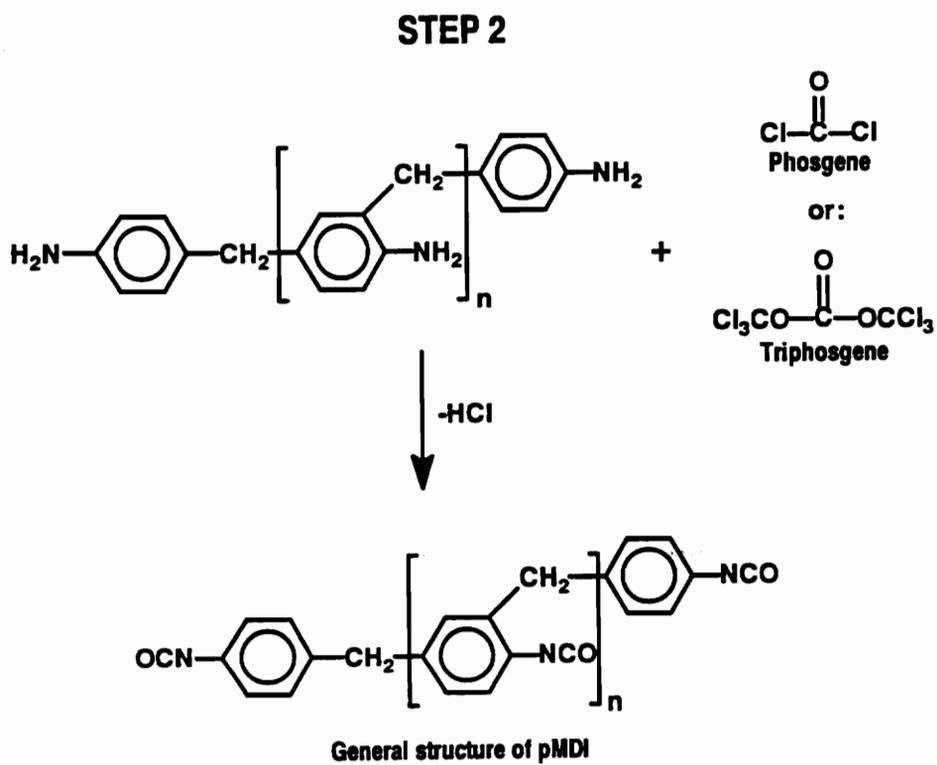
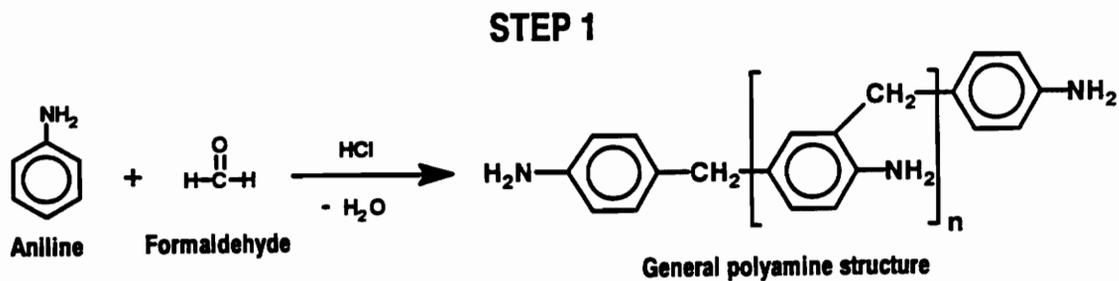
2.3.1. Introduction

The synthesis of pMDI is a two-step reaction beginning with the HCl catalyzed condensation of aniline with formaldehyde. The second step is the conversion of the resulting polyamine to polyisocyanate by phosgenation (Scheme II). The primary commercial product is an undistilled mixture consisting of about 50% 4,4'-isomer together with higher methylene-bridged species and a small amount of the 2,4'- and 2,2'-isomers. The degree of polymerization can reach as high as $n = 8$ [2], but the mean for commercial product is approximately $n = 0.8$ [61].

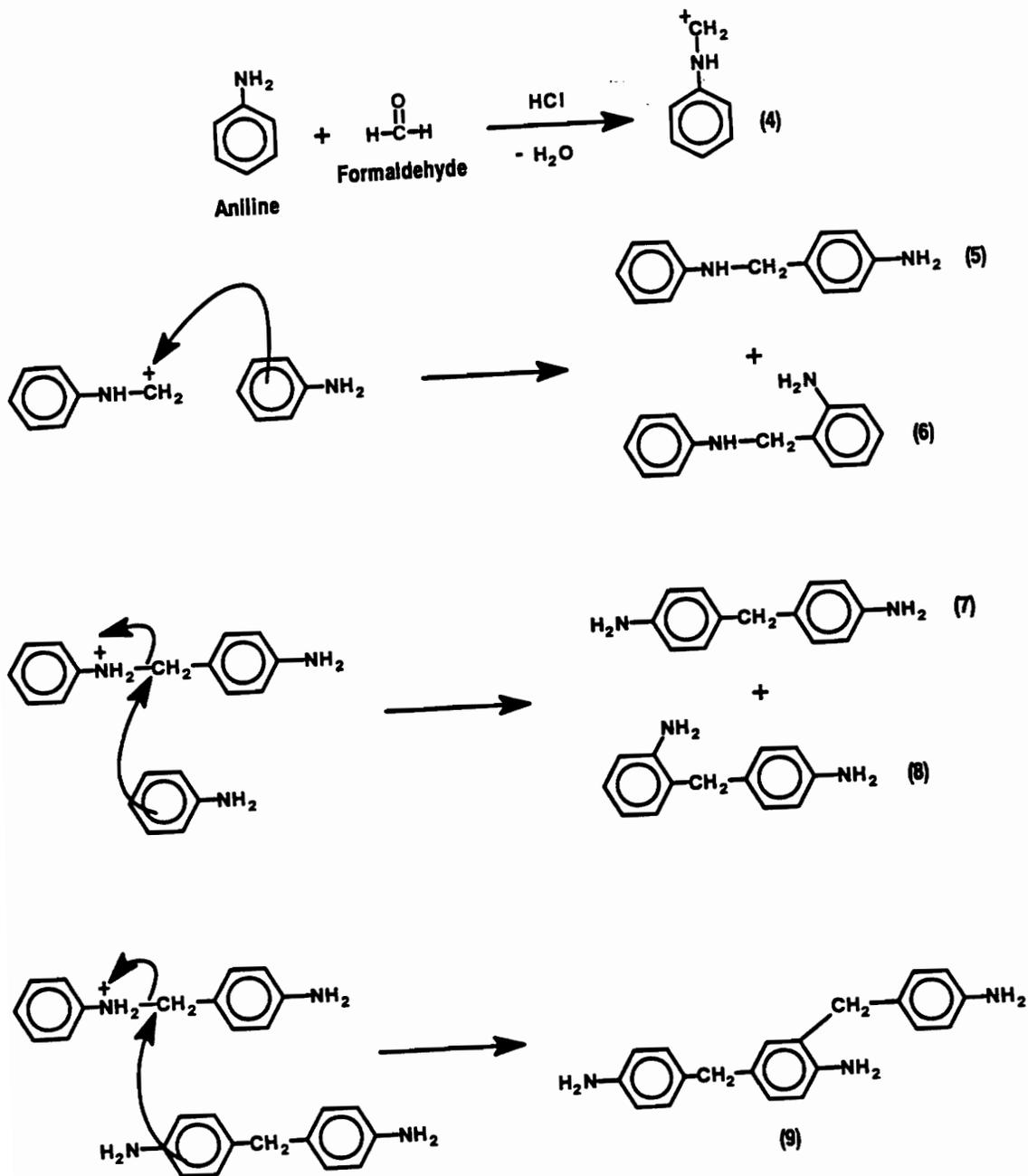
2.3.2. Synthesis of Polyamines

Much of the specific information regarding the aniline/formaldehyde condensation reaction is proprietary and the literature that is available is lacking in detail [61-65,67]. An excellent review article by Twitchett [61] discusses the reaction mechanism in detail (Scheme III), but does not provide the specific information necessary for the synthesis

Scheme II: The overall reaction scheme for the synthesis of polymeric MDI.



Scheme III: The simplified mechanism for the aniline/formaldehyde condensation.



of a fluid resin. The reaction begins with the addition of formaldehyde to aniline in the presence of HCl, producing an electrophile (4) with the elimination of water. This species then substitutes into an aromatic nucleus to give para- (5) and ortho- (6) substituted aminobenzylaniline by reaction with aniline, or higher polymeric species by reaction with analogues that have already been produced. The second step of the reaction is the conversion of secondary amine to primary amines. Secondary amines are protonated by HCl and subsequently attacked by a nonprotonated primary amine. If the attacking nucleophile is aniline, a diamine will be formed which is usually either the 4,4'-isomer (7) or the 2,4'-isomer (8). If the attacking nucleophile is the aromatic electrons of an already formed species, higher methylene-bridged polyamines (9) are formed. The resulting mixture can theoretically consist of a vast number of different species. As an example, there are three possible diamine isomers, seven possible triamine isomers, and fifteen possible tetra-amine isomers [61], although a smaller number actually predominate because of stereoselectivity.

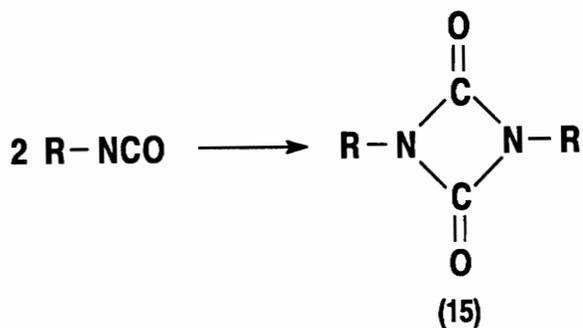
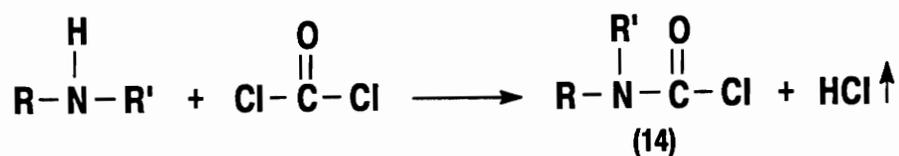
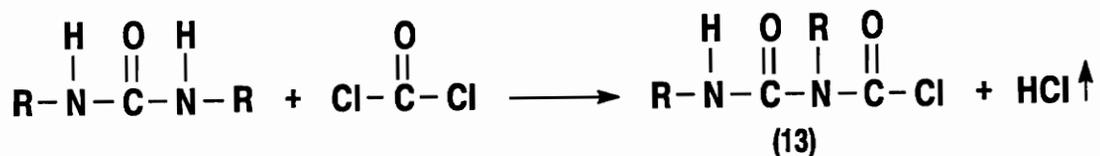
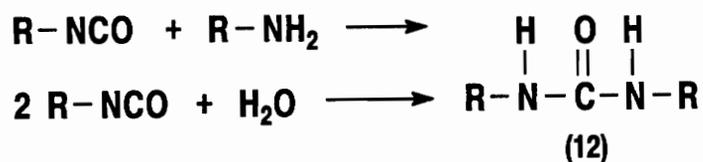
The polyamine composition can be varied greatly according to the conditions used, with the principle factors being the molar ratio of aniline/formaldehyde, the molar ratio of aniline/HCl, and the reaction time [61]. Without tight control of these parameters, the resin formed after phosgenation may be too viscous or even completely solid at room temperature. Large aniline/formaldehyde and aniline/HCl molar ratios favor the production of the 4,4'-diamine, whereas low ratios result in greater production of the higher methylene-bridged polyamines [61]. Unfortunately, specific values for these ratios

along with their corresponding reaction time which have been found to produce a suitable polyamine composition are not available in the literature. Instead, broad ranges have been cited from which vastly different polyamine compositions could be synthesized. Preferred ranges include an aniline/formaldehyde molar ratio of 1.6 to 2.1, aniline/HCl molar ratio of 2 to 6, and a reaction time of 2 to 18 hours [65].

2.3.3. Phosgenation of Polyamines

Commercial phosgenations are carried out by dissolving the polyamine in an inert solvent such as chloro- or dichlorobenzene and treating with phosgene [61]. For laboratory purposes, the crystalline solid triphosgene has been shown to be an effective substitute for the highly toxic phosgene gas [68]. The preferred amount of solvent ranges from 5 to 40 times the weight of polyamine, and the preferred molar ratio of phosgene/amine ranges from 2 to 10 [65]. The general reaction pathway, along with some potential products from side reactions, is shown in Scheme IV. Primary amines react with phosgene to first form primary carbamoyl chlorides (10) which are unstable and subsequently decompose to an isocyanate group (11) with the elimination of HCl. Numerous side reactions are possible but only several of the more important ones will be considered here. Ureas (12) can be formed by the reaction of isocyanate with residual amine or with any moisture that may be present in the system. It is also believed that these ureas react either with isocyanate to form biurets and polyurets or with phosgene to form N-carbonyl chlorides (13) [61]. Any residual secondary amine that remains in

Scheme IV: The phosgenation of amines, including potential side reactions.



the polyamine composition will react with phosgene to form a stable secondary carbamoyl chloride (14). Finally, MDI can be dimerized to substituted uretediones (15), and in fact, it is the dimer which is more thermodynamically stable at room temperature [61]. Both the formation of dimer and the presence of chlorine-containing impurities in the resulting pMDI resin are undesirable. As a result, it is necessary to heat the pMDI to approximately 200°C for 10 minutes and then quench cool it to room temperature [61,66]. This process decomposes the chlorine-containing impurities to phosgene and HCl gases, and dissociates the uretedione linkages to free isocyanate groups.

CHAPTER 3

OBJECTIVES-----

The primary objective of this study was to develop a technique by which to characterize the cure chemistry and morphology of the wood/polymeric MDI bondline. In particular, the extent and nature of the competing isocyanate/wood and isocyanate/water reactions were to be determined. Cure profiles for wood/pMDI composites were to be developed for the effects of wood precure moisture content, press temperature, and press time. It was a specific goal of this study to make the results as directly applicable as possible to the industrial manufacture of pMDI-bonded wood composites, and in particular oriented strand board. This meant the use of bonding conditions which are similar to those used for its manufacture.

CHAPTER 4

EXPERIMENTAL TECHNIQUES-----

4.1. REAGENTS

Nitrogen

Prepurified nitrogen (99.99%) (Airco) was regulated through a Drierite Gas Purifier Model L68GP packed with anhydrous calcium sulfate. After passing through the drying column, the dried nitrogen was regulated to 5-10 psi and connected to a glass nitrogen/vacuum manifold fitted with glass stopcocks. The vacuum manifold was connected to a Fisher Scientific Maxima Model D8A mechanical vacuum pump with an in-line cold trap and monometer.

4.1.1. Synthesis of Polyamines

Aniline. Aniline (Aldrich Chemical) was purified by vacuum distillation. The aniline changed from a light yellow color to clear upon purification. It was stored in a cool, dark place.

99% ¹⁵N-enriched Aniline. 99% ¹⁵N-enriched aniline (Cambridge Isotope Laboratories, Lot EA-138) was used as received to prevent loss of the expensive starting material. The labeled aniline was deep yellow in color, indicating that some impurities were present.

37% Aqueous Formaldehyde. 37% aqueous formaldehyde solution (Aldrich Chemical) was used as received.

37% Aqueous hydrochloric acid. 37% aqueous hydrochloric acid (HCl) solution (Aldrich Chemical) was used as received.

Chloroform. Chloroform (Fisher, Certified A.C.S.) was refluxed under a nitrogen atmosphere in the presence of anhydrous calcium chloride.

Double-distilled water. Water was distilled first in a Barnstead Fistream™ II GlassStill, then by refluxing for approximately 4 hours.

10N Sodium hydroxide. 10N aqueous sodium hydroxide (NaOH) (Fisher, Certified) was used as received.

4.1.2. Acetylation of Polyamines

Acetic anhydride. Acetic anhydride (Aldrich Chemical, 98%) was used as received.

Sulfuric acid. Concentrated sulfuric acid (Fisher, Certified A.C.S.) was used as received.

4.1.3. Phosgenation of Polyamines

Triphosgene. Triphosgene (Aldrich Chemical, 98%) was used as received. It was stored under nitrogen gas in a refrigerator.

1,2-Dichlorobenzene. Anhydrous 1,2-dichlorobenzene (ODCB) (Aldrich Chemical) was used as received.

4.1.4. Determination of Isocyanate Content

A number of reagents were used for the determination of isocyanate content via ASTM Standard D 5155-91, Test Method C.

Dibutylamine. Dibutylamine (Aldrich Chemical) was used as received.

Toluene. Toluene (Aldrich Chemical, 98%) was used as received.

Methanol. Methanol (Fisher, Certified A.C.S.) was used as received.

1,2,4-Trichlorobenzene. 1,2,4-trichlorobenzene (TCB) (Aldrich Chemical) was dried over Type 4A molecular sieves for several weeks prior to use.

4.1.5. Preparation of Wood Flakes

A block of 8/4 yellow poplar was purchased from Heavener Hardware and Lumber of Blacksburg, VA and then planed on all four sides. A section was cut off the end of the block with dimensions 1.90" × 1.95" × 6". This section was clear of noticeable defects and has a cross sectional area (1.90" × 1.95") nearly equal to that of the cellulose filter papers. The section was submerged in water at all times to help facilitate the cutting of good flakes. All flakes were cut from the radial face of the section to a thickness of 0.012"-0.015", which was the smallest thickness at which whole flakes could still be cut. Flakes were dried at $103 \pm 2^\circ\text{C}$ for 24 hours in order to obtain dry weights. To minimize the effect of surface deactivation on the experimental results, flakes were stored in the dark and always made into composites within two days of drying.

4.1.6. Miscellaneous

Chloroform-d (Aldrich, 99.8 atom % D), methyl sulfoxide-d₆ (Aldrich, 99.9 atom % D), acetone-d₆ (Aldrich, 99.8 atom % D), and pyridine-d₅ (Aldrich, 100 atom % D) were used as received for routine NMR analysis. Tin octoate (Pfaltz & Bauer) and phenylmercuric acetate (Aldrich, 97%) were used as received to catalyze the reaction between isocyanate and cellulose/wood.

4.2. SYNTHESIS OF POLYMERIC MDI

4.2.1. Synthesis of Polyamines

Three aniline:HCl molar ratios were studied prior to synthesis of a ¹⁵N-enriched material: 1.0:1.5, 1.5:1.0, and 3.0:1.0. In all cases, 4g (0.043 mol) aniline were used while the amount of 37% aqueous HCl solution was varied from 5.3 ml (0.0645 mol) to 2.4 ml (0.0287 mol) to 1.2 ml (0.0143 mol). The reaction apparatus was a 50 ml 3-neck round bottom flask equipped with a magnetic stir bar, septum, thermometer, condenser, and dry N₂ gas source. The HCl solution was added first using a pipet and diluted to 6N with double-distilled water. The reaction flask was submerged in a cold water bath to maintain the flask temperature below 50°C. The N₂ gas was also reduced to a very slow purge so as to prevent the loss of HCl vapors. Aniline was added slowly with stirring, followed by 37% aqueous formaldehyde (1.45 ml, 0.0194 mol) added dropwise with rapid stirring. The reaction temperature remained below 25°C and the solution took on a milky, tan-colored appearance. Heat was applied and the reaction mixtures were

refluxed for lengths of 2, 12, 17, and 24 hours. Reaction mixtures refluxed at about 100°C and turned a clear yellow color after about 30 minutes. After the desired reaction time, the mixtures were allowed to cool to room temperature and then added to a separatory funnel containing 30 ml chloroform. Two layers were formed with a yellow-colored aqueous phase on top and a clear organic phase on the bottom. 10N NaOH was added to the aqueous layer with swirling until it tested neutral on pH paper. At this time, the aqueous layer was bright white in color while the organic layer was yellow. The organic layer was removed and the remaining aqueous phase extracted with three 25 ml portions of chloroform to remove all organics. The combined organic phase was washed with double-distilled water until the aqueous layer tested neutral on pH paper, then dried over excess Na_2SO_4 . Chloroform was removed by rotational evaporation, followed by removal of residual aniline by vacuum distillation at 4 mm Hg up to a maximum temperature of 125°C.

4.2.2. Acetylation of Polyamines

The resulting polyamine was dissolved in 25 ml chloroform from which 10 ml was transferred to a 100 ml round bottom flask. The chloroform was rotavaped off until nearly constant weight. A large excess of acetic anhydride (15 ml) was added to the flask followed by 4 drops of concentrated sulfuric acid. The mixture was refluxed for 20 minutes under N_2 gas and with magnetic stirring. The resulting bright orange solution was added to 75 ml double-distilled water. Two phases formed with a clear aqueous

phase on top and a reddish-orange organic phase on the bottom. The solution was boiled on a hot plate with stirring until it became one phase. It was cooled to room temperature and added to a separatory funnel containing 25 ml chloroform. The organic phase was removed and the remaining aqueous phase rinsed with three 25 ml portions of chloroform. The total organic phase was washed with two 25 ml portions of double-distilled water and then dried over anhydrous Na_2SO_4 . Chloroform was removed by rotational evaporation.

4.2.3. Phosgenation of Polyamines

Polyamine which was not acetylated was dried overnight (about 12 hours) at roughly 10 mm Hg and 50°C . All reagents were thoroughly purged with N_2 gas before use. The polyamine was dissolved in 11 times its weight of dry 1,2-dichlorobenzene. Amine content for the polyamine was estimated based on two assumptions: 1) complete conversion of formaldehyde to methylene groups in the polyamine structure, and 2) complete conversion of secondary amine to primary amine. Moles of formaldehyde used is therefore assumed to be equal to the moles of methylene groups (0.0194 mol) formed in the product. The weight of methylene groups is subtracted from the total weight of polyamine. All remaining weight is assumed to be that of dehydroaniline (M.W. 92.13 g/mol) from which the moles of amine can be estimated. One mole of triphosgene is theoretically required for every three moles of amine in order to fully convert the polyamine to polyisocyanate. 1.14 times the theoretical amount of triphosgene was

dissolved in 10 times its weight of dry 1,2-dichlorobenzene. A 100 ml 3-neck round bottom flask was equipped with a large football-shaped magnetic stir bar, septum, thermometer, condenser, and dry N₂ gas. The entire apparatus was thoroughly flamed under a slow N₂ gas purge before adding reagents. Since the phosgenation reaction is exothermic, the reaction flask was submerged in a cold water bath to maintain the solution temperature below 50°C [65]. The triphosgene solution was added to the reaction flask, followed by the polyamine solution added as a continuous stream through a 19-gauge canula. A light yellow colored precipitate forms immediately upon addition of the polyamine. A large amount of this precipitate forms such that the final solution has a thick, creamy appearance. The maintenance of vigorous stirring (stir plate setting of 5½) throughout the reaction is critical to prevent these particles from clumping together. If the particles are allowed to clump together, heat transfer through them is poor and much will remain as solid waste in the final product. This is because the particles do not go into solution until near the boiling point of ODCB (which is 178°C). After addition of the entire polyamine solution to the reaction flask, the cold water bath was removed and replaced with a silicone oil bath for heating. HCl gas bubbles become visible in the solution at about 80°C, but the reaction does not become vigorous until between 120°-150°C. The precipitate dissolved into solution at about 170°C when the solution had been stirred vigorously, but remained as a solid when the particles were able to clump together. It took about 30 minutes for the solution temperature to reach 175°C where it was held for 30 minutes. The temperature was reduced to 150°C and the

solution degassed for 15 minutes by blowing N₂ gas directly into the solution through a 19-gauge syringe needle. After transferring the solution to a 100 ml round bottom flask, the 1,2-dichlorobenzene was removed by vacuum distillation at roughly 10 mm Hg and 90°C. Note that it is still crucial to keep the isocyanate in an inert atmosphere during all these procedures. In order to remove chlorine-containing impurities and to break down uretidione linkages formed by the dimerization of isocyanate, the product was heat treated under a steady stream of N₂ gas at 195°C for 5 minutes followed by degassing at 195°C for an additional 5 minutes. Heat treatment was performed by lowering the flask into a silicone oil bath, raising the oil temperature to about 205°C, and maintaining at that temperature for 5 minutes. Experience showed that an oil temperature of 205°C produced a resin temperature of about 195°C. The isocyanate was quench cooled by spraying the reaction flask with acetone and then submerging the flask in a cold water bath.

4.2.4. Synthesis of 99% ¹⁵N-labeled Polymeric MDI

All procedures for the synthesis of the ¹⁵N-labeled pMDI were identical to those described above, except: 1) the reaction was scaled up to 10g aniline, and 2) the optimum conditions for the polyamine condensation as determined from the preceding experiments were employed. These conditions were determined to be aniline:formaldehyde of 2.2:1.0, aniline:HCl of 1.0:1.5, and a reaction time of 6 hours. Reagents used were 10g (0.107 mol) 99% ¹⁵N-aniline, 13.25 ml (0.161 mol) 37%

aqueous HCl diluted with 13.75 ml double-distilled water, and 3.62 ml (0.0484 mol) 37% aqueous formaldehyde. The only other change from the preceding polyamine synthesis was that the reaction flask was now a 100 ml 3-neck round bottom instead of a 50 ml. The reaction flask for the phosgenation reaction is a 250 ml 3-neck round bottom. All other procedures remain the same as discussed in the previous section.

4.3. PREPARATION OF CELLULOSE/¹⁵N-pMDI COMPOSITES

4.3.1. Variable Cellulose Precure Moisture Content

Common cellulose filter papers (Fisher, Type P8) were dried under vacuum at about 1 mm Hg and 50°C for at least 24 hours, then conditioned to various equilibrium moisture contents (EMC's). Those filter papers which were to be bonded dry were vacuum dried at 1 mm Hg and 50°C for 48 hours. Filter papers straight out of the box at room conditions had a moisture content of 2.1%. Several others were tested at 3.3% MC by storing over a saturated NaCl solution for several days. Filter papers stored in a sealed container over water had an EMC of 23%. In order to reach the intermediate moisture levels, filter papers had to be saturated by storing over water and then allowed to lose moisture in the open atmosphere until the desired moisture content was reached. In all, seven different cellulose precure moisture contents were used: Dry, 2.1%, 3.3%, 6.3%, 7.3%, 8.1%, and 23%. Three composites were made from filter papers at room conditions (2.1% MC) in order to test the reproducibility of the ¹⁵N CP/MAS technique. Composites were made of the ¹⁵N-labeled pMDI sandwiched between two filter papers.

Resin was applied in the open atmosphere using a teflon coated spatula at a loading of 25% of the total composite weight. This resin loading was determined to be the lowest amount possible while still achieving equal distribution over the entire surface area of one side of one filter paper. No resin was applied directly to the second filter paper. Composites were pressed between teflon sheets using a Micromet Instruments MP-2000 Minipress at 120°C and 50 psi platen pressure for 60 minutes. Samples were then placed in individual sealed containers under N₂ gas and stored over dessicant in a freezer to prevent postcure reactions.

4.3.2. Catalyzed Cellulose/¹⁵N-pMDI Composite

In order to promote the formation of urethane linkages between the isocyanate adhesive and cellulose, a tin octoate catalyst was used to make one composite. A solution was made consisting of 0.02g tin octoate in 10 ml chloroform. Two cellulose filter papers were dried at 1 mm Hg and 50°C for 24 hours in order to determine the dry weights. 1 ml of the tin octoate solution was added to each filter paper with a pipet. The chloroform rapidly evaporated off, leaving behind the tin octoate at a concentration of roughly 1% by weight of dry cellulose. The filter papers were then redried at 1 mm Hg and 50°C for 24 hours. Resin was applied in the open atmosphere at a loading of 25% of the total composite weight. The composite was pressed between teflon sheets at 50 psi platen pressure and 120°C for 60 minutes.

4.3.3. Variable Degree of ¹⁵N-labeling

Cellulose filter papers were used straight from the box (2% MC) for these composites. Three composites were made using resins with different degrees of ¹⁵N-labeling. One composite was made by using only the 99% ¹⁵N-labeled pMDI synthesized in our lab. A second resin was made at 54.5% ¹⁵N content by mixing 0.0888g of 100% ¹⁵N-pMDI with 0.0740g of unlabeled Rubinate[®] MF-184, a commercial pMDI resin produced by ICI Polyurethanes. The two resins were combined in a 10 ml round bottom flask to which 1 ml dry chloroform was added to ensure good mixing. The chloroform was then evaporated off under a slow N₂ purge. The third resin was made at 73.3% ¹⁵N content by mixing 0.1409g of 100% ¹⁵N-pMDI with 0.0512g of unlabeled Rubinate[®] MF-184. These resins were applied in the open atmosphere at a loading of 25% of the total composite weight. Composites were pressed between teflon sheets at 50 psi platen pressure and 120°C for 60 minutes. Due to time limitations, these composites will not be analyzed as part of this study, but rather at a future time by Jianwen Ni. The method of preparation was included, however, for future reference.

4.4. PREPARATION OF WOOD/¹⁵N-pMDI COMPOSITES

All wood/¹⁵N-pMDI composites were cured at a resin loading of 17% of the total composite weight. Resin was applied to one of the flakes in the open atmosphere using a teflon coated spatula. The second flake was then placed on top, sandwiching the resin in between. The total time that was required to spread the resin and place the composite

into the press ranged from 3-4 minutes.

4.4.1. Variable Wood Precure Moisture Content

One composite was made using dry wood flakes straight out of the oven. Another was made with flakes which were equilibrated to room conditions (4.5% MC). Flakes stored in a sealed container over water reached 31% moisture. Intermediate moisture contents were once again reached by storing over water until saturated and then allowing them to lose moisture in the open atmosphere. In all, six wood precure moisture contents were used: Dry, 4.5%, 7.6%, 11.5%, 15.0%, 31%. These composites were pressed between teflon at 50 psi platen pressure and 120°C for 60 minutes.

4.4.2. Variable Cure Temperature

Five different cure temperatures were studied: 120°, 140°, 159°, 172°, and 185°C. A temperature of 120°C is similar to target core temperatures used in the production of oriented strand board (OSB). 185°C is similar to platen temperatures used in the production of OSB. All flakes used in this experiment were equilibrated to room conditions (4.5%). Composites were pressed between teflon at 50 psi platen pressure and the corresponding cure temperature for 140 seconds. This reduced press time of 140 seconds was chosen as one which is realistic for the production of OSB.

4.4.3. Variable Cure Time

The effect of cure time was studied at both extremes of the temperature study (i.e., at 120° and 185°C). Six different cure times were studied: 140 sec, 160 sec, 3 min, 4 min, 10 min, and 60 minutes. All flakes were equilibrated to room conditions (4.5%) and pressed between teflon sheets. One series of six composites was pressed at 50 psi platen pressure, 120°C, and the corresponding cure time. A second series of six composites was made at 50 psi platen pressure, 185°C, and the corresponding cure time.

4.4.4. Catalyzed Wood/¹⁵N-pMDI Composites

Tin Octoate catalyst. Two wood flakes were dried at $103 \pm 2^\circ\text{C}$ for 24 hours to obtain the dry weights (total 0.6190g). A solution was made consisting of 0.02g tin octoate in 10 ml chloroform. 1.5 ml of the tin octoate solution was pipeted onto each flake for a target concentration of 1% catalyst. The flakes were then redried at 1 mm Hg and 50°C for 24 hours. The new dry weight indicated an actual catalyst concentration of 1.1%. Resin was then applied rapidly in the open atmosphere to one of the flakes at a loading of 18% of the total composite weight. The composite was pressed at 50 psi platen pressure and 120°C for 60 minutes.

Phenylmercuric Acetate catalyst. Two wood flakes were cut and dried at $103 \pm 2^\circ\text{C}$ for 24 hours (total dry weight 0.4510g). A solution was made consisting of 0.2545g phenylmercuric acetate in 10 ml of acetone. 1 ml of this solution was then pipeted onto each wood flake (target 10 wt.% catalyst). The flakes were then redried at 1 mm Hg

and 40°C for 36 hours. The vacuum was released by blowing dry argon gas into the vacuum oven. The flakes were removed from the oven with the argon gas still blowing through, placed into a container, blown out with argon, and sealed. An Atmosbag (Aldrich Chemical) had previously been equipped with an analytical balance, ¹⁵N-pMDI resin, and a teflon coated spatula. The container with the flakes was placed into the Atmosbag which was then sealed, thoroughly purged with argon, then inflated with argon. The new dry weight of the flakes indicated a catalyst concentration of 9.5%. Resin was applied to one flake at a loading of 20 wt. % of the total composite weight. The composite was quickly removed from the Atmosbag with argon gas blowing through and then pressed at 50 psi platen pressure and 120°C for 60 minutes. After pressing there was absolutely no visible ooze out of the resin, which was not characteristic to the other composites.

4.5. SYNTHESIS OF ¹⁵N-LABELED URETHANE

A reflux apparatus was assembled consisting of a 50 ml 3-neck round bottom flask, magnetic stir bar, septa, thermometer, condenser, and dry N₂ gas. Methanol had been previously distilled over anhydrous calcium chloride and a slow N₂ purge. 20 ml of methanol were added to the flask followed by 1 drop (0.0113g) of tin octoate catalyst. 11 drops (0.1314g) of the ¹⁵N-pMDI were added to the flask with rapid stirring. The solution was heated to reflux for 40 minutes upon which it became very light yellow in color. The solution was cooled down to room temperature and the methanol rotavaped

off. The product, an orangish-brown colored solid, was ground into a fine powder for characterization.

4.6. CHARACTERIZATION TECHNIQUES

4.6.1. Isocyanate Content Determinations

Isocyanate content was measured for the ^{15}N -labeled resin that was synthesized in our lab. Procedures were followed from ASTM Standard D 5155-91 - "Standard Test Method for Polyurethane Raw Materials: Determination of the Isocyanate Content of Aromatic Isocyanates". Test Method C (unheated trichlorobenzene-toluene-dibutylamine) was used. A dibutylamine solution (2N) was prepared by diluting 130g (169.5 ml) of dibutylamine to 500 ml total volume with toluene (i.e., 330.5 ml toluene) in a 1L reagent bottle. Approximately $\frac{1}{2}$ inch of Type 4A molecular sieves were added to the bottle. Methanolic HCl (1N) solution was prepared by adding 78.85g of 37% aqueous HCl (65.7 ml, 0.8 mol HCl) to 734.3 ml of methanol in a 1L reagent bottle. The 37% HCl solution was measured by weight rather than volume for best accuracy. The methanolic HCl solution was standardized with three primary standard solutions of 0.20-0.25g Na_2CO_3 in 50 ml water. 2 drops of methyl orange (Aldrich, 0.1 wt. % aqueous solution) were added to the primary standards which were then titrated with methanolic HCl until the color matched that of a 0.05N potassium acid phthalate solution (pH 4.0) with two drops of methyl orange. The mean normality of the methanolic HCl solution was determined to be 0.938N (standard deviation = 0.006).

Due to the expensive nature of the ^{15}N -pMDI resin, procedures for the isocyanate content determinations were scaled down to 10% of the volumes stated in Test Method C. In order to practice this technique and to determine its accuracy when scaled down to 10%, measurements were first performed on commercial Isonate MDI/polyol resin (Dow Chemical Company) with a manufacturer stated isocyanate content of 29.23%. Three samples tested at the 10% scale were determined to have a mean isocyanate content of 30.07% ($\sigma = 0.087$). This degree of error (2.9%) was deemed acceptable for the purposes of this study. Two tests were performed on the ^{15}N -pMDI synthesized in our lab. Isocyanate contents were determined to be 25.64% and 25.55% (Mean = 25.60%).

4.6.2. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopy was performed on a Nicolet 5 SXC spectrophotometer. Spectra of the various pMDI resins which were synthesized, including the ^{15}N -labeled pMDI, were obtained by sandwiching several milligrams of the sample between two KBr pellets. Cellulose and wood composites were ground into 60 mesh particles using a Wiley mill and then made into KBr pellets.

4.6.3. Nuclear Magnetic Resonance (NMR) Spectroscopy (solution techniques)

All solution state NMR spectra were obtained at room temperature from a Varian Unity-400 MHz spectrometer. Samples were prepared by adding 25-50 mg of sample

to 1 ml of deuterated solvent (chloroform-d, acetone-d₆, DMSO-d₆, or pyridine-d₅) in a 5 ml round bottom flask. The solution was then transferred to either Wilmad 507 or 550 PP NMR tubes.

¹H NMR. ¹H NMR spectra were acquired using 16 scans. All spectra were referenced internally to tetramethylsilane at 0 ppm.

¹³C NMR. ¹³C NMR spectra were acquired using 300-960 scans at a frequency of 100.577 MHz. Most acetylated polyamines were acquired for 300 scans while the spectra of pMDI resins were acquired for 960 scans. Scans were accumulated using complete proton decoupling. All spectra were referenced internally to tetramethylsilane at 0 ppm.

¹⁵N NMR. ¹⁵N solution NMR spectra were obtained for the ¹⁵N-pMDI resin and the ¹⁵N-labeled urethane synthesized for this study. 92 scans were accumulated at a frequency of 40.543 MHz.

4.6.4. ¹⁵N CP/MAS NMR (solid state)

¹⁵N CP/MAS NMR spectra were obtained at room temperature on a Bruker MSL-300 MHz spectrometer with a 7 mm Probenkopf MAS.07.D8 probe. The ¹⁵N frequency was 30.4 MHz. A bullet-type zirconium oxide rotor fitted with a Kel-f cap was used. Small circles were punched out of the composites using a paper hole puncher, stacked into the rotor, and filled in and around with powdered aluminum oxide to facilitate rapid spinning. The ¹H channel was tuned using adamantane while ¹⁵N-glycine was used to set

the Hartmann-Hahn condition. Standard phase cycling was used during acquisition. Common parameters were set as follows: Recycle delay (D0) = 6 sec, Dwell time (D3) = 25 μ sec, and Acquisition time (D7) = 50 msec. Variable contact time experiments were performed on all composites. All samples were spun at a rotor speed of 4100-4150 Hz. Spectra were referenced externally to ^{15}N -glycine at 31 ppm.

Several additional experiments were performed using a variable spin lock period prior to a fixed contact time. Three experiments were performed on a cellulose composite using contact times of 1.5, 3.0, and 5.0 msec. All experiments on wood composites used a contact time of 5.0 msec. The proton 90° pulse was 8 μ sec in duration and all other parameters were the same as those described above.

Cellulose/ ^{15}N -pMDI Composites. Experiments on cellulose composites used a ^1H 90° pulse which was 10 μ sec in duration. CP variable contact time experiments were performed using 16 different contact times: 0.2, 0.5, 0.8, 1, 1.5, 2, 2.5, 3, 4, 5, 7, 9, 11, 13, 15, and 18 msec. 200 scans were collected at each contact time and then Fourier transformed with a line broadening of 15 Hz.

Wood/ ^{15}N -pMDI Composites. Experiments on wood composites used a ^1H 90° pulse which was 8 μ sec in duration. CP variable contact time experiments were performed for most samples at the same 16 contact times used for cellulose composites. For the first group of wood composites that were cured as a function of precure moisture content, three additional contact times were added: 0.05, 0.1, and 0.15 msec. These contact times had to be added so that the T_{NH} relaxation parameter could be calculated for

protonated species. The signal to noise ratio was poor after 200 scans so acquisitions were increased to 400 scans for all wood composites. FID's were Fourier transformed with a line broadening of 50 Hz.

¹⁵N-labeled Urethane. The product from the reaction of ¹⁵N-pMDI with dry methanol was observed for 200 scans at a contact time of 2 msec. The ¹H 90° pulse was 10 μsec in duration and the FID was Fourier transformed with a line broadening of 15 Hz.

CHAPTER 5

SYNTHESIS OF POLYMERIC MDI-----

5.1. INTRODUCTION

The synthesis of pMDI is a two-step reaction beginning with the HCl catalyzed condensation of aniline with formaldehyde. The second step is the conversion of the resulting polyamine to polyisocyanate by phosgenation. Much of the literature regarding the aniline/formaldehyde condensation is proprietary and the literature that is available is lacking in detail [61-67]. This is unfortunate since the formation of a suitable polyamine is critical for the synthesis of a fluid pMDI resin.

As the literature has shown [61], polyamine molecular weight is influenced primarily by three variables: 1) aniline:formaldehyde ratio, 2) aniline:HCl ratio, and 3) reaction time. However, specific values for these ratios along with their corresponding reaction time which produce a suitable polyamine composition are not available in the literature. Instead, broad ranges have been cited from which vastly different polyamine compositions could be synthesized [65]. Yet without tight control of these variables the resin may either be too viscous or even completely solid at room temperature. As a result, it was necessary to begin this study with a cursory examination of the aniline/formaldehyde condensation before an attempt could be made to synthesize a desirable ^{15}N -pMDI resin.

5.2. RESULTS AND DISCUSSION

5.2.1. Polyamine Synthesis

As mentioned in the literature [61,65] and determined in preliminary experiments, it was found that an aniline:formaldehyde ratio of 2.2:1.0 yields favorable resin properties so this variable was not studied further. Table 1 displays the results of three sets of experiments performed to study the effects of aniline:HCl ratio and reaction time on the polyamine molecular weight. The polyamines from these experiments were then acetylated to remove the amine proton resonance from the ^1H NMR spectrum (Figure 1). Due to hydrogen bonding effects, the amine proton chemical shift varies with the concentration of the NMR sample solution [34]. This was a particular problem for the polyamines of this study because the amine proton resonance often overlapped with the methylene protons, making integration of that region impossible. By acetylating the polyamines, the amine resonance was replaced with an amide proton resonance which was well resolved from any other resonances (δ 9.2-9.8). As mentioned earlier, some reaction conditions can cause a significant amount of residual secondary amine that was not converted to primary amine during the second step of the aniline/formaldehyde condensation. The chemical shift of methylene protons adjacent to acetylated secondary amine appears to be shifted up-field to δ 4.7-5.1 due to electron deshielding.

The number average molecular weight of the polyamines can be obtained from the ratio of the integrals of the aromatic protons (6.9-7.6 ppm) to the benzylic protons (3.5-4.1 ppm) obtained from solution state ^1H NMR (Figure 2). From the characteristic

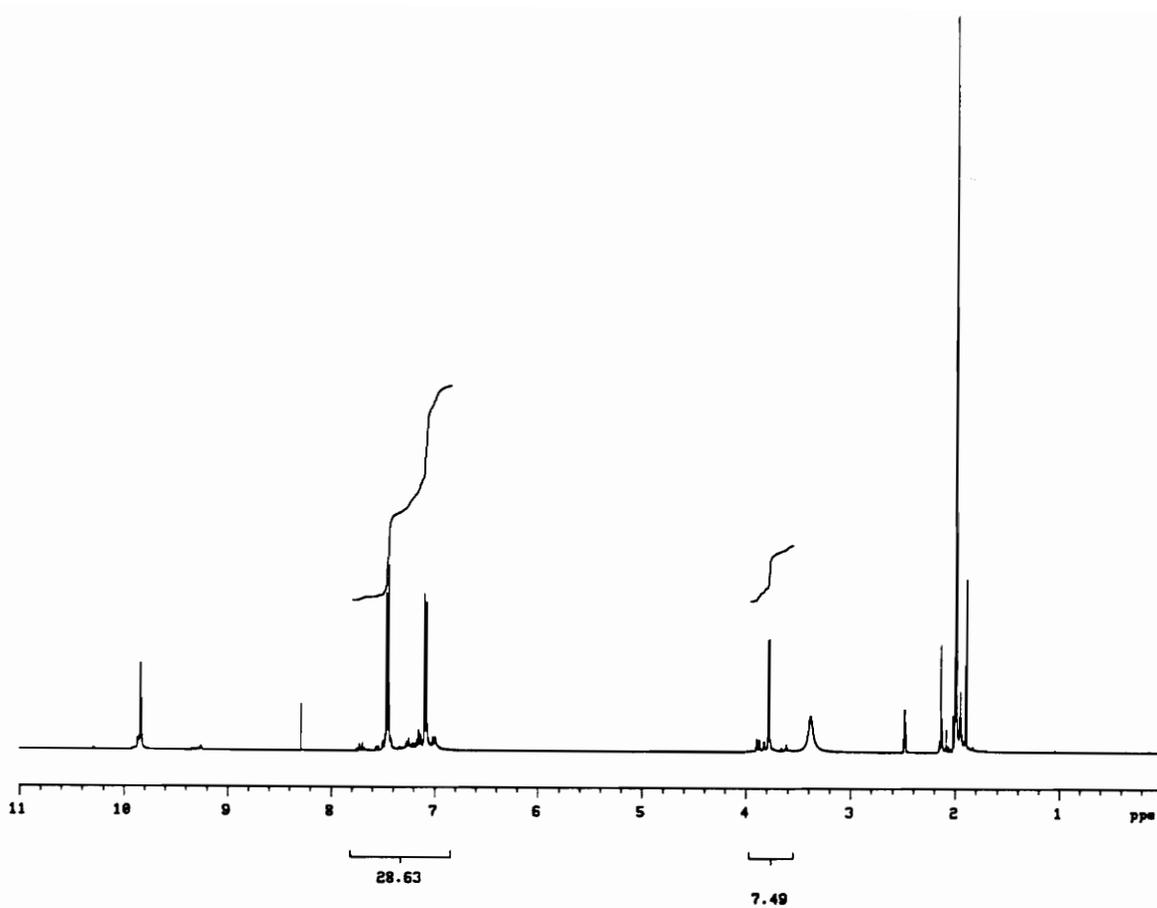


Figure 1: Solution state ^1H NMR of a typical polyamine synthesized in this study, integrated to show the benzylic ($\delta 3.5-4.1$) and aromatic ($\delta 6.9-7.6$) proton regions.

Table 1: Molecular Weight Data of Polyamines Calculated from Solution State ^1H NMR as a Function of Aniline:HCl Ratio and Reaction Time.

Aniline:HCl Ratio	Reaction Time (hours)	Aromatic:Benzylic Ratio	Average Molecular Weight
1.0:1.5	2	3.6	220
	12	3.4	235
	17	3.3	250
	24	3.4	241
1.5:1.0	2	3.6	224
	12	3.7	212
	17	4.0	198
	24	3.7	212
3.0:1.0	2	4.0	198
	12	4.0	198
	17	4.0	198
	24	4.0	198

polyamine structure in Scheme II, we can define an upper theoretical limit for this ratio of 4.0 for pure methylenedianiline ($n = 0$) and a lower limit of 1.5 for infinite molecular weight material ($n = \infty$). The ratios in Table 1 indicate that the polyamines synthesized are primarily $n = 0$ and $n = 1$ material.

It has been stated that increasing the aniline:HCl ratio favors the production of methylenedianiline [61]. Indeed, such a trend is observed in Table 1 for a given reaction time. Note that at an aniline:HCl ratio of 3.0:1.0 the dimer was essentially produced at all reaction times. The effect of reaction time can be seen to be dependent on the aniline:HCl ratio. At a ratio of 1.0:1.5, molecular weight increases with reaction time from 2 to 17 hours and then for unknown reasons decreases after 24 hours of reaction. When the ratio is reversed to 1.5:1.0, molecular weight decreases with reaction time over the same range. After 17 hours the polyamine becomes essentially dimer, but then increases in molecular weight after 24 hours of reaction. While no error analysis is given for the integral ratios in Table 1, it is believed that the minor molecular weight differences shown are indeed significant.

5.2.2. Synthesis of 99% ^{15}N -labeled Polymeric MDI

Using the optimum conditions for the polyamine condensation reaction as determined from the previous experiments, a ^{15}N -labeled polyamine was synthesized. Aniline:HCl was chosen to be 1.0:1.5 because this produced a suitable polyamine for the synthesis of a fluid pMDI resin. A reaction time of 6 hours was chosen because the product

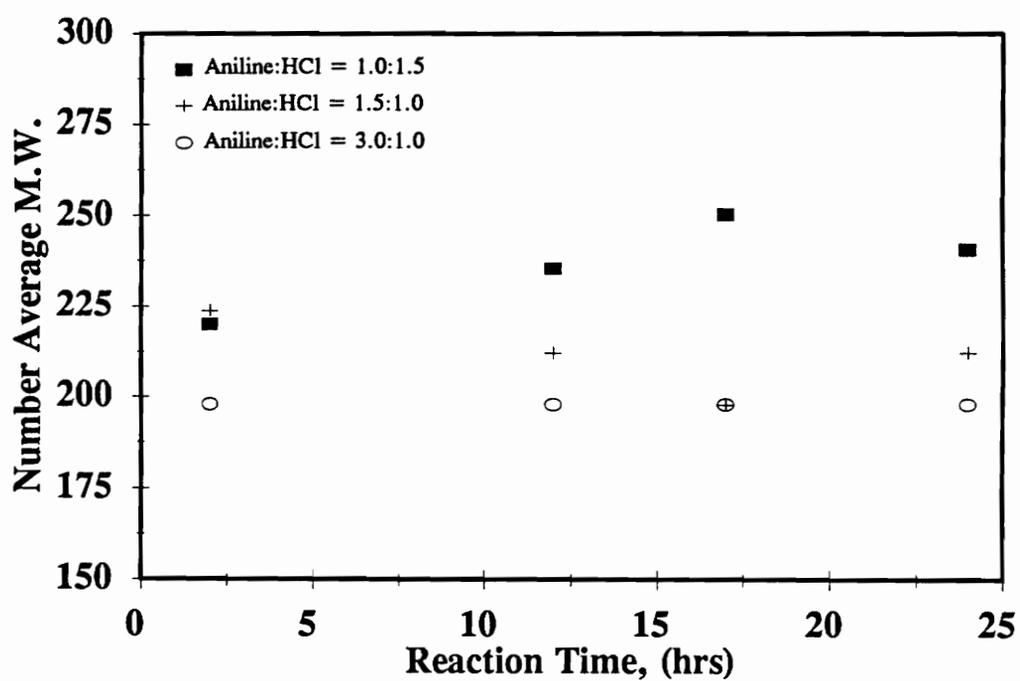


Figure 2: Polyamine number average molecular weight calculated from ^1H NMR as a function of the aniline:HCl ratio and reaction time.

viscosity was favorable and the concentration of residual secondary amine is minimized. Twitchett [61] has discussed in detail the need to minimize residual secondary amine, which is formed as a reaction intermediary during the condensation reaction. If a proper combination of reaction time and aniline:HCl are employed, virtually all secondary amine should be converted to the desired primary amine. As in the previous experiments, triphosgene was used to carry out the phosgenation. The resulting ^{15}N -pMDI resin was produced in high yield ($>90\%$), had low viscosity and an isocyanate content of 25.60%, and was structurally similar to commercial resin according to ^1H (Figure 3) and ^{13}C (Figure 4) solution state NMR.

5.3. CONCLUSIONS

A cursory examination of the aniline/formaldehyde condensation reaction was performed due to a lack of detailed information in the literature. Preliminary experiments determined that an aniline:formaldehyde ratio of 2.2:1.0 yields a polyamine capable of producing a fluid pMDI resin. Number average molecular weight data obtained from solution state ^1H NMR indicates that increasing the aniline:HCl ratio for a given reaction time favors the production of methylenedianiline. The effect of reaction time was noted to be dependent on the aniline:HCl ratio. At a ratio of 1.0:1.5, molecular weight increases with reaction time from 2 to 17 hours. When the ratio is reversed to 1.5:1.0, molecular weight decreases over the same range, becoming essentially methylenedianiline after 17 hours. For unknown reasons the trend in

polyamine molecular weight reverses sometime between 17 and 24 hours for both aniline:HCl ratios. At an aniline:HCl ratio of 3.0:1.0, methylenedianiline was produced at all reaction times from 2 to 24 hours.

Using the optimum conditions for the aniline/formaldehyde condensation reaction, a 99% ^{15}N -enriched pMDI resin with desirable adhesive properties was successfully synthesized. Aniline:HCl of 1.0:1.5 was used because this ratio produced a polyamine suitable for the synthesis of a fluid pMDI resin. A reaction time of 6 hours was used because the product viscosity was favorable and the concentration of residual secondary amine was minimal. Triphosgene, a crystalline solid, proved to be an effective substitute for the highly toxic phosgene gas. The resulting ^{15}N -pMDI resin was synthesized in high yield (>90%), had low viscosity and an isocyanate content of 25.60%, and was structurally similar to commercial resin by solution state ^1H and ^{13}C NMR.

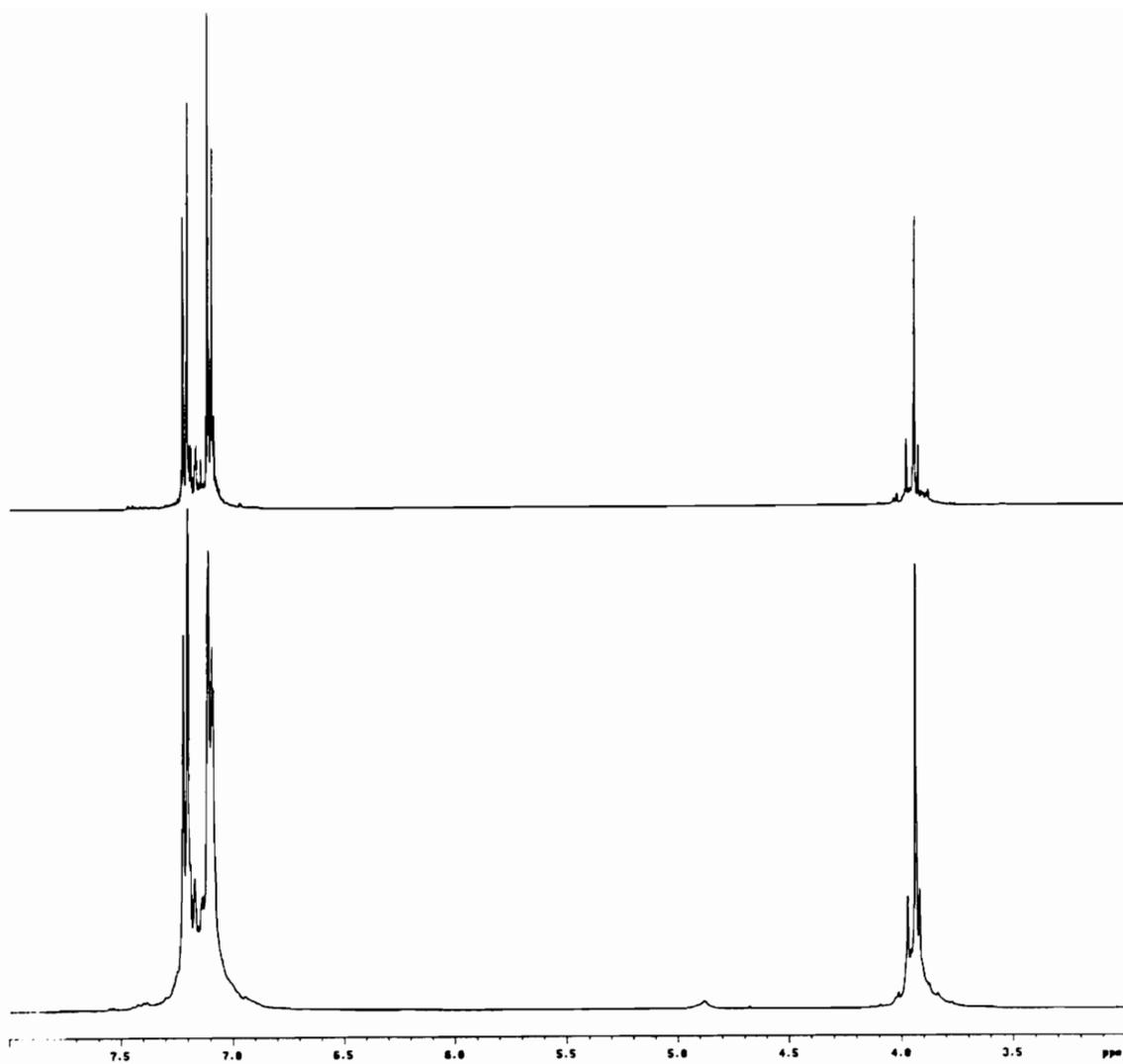


Figure 3: Solution state ¹H NMR spectra of the ¹⁵N-enriched pMDI resin synthesized for this study (bottom) and ICI Rubinate MF-184 commercial resin (top). Samples were run in acetone-d₆ and referenced to tetramethylsilane at 0 ppm.

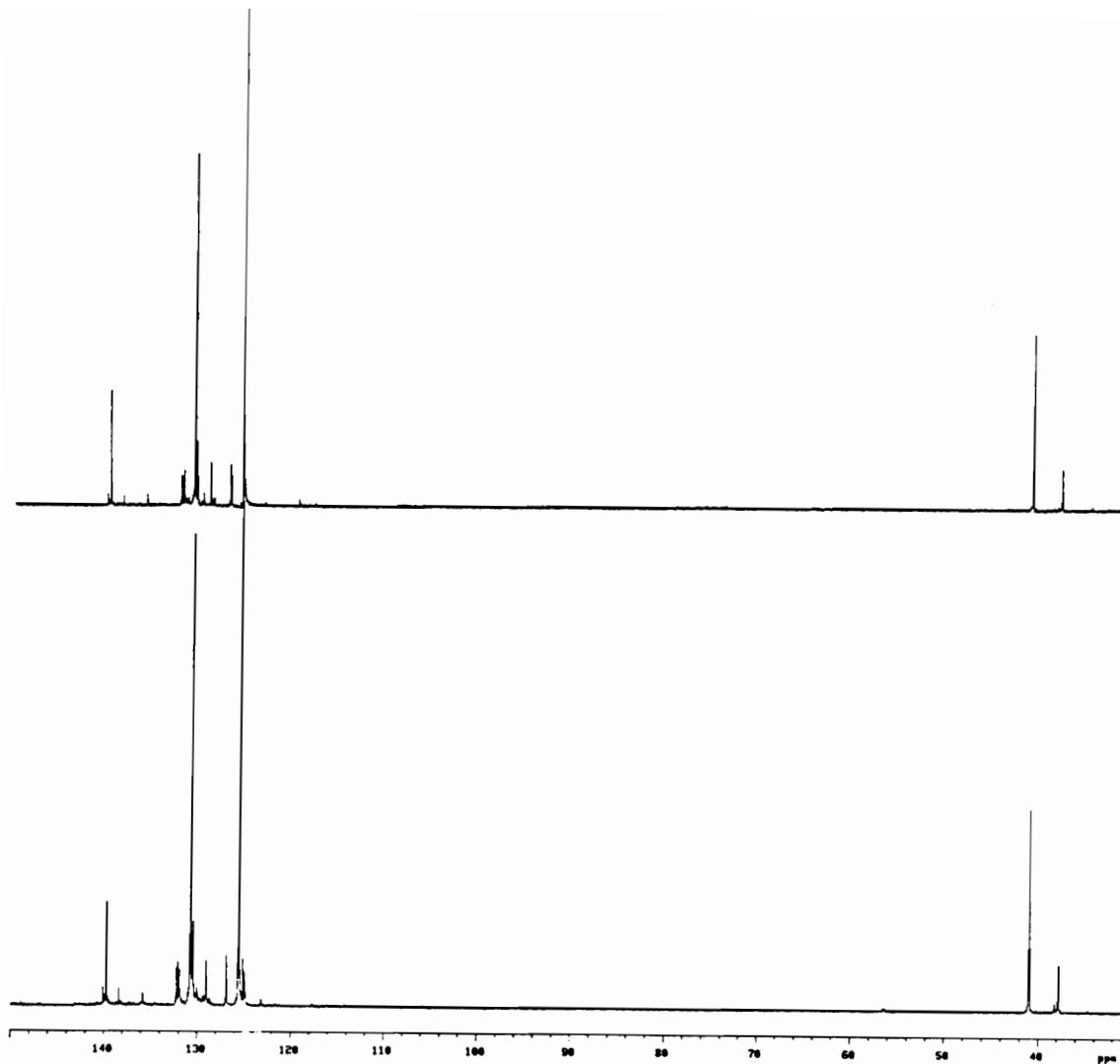


Figure 4: Solution state ^{13}C NMR spectra of the ^{15}N -enriched PMDI resin synthesized for this study (bottom) and ICI Rubinate MF-184 commercial resin (top). Samples were run in acetone- d_6 and referenced to tetramethylsilane at 0 ppm.

CHAPTER 6

CELLULOSE/¹⁵N-pMDI COMPOSITES-----

6.1. INTRODUCTION

The study of isocyanate-wood adhesion began with the work of Morak and coworkers [19-21]. They learned that diisocyanates readily reacted with wood fiber, thus increasing the strength of paper products. Rowell et al. extended this by demonstrating the stability of urethane bonds formed between wood and isocyanates under specialized conditions [22-24]. Later, Owen and coworkers founded some of the first chemical analyses that had a direct bearing upon the adhesive mechanism in wood-isocyanate bonding [25]. They demonstrated by infrared spectroscopy that urethane bonds could be formed under anhydrous conditions when an excess of isocyanate was used on wood [17,25]. Others have used FTIR and DSC to reveal the domination of polyurea formation when moisture is present [2,28]. Most studies to date, however, have utilized special conditions such as small, monofunctional isocyanates [22-25], large excesses of isocyanate [17], and the use of wood swelling solvents as a carrier of the isocyanate into the wood microstructure [19-21,25]. Studies of the wood-isocyanate reaction under conditions common to gluing operations (i.e., the production of oriented strand board) are curiously lacking. This lack of information is likely due to the chemical complexity of wood and the associated problems with techniques such as infrared spectroscopy which gives multiple overlapping signals in the carbonyl region when observing isocyanate-

bonded wood.

This chapter introduces ^{15}N CP/MAS NMR as a technique for probing these complex composite systems. Model cellulose/ ^{15}N -pMDI composites were chosen for study prior to wood composites in order to establish the feasibility of this technique. Cellulose composites have a more homogeneous weight distribution than solid wood composites, facilitating the required rapid spinning. CP/MAS NMR is ideally suited for the study of cured resin systems [40-48]. In particular, the usefulness of this technique for studying wood adhesives has been expressed [49]. CP/MAS allows the study of molecular phenomena within the composite without disrupting the solid state. Molecular events in the solid give rise to the macroscopic performance of materials and as such makes study of the intact solid most interesting.

^{13}C CP/MAS is the most common magnetic resonance technique used to probe polymeric solids. However, the ^{13}C spectrum of a pMDI composite is complicated by overlapping resonances from the resin and the substrate. ^{15}N NMR offers the advantage of direct observation of the resin chemistry. No additional resonances are present from cellulosic or wood substrates, and each resonance from the resin provides concise information regarding cure chemistry. Fewer resonances combined with a broad spectral width makes interpretation of ^{15}N spectra straightforward for these systems. Indeed, the advantages of ^{15}N CP/MAS over ^{13}C experiments have recently been demonstrated for the study of MDI-based resin systems [55-58]. The disadvantages associated with using the ^{15}N nucleus include low natural abundance (0.37%) and a small magnetogyric ratio,

both of which usually make isotopic enrichment necessary in order to increase sensitivity.

6.2. RESULTS AND DISCUSSION

6.2.1. Effect of Moisture on Cure Chemistry

A series of composites using different cellulose precure moisture contents were cured at 25 wt. % resin, 50 psi platen pressure, and 120°C for 60 minutes. While this may seem to be a very high resin loading, it must be emphasized that these composites have continuous bondlines. They are probably not very different from the localized, "spot-weld" resin loadings that are characteristic of industrial wood composites which have discontinuous bondlines. Figure 5 shows the ^{15}N CP/MAS NMR spectra displaying the effect of moisture on cure chemistry. Four distinct resonances are present in the spectra. The resonance at 44 ppm is due to residual isocyanate. The resonance at 104 ppm corresponds to urea nitrogens formed by the reaction of isocyanate with amines, the amines being produced by the reaction of isocyanate with water. Further reaction of urea with isocyanate is shown by the presence of amide (111 ppm) and imide (138 ppm) nitrogens of a biuret network. Note that a small shoulder appears on the isocyanate peak at 52 ppm for the composite cured at 23% moisture content. This resonance is due to residual amine groups which have not undergone the reaction with isocyanate to form polyurea. Identification of resonances is based upon ^{15}N chemical shifts previously reported in the literature for isocyanate-based resins [55]. Note that there is also a small resonance at 130 ppm. This resonance is particularly noticeable for the composite cured

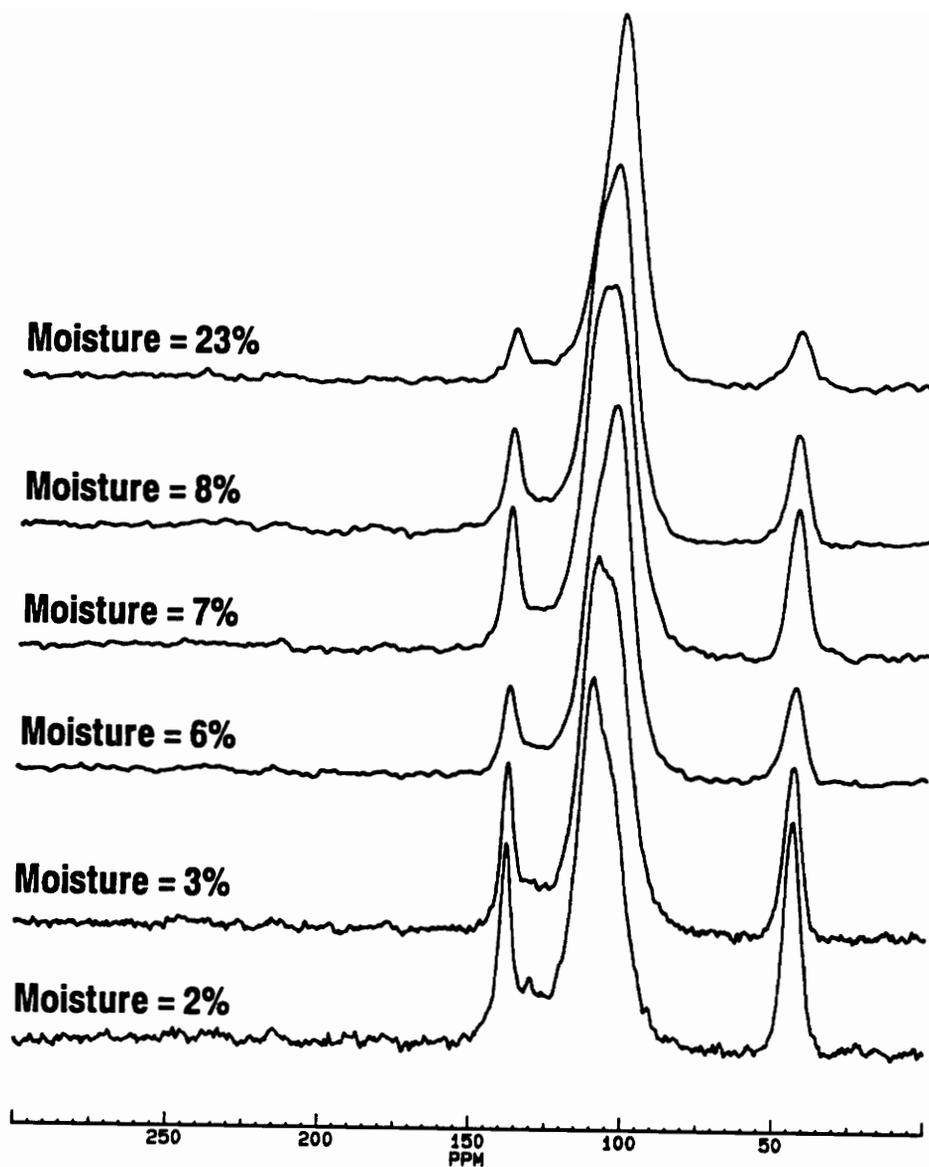


Figure 5: ^{15}N CP/MAS NMR spectra of cellulose/ ^{15}N -pMDI composites as a function of cellulose pre-cure moisture content. Contact time is 2 msec and spectra are referenced to ^{15}N -glycine at 31 ppm.

at 2% moisture, but visibly decreases at the higher moisture levels. The exact identity of this resonance is currently unknown, but it displays a slow cross-polarization rate characteristic of a nonprotonated species. Based solely on the chemical shift it is unlikely that this resonance is from uretedione (δ 145 ppm [55]) or isocyanurate (δ 149 ppm [55]) linkages, which are formed by the dimerization and trimerization of isocyanates, respectively.

The spectra clearly show the dominant influence of water on the cure chemistry. At low moisture contents (<3.3%) the isocyanate reacts first with water to form primary amines, which in turn react with isocyanate to form polyureas. Much of the polyurea also reacts with residual isocyanate to form biuret structures. Some residual polyurea remains as revealed by the shoulder at 104 ppm on the amide nitrogen resonance (Figure 5, 2% and 3% MC). As the moisture is increased to 6%, the cure chemistry shifts to primarily polyurea type structures. The high concentration of water molecules, combined with their greater mobility compared to polyurea molecules, results in less biuret formation. The amide nitrogen is reduced to a shoulder at 111 ppm on the urea nitrogen resonance and a significant decrease in imide nitrogen (138 ppm) intensity can also be noted. When the cellulose is saturated at 23% moisture, an overwhelming dominance of urea formation is noted.

No indication of urethane formation is seen in any of the samples. In fact, on three separate attempts dry cellulose papers did not bond under the curing conditions described earlier. In each instance of bonding dry papers, the composites were easily peeled apart

by hand after pressing and most of the resin remained as a liquid. Only upon addition of a suitable catalyst, stannous octoate, was adhesion of the dry papers achieved. The cure chemistry of this catalyzed composite shows a prominent peak at 103 ppm which corresponds to the urethane nitrogen formed by reaction between isocyanate and cellulose hydroxyls (Figure 6). Note also the difficulty of achieving complete dryness with cellulose as biuret formation is evidenced by the imide (138 ppm) nitrogen resonance. Also shown in Figure 6 are the urethane product from the reaction of ^{15}N -pMDI with dry methanol, and for comparison a cellulose composite cured at 2% moisture. There does not appear to be a significant amount of urethane formation, if any, in the composite even when cured at such a low moisture content. The long press time of 60 minutes was chosen to establish a reference point of "complete cure". This length of time was expected to allow urethane formation to take place, if possible, under these bonding conditions. It is evident, however, that the amide, urea, and urethane nitrogens are not well resolved in ^{15}N solid state spectra. Therefore, it is conceivable that low amounts of urethane formation are undetectable.

The peak intensities shown in Figure 5 can be used to approximate the relative concentrations of the various species present in the bondline. However, for a given contact time, cross-polarization and rotating-frame relaxation rates are not the same for all types of nitrogen. Direct comparisons of intensities at a given contact time are therefore inaccurate. Equation 1 which was cited in Chapter 2 was used to convert these intensities at a given contact time to a standardized value, I^* , corrected for variations in

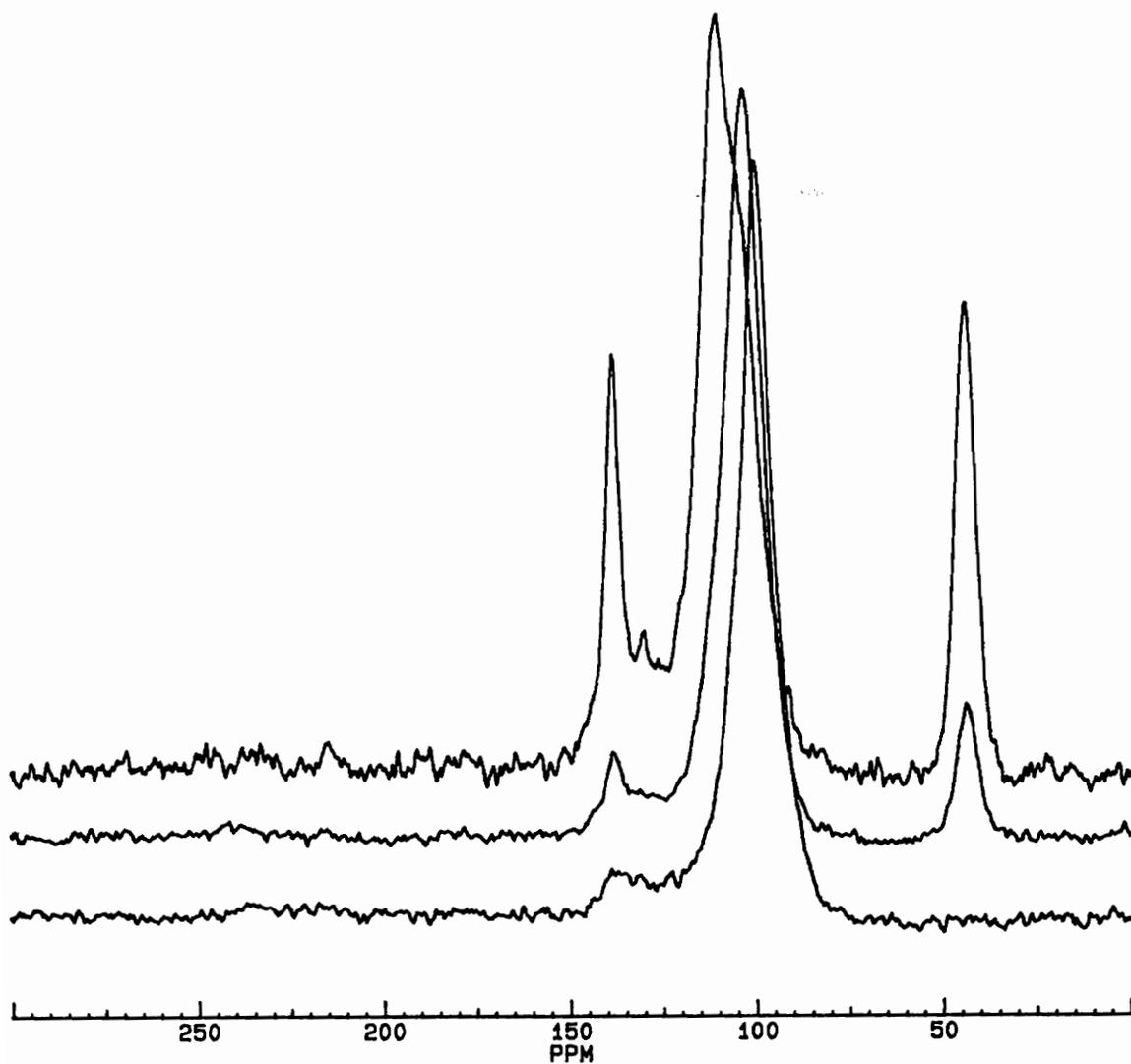


Figure 6: ^{15}N CP/MAS NMR spectra of a cellulose/ ^{15}N -pMDI composite cured at 2% moisture (top), cellulose/ ^{15}N -pMDI composite cured dry with 1% stannous octoate (middle), and the urethane product from reaction of ^{15}N -pMDI with dry methanol (bottom).

rotating-frame and cross-polarization relaxation rates [55,59]:

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

Table 2 provides the relaxation parameters and corrected relative intensities for the major peaks of each composite. The relaxation parameters, T_{NH} and $T_{1\rho H}$, are obtained by fitting the signal intensity versus contact time data to Equation 1. The corrected relative intensity is simply the corrected intensity for a desired peak divided by the sum of all corrected intensities. It is in essence the percent composition of each chemical moiety present at the bondline. Note that only the major peak of the overlapping urea and amide nitrogen resonances was assessed. The overlap in this area made it impossible to correctly evaluate signal intensities for both resonances, and deconvolution was not attempted. The corrected relative intensity values confirm the trends discussed earlier (Figure 7). With the exception of the composite cured at 7.3% moisture, a clear increase in urea content is observed with increasing precure moisture content. The source of this discontinuity is not clear and may be attributable to random error. The imide nitrogen concentration appears to be relatively constant up to 8% moisture. Beyond 8% the imide concentration decreases, indicating the shift toward greater residual polyurea and less biuret formation as evidenced in Figure 5. A gradual decrease in residual isocyanate content is also noted, but it is interesting that some is still present even after curing for 60 minutes at 23% moisture.

The variability of this technique was tested by making three identical composites at 2% moisture content. This moisture content was chosen because it was the easiest to

Table 2: Effect of Moisture Content on the Relaxation Parameters and Relative Intensity of Major Peaks for ¹⁵N-Enriched pMDI/Cellulose Composites.^a

Moisture (%)	Peak ^b (ppm)	T _{NH} ^c (ms)	T _{1ρH} ^c (ms)	I*/I(4 ms)	Rel Int (I), %	
					uncorr	corr ^d
2.1 ^e	44	2.5 (0.13)	12.9 (0.97)	1.48	39.2	32.2 (4.0)
	104	—	—	—	—	—
	111	0.07 (~ 0)	4.9 (0.05)	2.15	30.3	39.9 (4.5)
	138	2.5 (0.20)	8.3 (0.16)	1.60	30.5	27.9 (0.8)
3.3	44	2.5	12.1	1.64	32.3	23.3
	104	—	—	—	—	—
	111	0.07	4.5	2.40	36.4	56.7
	138	2.4	8.7	1.54	31.3	20.0
6.3	44	3.5	14.2	1.87	26.5	23.8
	104	0.07	5.5	2.04	48.8	52.0
	111	—	—	—	—	—
	138	3.6	7.9	1.73	24.7	24.2
7.3	44	3.0	12.3	2.06	32.4	27.2
	104	0.07	4.9	2.22	37.7	41.9
	111	—	—	—	—	—
	138	3.4	6.7	1.67	29.9	30.9
8.1	44	2.3	26.4	1.48	28.2	20.8
	104	0.07	5.4	2.08	46.1	56.7
	111	—	—	—	—	—
	138	2.5	12.5	1.25	25.7	22.4
23	44	3.5	13.1	2.07	19.5	15.7
	104	0.07	5.2	2.12	64.7	68.1
	111	—	—	—	—	—
	138	3.9	7.4	1.62	15.8	16.2

^a Cured at 25 wt. % resin, 50 psi, and 120°C for 60 minutes.

^b Chemical shifts of ¹⁵N resonances referenced to glycine at 31 ppm.

^c The mean error is ±10% for T_{NH} values and ±12% for T_{1ρH} values.

^d Calculated from corrected peak intensities at a contact time of 4 msec.

^e Average of three repetitions at this condition. Standard deviations shown in parentheses.

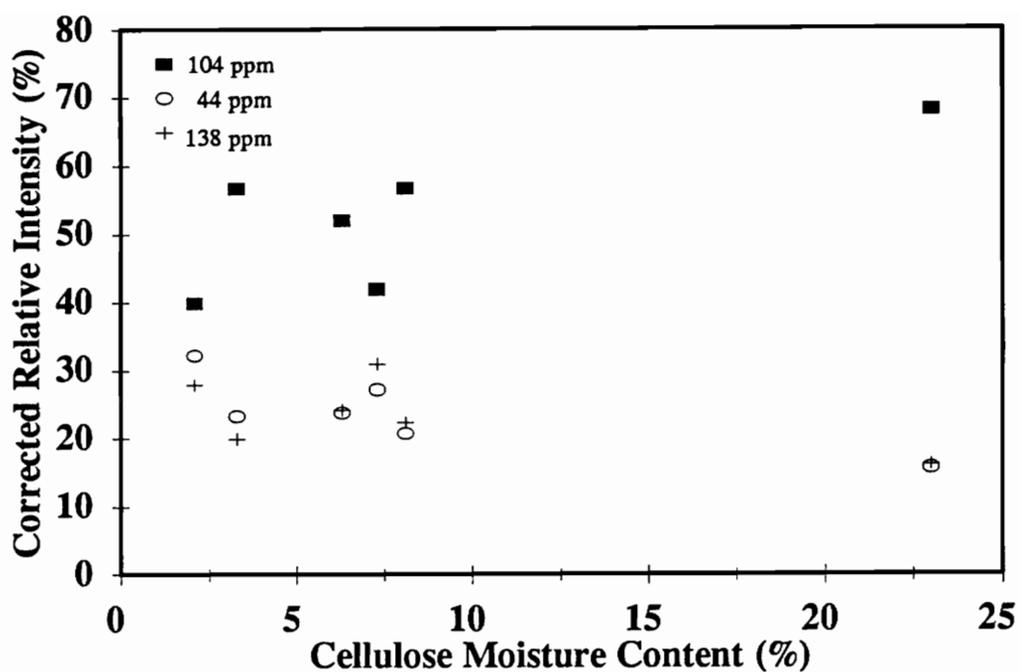


Figure 7: The corrected relative intensity, or percent composition, of the major chemical moieties present in the bondline of cellulose/¹⁵N-pMDI composites as a function of cellulose precure moisture content.

replicate since the composites were simply equilibrated to room conditions. Mean values are given in Table 2 with standard deviations shown in parentheses. The results indicate good reproducibility for both T_{NH} and $T_{1\rho\text{H}}$ relaxation values as well as for the corrected relative intensities.

6.2.2. Effect of Moisture on Bondline Morphology

Figure 8 displays the $T_{1\rho\text{H}}$ values from Table 2 for each nitrogen moiety as a function of cellulose moisture content. Again, due to signal overlap the composite relaxation of the amide and urea signals is shown. Note that the amide/urea relaxation rate is very fast and unchanging as a function of precure moisture. The relaxation rates of the isocyanate and imide nitrogens also remain constant with the exception of the discontinuity at 8.1%. Ordinarily, this would be evidence for a phase separated bondline in which the isocyanate, urea, and biuret structures exist in separate phases which possess distinct relaxation rates. However, notice that at precure moisture contents below 6% the biuret amide peak is the major component in the amide/urea composite signal. Given this, the relaxation rates in Table 2 seem to suggest that the amide and imide nitrogens of biuret structures have significantly different relaxation rates while only being separated by one carbon atom.

This irregularity indicates that these $T_{1\rho\text{H}}$ values are being affected by something other than spin diffusion and molecular mobility. Keep in mind that this data has come from variable contact time experiments in which signal intensity is monitored as a

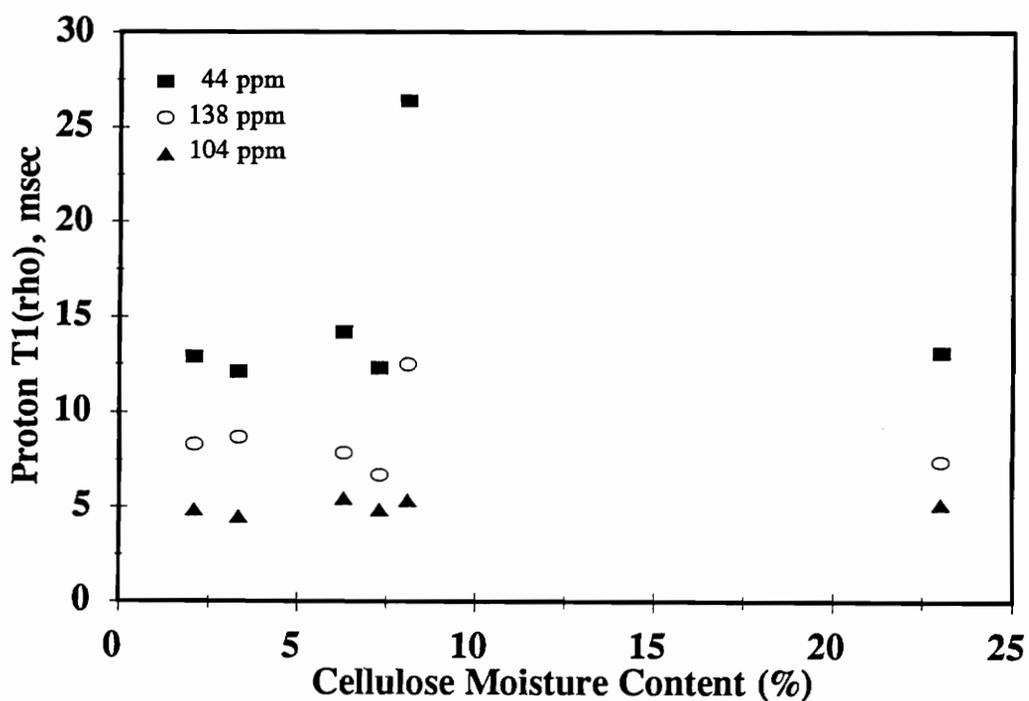


Figure 8: $T_{1\rho H}$ values calculated from cross-polarization variable contact time experiments for chemical moieties present in the bondline of cellulose/ ^{15}N -pMDI composites versus cellulose precure moisture. Mean error for these values is $\pm 12\%$.

function of the period of Hartmann-Hahn contact. In other words, the processes of cross-polarization and proton rotating-frame relaxation are effectively in competition. This is typically of little concern for protonated species which cross-polarize very rapidly. However, notice that the nonprotonated isocyanate and imide nitrogens have excessively long cross-polarization rates which are of the same magnitude as the $T_{1\rho H}$. Inspection of Equation 1 demonstrates that excessively long cross-polarization rates could serve to artificially inflate the values of $T_{1\rho H}$ due to the latent effects of long range cross-polarization. The interaction of cross-polarization and proton rotating-frame processes can be avoided by spin locking the proton reservoir for variable times prior to a fixed period of Hartmann-Hahn contact. Table 3 shows the $T_{1\rho H}$ values measured in the composite cured at 2.1% pre-cure moisture using a variable spin lock prior to a fixed contact period. Three separate experiments were performed using fixed contact times of 1.5, 3.0, and 5.0 ms. The data in Table 3 show that all nitrogen species in this composite are relaxing rapidly with a similar $T_{1\rho H}$ of about 4.5 ms. This is very similar to the $T_{1\rho H}$ of the protonated amide/urea peaks measured with the variable contact time experiment (Table 2). This finding indicates the cross-polarization and proton rotating-frame relaxation processes are interacting in the variable contact time experiment for nonprotonated nitrogens. In other words, variable contact time experiments produce artificially high values of $T_{1\rho H}$ for the imide and isocyanate peaks, while values for the amide/urea composite peak appear to be accurate. Since the corrected signal intensities are calculated using the $T_{1\rho H}$ relaxation parameter, trends in the percent composition as

Table 3: $T_{1\rho H}$ Values Measured Using a Variable Spin Lock Period Prior to a Fixed Contact Time for a Cellulose/ ^{15}N -pMDI Composite^a.

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

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

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

^c All $T_{1\rho H}$ measurements are listed in msec.

shown in Figure 7 can only be used qualitatively. Also, the conclusion drawn from the variable spin lock experiment must be that the cured resin in these composites is probably not phase separated.

Relaxation studies such as these may also be used to probe the character of the residual isocyanate present in these model composites. Residual isocyanate may be present either in the form of free, unreacted pMDI molecules or as dangling ends from partially reacted molecules which are in turn part of a polyurea or biuret structure. Chemical shift information cannot distinguish between these two isocyanate types. However, it is plausible that free isocyanate and dangling isocyanate would have substantially different mobilities. In this instance, each type might contribute to the total signal intensity of the isocyanate resonance and be manifested as biexponential signal decay. On the other hand, simple monoexponential decay would suggest that the isocyanate signal is derived solely from groups within one motional regime. Isocyanate groups within a single motional regime would be consistent with the presence of a single type of isocyanate, presumably those attached to the network as dangling ends rather than free molecules. This topic has been treated thoroughly by Duff and Maciel who have used ^{15}N CP/MAS variable contact time experiments on MDI-based isocyanurate resins [55]. All cellulose/ ^{15}N -pMDI composites in this study show simple monoexponential decay for the isocyanate signal whether using variable contact time or variable spin lock (prior to fixed contact) experiments. This is in agreement with the findings of Duff and Maciel, suggesting that residual isocyanate is present in one form, probably that which

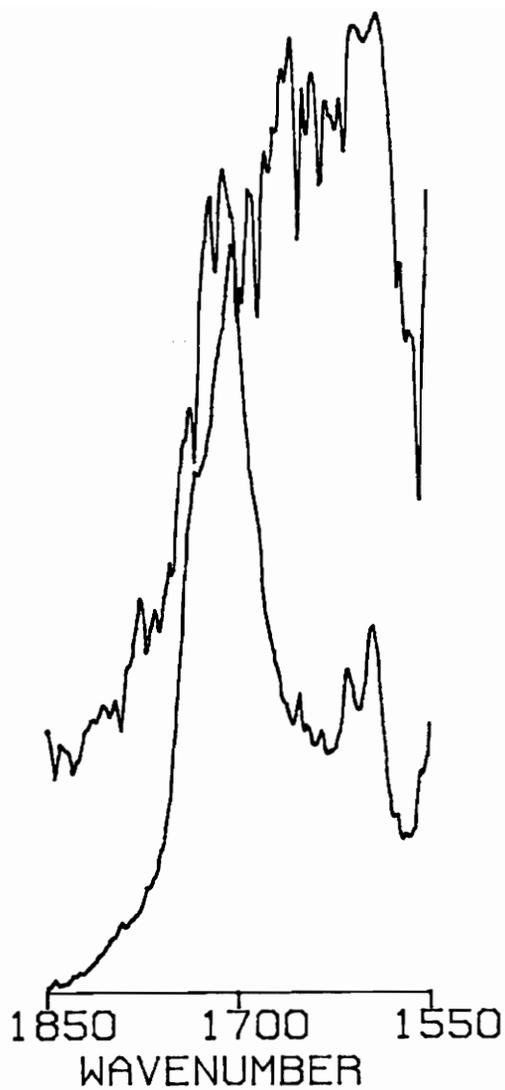


Figure 9: FTIR of a cellulose/¹⁵N-pMDI composite cured at 2% moisture (top) and the urethane product from reaction of ¹⁵N-pMDI with dry methanol (bottom), expanded to show the carbonyl region.

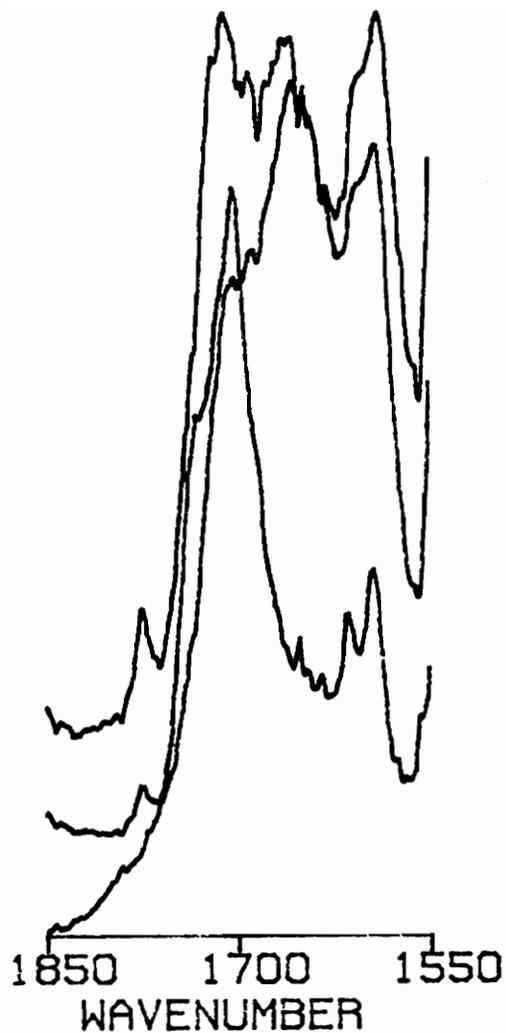


Figure 10: FTIR of a cellulose/¹⁵N-pMDI composite cured at 23% moisture (top), a cellulose/¹⁵N-pMDI composite cured dry with 1% stannous octoate (middle), and the urethane product from reaction of ¹⁵N-pMDI with dry methanol (bottom). The spectra are expanded to display the carbonyl region.

is anchored to the cured network. This conclusion should be supported by the observation of simple monoexponential decay of ^{15}N T_1 or $T_{1\rho}$. Interestingly, Duff and Maciel do show that the isocyanate ^{15}N T_1 exhibits single exponential decay, supporting the contention that residual isocyanate is present in one motional regime.

6.2.3. Characterization Using FTIR

As a means for comparison, several of the cellulose/ ^{15}N -pMDI composites were analyzed using FTIR. Figure 9 shows a portion of the FTIR spectra for a composite cured at 2% moisture and the urethane product from the anhydrous, stannous octoate catalyzed reaction of ^{15}N -pMDI with methanol. The spectra are expanded to display the carbonyl region which provides the most useful information for these systems. The model urethane compound from reaction of ^{15}N -pMDI with methanol displays the characteristic carbonyl absorption at 1701 cm^{-1} [31,32]. The spectrum for the composite that was cured at 2% moisture is more complex. From the ^{15}N CP/MAS spectrum (Figure 5), it is concluded that a number of carbonyl types are present in the bondline. There are the carbonyl groups associated with residual urea as well as those which are incorporated into the different stages of biuret and/or polyuret formation. Indeed, this region ($1650\text{-}1800\text{ cm}^{-1}$) of the FTIR spectrum is extremely complicated. At least ten absorbances can be noted in the region, many of them overlapping one another. As a result, identification of each absorbance is very difficult and well beyond the scope of this study.

One of the major absorbances (1650 cm^{-1}) has been identified as characteristic of a urea carbonyl [32]. Unfortunately, it is not as easy to detect whether small amounts of urethane linkages are present. A close comparison of the two spectra in Figure 9 may indicate that a small shoulder exists in the spectrum of the composite which has the same absorption frequency as the model urethane carbonyl. However, since it is not well resolved from the larger absorption it is unknown whether this is actually a shoulder representative of a different carbonyl type. There is an absorption at 1712 cm^{-1} which is consistent with the value reported by Owen et al. [17] for the isocyanate-cellulose reaction. This could be an indication that a small amount of urethane formation did take place in the composite. However, this absorption is still as intense in the composite that was cured at 23% moisture (Figure 10). This is quite surprising since the isocyanate/water reaction is expected to completely dominate the cure chemistry at such a high moisture content, as confirmed by the ^{15}N CP/MAS results. Furthermore, the catalyzed ^{15}N -pMDI/cellulose composite that was cured dry does not display an absorption at that frequency (Figure 10). Instead, Figure 10 clearly shows that the catalyzed composite has an absorption at 1701 cm^{-1} that matches the model urethane carbonyl absorption. This information disputes the identification of the 1712 cm^{-1} absorbance as characteristic of a urethane carbonyl. It might be that this absorbance represents one of the numerous other carbonyl types that can be formed when curing isocyanate resins in the presence of water.

6.3. CONCLUSIONS

Model cellulose/¹⁵N-pMDI composites were cured at various cellulose precure moisture contents. The ¹⁵N CP/MAS NMR spectra clearly show the dominance of the isocyanate-water reaction on the cure chemistry. Four prominent resonances are present in the spectra: residual isocyanate (44 ppm), polyurea (104 ppm), and the amide (111 ppm) and imide (138 ppm) nitrogens of biuret type structures. There is also evidence of some residual amine groups (52 ppm) in the composite cured at 23% moisture and an unknown resonance (130 ppm) that is most pronounced in the composites cured at low moisture. The cure chemistry at low precure moisture contents is primarily biuret type structures with some residual polyurea and a significant amount of unreacted isocyanate. When the moisture is increased to 6%, the cure chemistry is primarily polyurea type structures with less biuret formation and residual isocyanate. Even at 23% moisture, however, some residual isocyanate remains in the bondline.

Significant urethane formation was not detected at any moisture level. In fact, three separate attempts to bond dry cellulose papers failed. In each instance the composites were easily peeled apart by hand after pressing and much of the resin remained as a liquid. Low levels of urethane formation in any of the samples cannot be completely discounted by ¹⁵N CP/MAS, however, since they could be obscured by signal overlap with urea and amide nitrogens. FTIR results proved to be inconclusive as well.

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

frame relaxation processes. As a result, corrected relative intensity data provide only qualitative information regarding the percent composition of each nitrogen moiety present in the bondline. A more direct measurement of the $T_{1\rho H}$ is obtained from experiments using a variable spin lock prior to the fixed contact time. Results from one of these experiments on a composite that was cured at 2% moisture indicate that the cured resin is probably a homogeneous continuum.

Lastly, it has been demonstrated that ^{15}N CP/MAS NMR is a powerful technique for elucidating fine structural and morphological information from these complex composite systems. A useful procedure for the analysis of solid wood/pMDI composites has been established.

CHAPTER 7

WOOD/¹⁵N-pMDI COMPOSITES VS. PRECURE MOISTURE CONTENT-----

7.1. INTRODUCTION

One of the primary variables in consolidating wood-based composites is the precure moisture content of the wood furnish. While pMDI resins have been demonstrated to possess greater flexibility in the furnish moisture content than PF resins [2,5-14], it is still an important consideration. Studies have shown that pMDI-bonded waferboard [2,10,13,14], hardboard [6,7], and medium density fiberboard [11,12] can be consolidated with excellent properties using 10-12% wood moisture content. In fact, Johns et al. [11] noted that internal bond strengths of pMDI-bonded MDF are not sufficiently high when cured below 10% mat moisture content. Since the internal bond strength is a good indication of adhesion, this conclusion speaks directly to the curing behavior of pMDI in different moisture level environments. In fact, the macroscopic properties of a composite material in general are often directly associated to the microscopic properties of the cured resin system.

As discussed earlier, isocyanates react readily with water to form ureas. These ureas may undergo varying degrees of further reaction with residual isocyanate to form biuret and polyuret type structures. The exact nature of the isocyanate/water reaction will therefore affect the cure chemistry, and as a result, the adhesive mechanism of pMDI-bonded wood composites. This in turn could affect the macroscopic performance

of the composite which is of great interest to the board manufacturer. It is certainly expected that the precure wood moisture content plays an important role in the extent and nature of the isocyanate/water reaction. As such, it is of great interest when studying the cure behavior of pMDI-bonded wood composites.

7.2. RESULTS AND DISCUSSION

7.2.1. Effect of Moisture on Cure Chemistry

A series of wood/¹⁵N-pMDI composites were made using precure moisture contents of 0%, 4.5%, 8%, 12%, 15%, and 31%. The composites, consisting of two wood flakes with 17 wt. % resin sandwiched between, were cured at 50 psi platen pressure and 120°C for 60 minutes. Figure 11 displays the ¹⁵N CP/MAS NMR spectra of these composites as a function of moisture content. The composite that was cured at 15% moisture was eliminated from Figure 11 for space considerations since it was identical in appearance to the composite cured at 12%. As in the cellulose composites, there are four major resonances in the spectra: residual isocyanate (44 ppm), polyurea (104 ppm), and the amide (111 ppm) and imide (138 ppm) nitrogens of a biuret type network. Some residual amine is also noted as a shoulder on the isocyanate resonance at 52 ppm, especially in the composites cured above 12% moisture. Also present is the unknown resonance at 130 ppm that was present in the cellulose composites. However, in the wood composites this resonance is noticeable at all of the precure moisture levels. Recall that for the cellulose composites it had its greatest intensity at 2% and then visibly

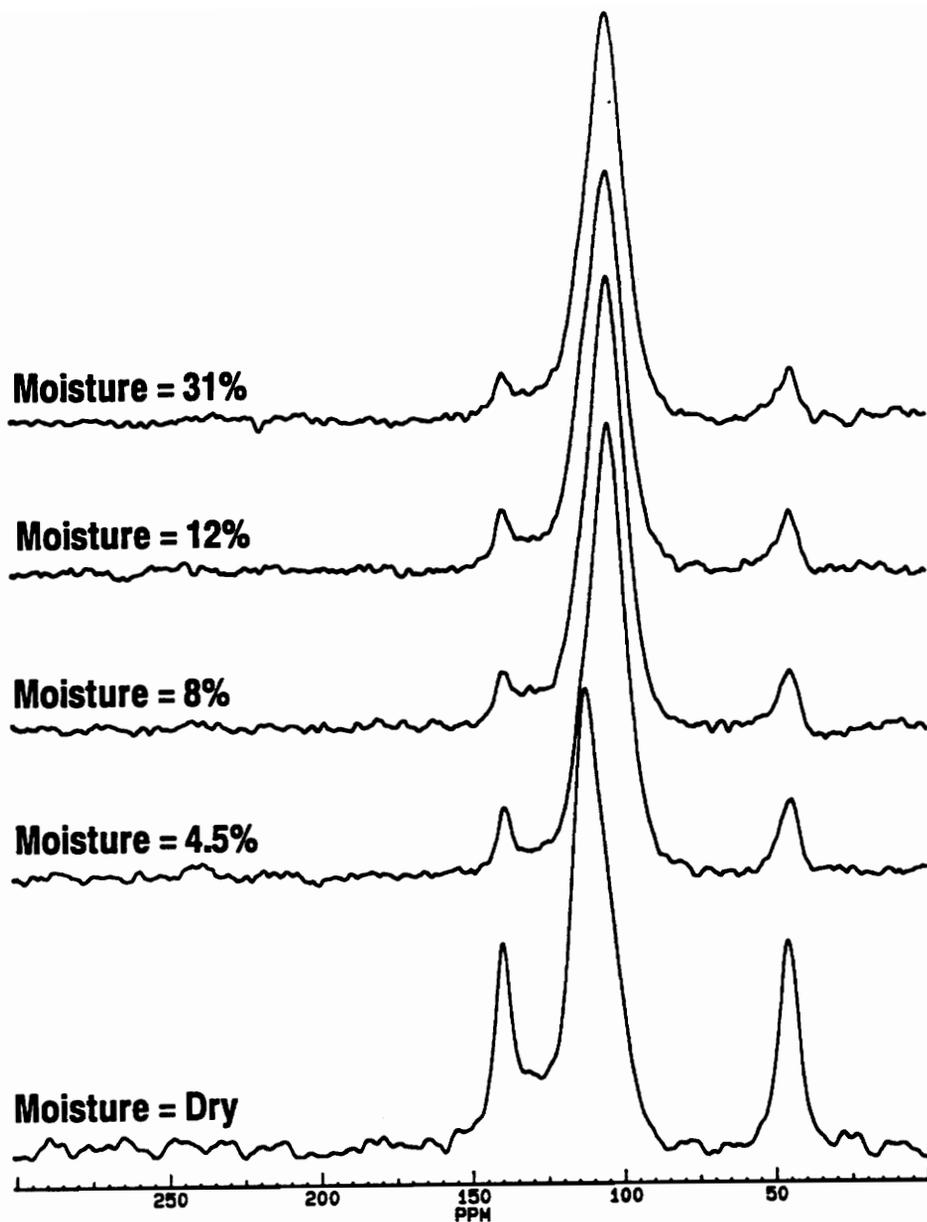


Figure 11: ^{15}N CP/MAS NMR spectra of solid wood/ ^{15}N -pMDI composites as a function of wood precure moisture content. Contact time is 2 msec and spectra are referenced to ^{15}N -glycine at 31 ppm.

decreased at the higher moisture contents.

Once again, the dominance of water on the cure chemistry is evidenced in the spectra. The significant amount of biuret formation in the composite cured "dry", as evidenced by the intense amide and imide resonances, clearly demonstrates the difficulty of achieving and maintaining complete dryness in wood. The composite was made with flakes taken directly from the oven after drying at $103 \pm 2^\circ\text{C}$ for 24 hours and then applying the resin quickly in the open atmosphere. The total time in which the flakes were exposed to the atmosphere is estimated to be 3-5 minutes. Yet this small amount of moisture that was taken up by the flakes during that time was enough to completely dominate the cure reactions. The isocyanate reacted first with the available moisture to form polyurea. When the water was consumed, some of the excess isocyanate reacted with these polyureas to form various biuret type structures. Some residual polyurea remains in the bondline as evidenced by the shoulder on the amide nitrogen resonance at 104 ppm. There is also a large amount of residual isocyanate. When moisture is present at 4.5% or more, the cure is dominated by the isocyanate/water reaction. The primary reaction product is clearly polyurea, with significantly less biuret formation and residual isocyanate. As mentioned earlier, it is likely the great excess of water molecules in these composites and perhaps to some extent their greater mobility compared to the polyurea molecules which leads to less biuret formation. An interesting observation is that the cure chemistry does not visibly change beyond 4.5% moisture (roughly a 400% excess of water over -NCO groups), not even when cured as high as 31%. There does

appear to be slightly more residual amine at the high precure moistures, but the levels of biuret formation, and most interestingly, residual isocyanate do not appear to decrease any further. It may be that upon significant formation of polyurea and biuret structures a certain amount of isocyanate becomes "trapped" inside the network in locations that are inaccessible to further reaction.

The corrected relative intensity values calculated for each composite support the trends discussed above (Table 4 and Figure 12). Recall, however, that these values can only be used in a qualitative manner for CP variable contact time experiments. This is because of the artificial inflation of the $T_{1\rho H}$ for nonprotonated nitrogens due to an interaction between cross-polarization and rotating-frame relaxation processes. This issue was thoroughly addressed in the discussion of cellulose composites (Section 6.2.2, pages 67-69). The composite cured "dry" has significant amounts of residual isocyanate and imide nitrogens as a percentage of the total composition. The large concentration of imide nitrogens confirms that significant biuret formation occurred in this composite. When the precure moisture is increased to 4.5%, there is a drastic increase in the polyurea concentration along with accompanying decreases in imide and residual isocyanate. Consistent with the earlier observation that the cure chemistry did not change beyond 4.5% are the relatively flat slopes in Figure 12 beyond this MC. Indeed, it does not appear that additional moisture has a major effect on the cure chemistry of pMDI-bonded wood composites beyond a certain moisture level. Furthermore, it appears that this MC is well within the realm of those commonly used in the processing of wood

Table 4: Effect of Moisture Content on the Relaxation Parameters and Relative Intensity of Major Peaks for ¹⁵N-Enriched pMDI/Solid Wood Composites.^a

Moisture (%)	Peak ^b (ppm)	T _{NH} ^c (ms)	T _{1ρH} ^c (ms)	I*/I(4 ms)	Rel Int (I), %	
					uncorr	corr ^d
Dry ^e	44	2.8	17.4	1.56	33.0	31.2
	104	---	---	---	---	---
	111	0.10	5.8	1.91	35.4	39.8
	138	2.4	9.4	1.61	31.6	29.0
4.5	44	3.4	11.7	2.03	19.7	17.1
	104	0.11	5.3	2.05	62.8	64.9
	111	---	---	---	---	---
	138	3.7	6.6	1.72	17.5	17.9
7.6	44	6.6	6.5	2.50	18.2	20.7
	104	0.18	4.7	2.28	67.7	64.5
	111	---	---	---	---	---
	138	4.8	6.3	2.71	14.1	14.8
11.5	44	3.1	14.9	1.60	17.6	14.5
	104	0.10	5.3	2.07	64.8	70.7
	111	---	---	---	---	---
	138	2.8	9.8	1.57	17.6	14.8
15.0	44	6.8	6.7	1.62	15.2	19.8
	104	0.09	5.0	2.21	69.8	69.2
	111	---	---	---	---	---
	138	2.6	9.3	2.90	15.1	11.0
31.1	44	6.6	6.4	2.72	15.9	20.0
	104	0.09	4.9	2.21	69.5	63.5
	111	---	---	---	---	---
	138	5.7	5.6	3.06	14.6	16.5

^a Cured at 17 wt. % resin, 50 psi, and 120°C for 60 minutes.

^b Chemical shifts of ¹⁵N resonances referenced to glycine at 31 ppm.

^c The mean error is ±15% for T_{NH} values and ±16% for T_{1ρH} values.

^d Calculated from the corrected peak intensities at a contact time of 4 msec.

^e Dried at 103±2°C for 48 hours. Note some moisture is still present.

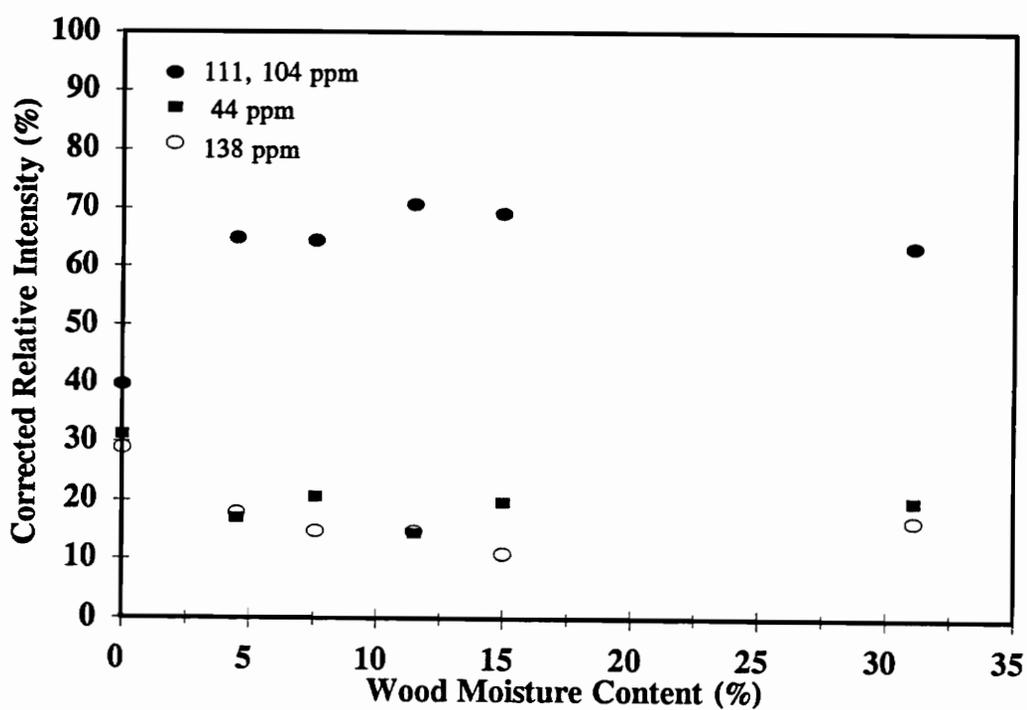


Figure 12: The corrected relative intensity, or percent composition, of the major chemical moieties present in the bondline of wood/¹⁵N-pMDI composites cured as a function of wood precure moisture content.

composite boards using pMDI resin.

As with the cellulose composites discussed earlier, there is not a clear indication of urethane formation in any of the samples. Even the composite that was cured "dry" was dominated by the small amount of moisture that was present. An increase in the breadth of the amide/urea resonance on the righthand side can be an indication of urethane formation, but this is not apparent in any of the composites. As a result, it was assumed that urethane formation did not take place to any significant extent. A catalyst was employed once again to force the isocyanate/wood reaction so that a wood-containing urethane resonance could be obtained for comparison. The first attempt to force the reaction used 1% stannous octoate catalyst on a composite that was cured dry. The spectrum for this composite is very similar to the one that had been cured at 4.5% moisture, perhaps indicating that water had dominated the cure (Figure 13). There is not even a small shoulder visible on the urea nitrogen resonance where the urethane peak would be overlapped. As a result, it was once again assumed that no urethane formation had occurred even when the catalyst was employed.

A second attempt was made to force the isocyanate/wood reaction so that a urethane resonance could be obtained for comparison. Phenylmercuric acetate, a catalyst that has been shown to be very effective in promoting the isocyanate/hydroxyl reaction (even secondary hydroxyls) in urethane systems while blocking the isocyanate/water reaction [69], was used in the second attempt. The catalyzed flakes were dried for 36 hours at 40°C and about 1 mm Hg, then removed to an argon atmosphere under which the resin

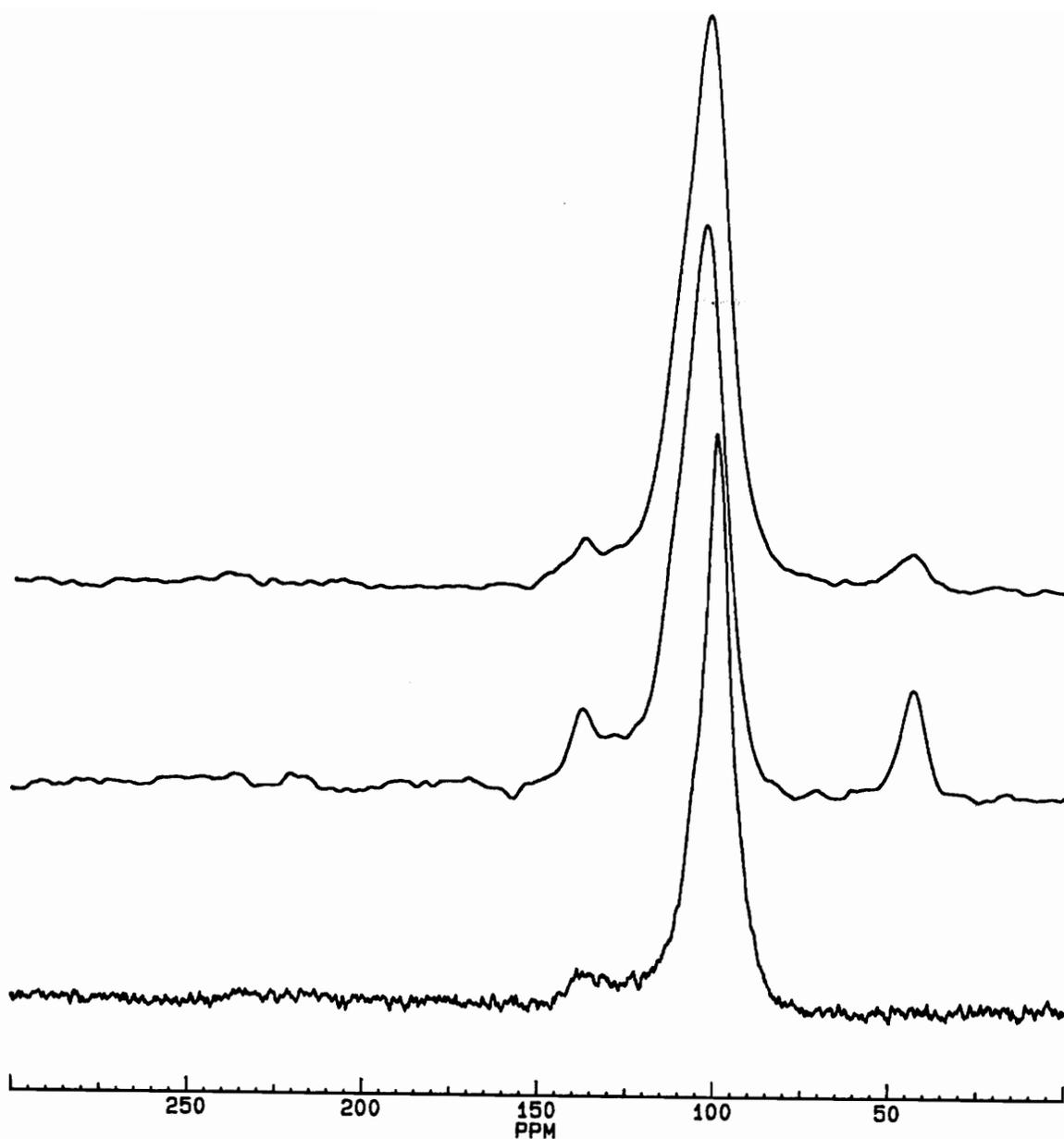


Figure 13: ^{15}N CP/MAS NMR spectra of a wood/ ^{15}N -pMDI composite cured at 4.5% moisture (top), wood/ ^{15}N -pMDI composite cured dry with 1% stannous octoate (middle), and the urethane product from reaction of ^{15}N -pMDI with dry methanol (bottom).

was applied. Furthermore, 10% catalyst was used this time since the only objective was to force a urethane bond and not to test feasible catalyst systems for these composites. The ^{15}N CP/MAS spectrum of this composite shows a resonance centered at 103 ppm (Figure 14), identified as the urethane signal. Also shown for comparison in Figure 14 is the composite that was cured at 4.5% moisture. Note that there is only a very small difference between the two spectra. Even though the urethane resonance appears at a slightly lower chemical shift, it is evident that very large amounts would have to be present before it would be noticeable in the spectrum. As a result, it is concluded that the urea and urethane resonances in wood/ ^{15}N -pMDI composites are simply not resolved well enough to detect moderate or low levels of urethane formation.

7.2.2. Effect of Moisture on Bondline Morphology

The ratio of amide to imide nitrogens from Table 4 provides qualitative information about the crosslink density of biuret structures. The data can only be viewed qualitatively since it is calculated from the corrected relative intensities, which in turn are determined using the $T_{1\rho\text{H}}$. As discussed in the previous Chapter (see pages 67-69), the $T_{1\rho\text{H}}$ values of nonprotonated nitrogens from CP variable contact time experiments are artificially high.

Recall that biurets form when an isocyanate group reacts at one of the active hydrogen sites of a urea. The resulting biuret can also react with isocyanate at either of its active amide hydrogens to form a triuret, and so on. From the corrected relative

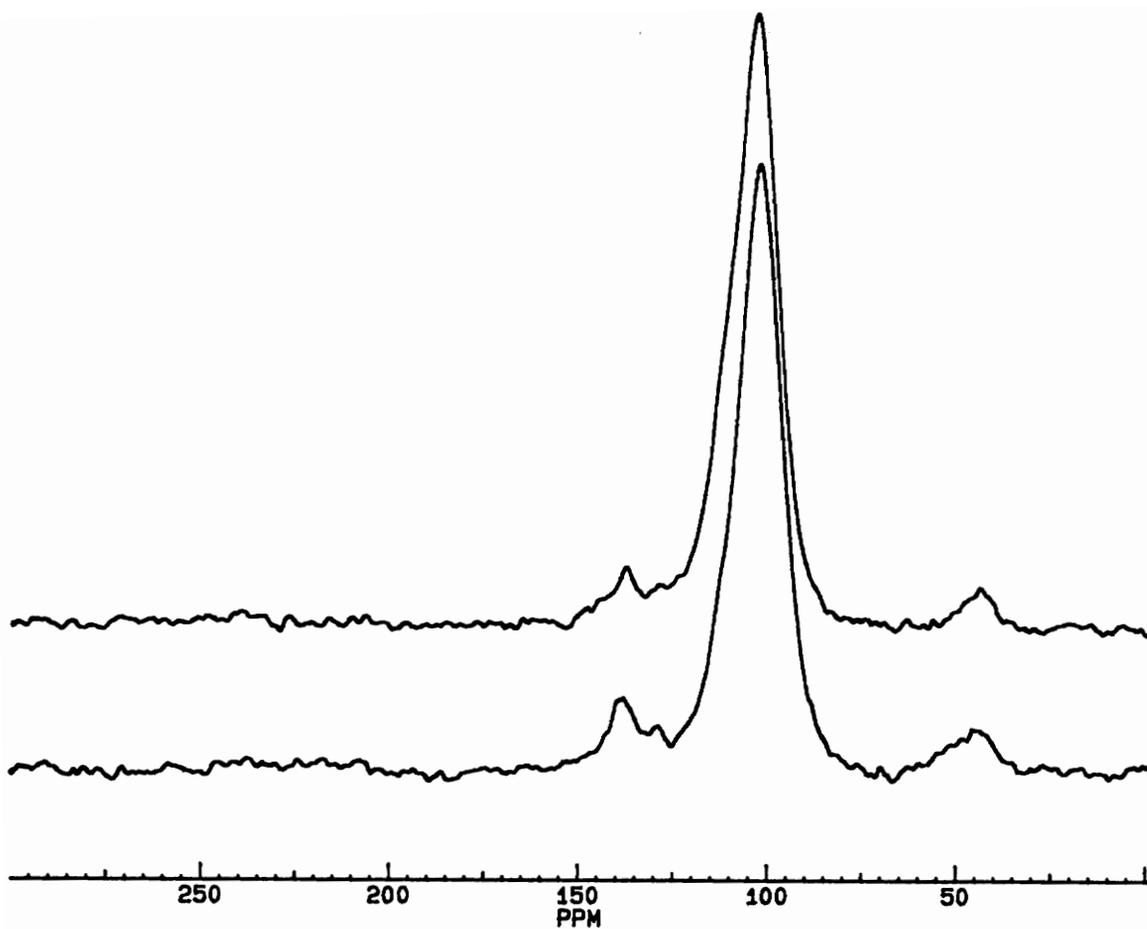


Figure 14: ^{15}N CP/MAS NMR spectra of a wood/ ^{15}N -pMDI composite cured at 4.5% moisture (top) and a wood/ ^{15}N -pMDI composite cured dry with 9.5% phenylmercuric acetate (bottom).

intensities in Table 4, the ratio of amide/imide nitrogens is 1.37 for the composite cured dry (this information is available only for the composite cured dry, where the amide peak is well resolved). Theoretical limits for this ratio are 2.0 for a perfect biuret and 0 for an infinite molecular weight polyuret in which all amide functionalities have reacted with isocyanate to leave only imide nitrogens. A ratio of 1.37 indicates that the cured resin is quite highly crosslinked, having a significant amount of polyuret character. The composite had very little water present when it was cured. It seems likely that the isocyanate reacted first with the available water to form polyurea. When the water was consumed, such a large excess of unreacted isocyanate remained that it reacted with much of the polyurea and then with many of the subsequent amide hydrogen sites of the biuret. Although no proof is given, it is expected that less polyuret formation occurs at the higher precure moisture contents.

The effect of precure wood moisture content on the $T_{1\rho H}$ relaxation parameter (calculated from CP variable contact time experiments) is shown in Figure 15. As noted earlier in the cellulose composites, the combined urea/amide relaxation rate is rapid and unchanging over the moisture range. Unfortunately, there is some scatter in the data for the isocyanate (44 ppm) and imide (138 ppm) nitrogens. Even with the scatter, it appears that there is a downward trend in the $T_{1\rho H}$ for residual isocyanate with increasing precure moisture. In fact, with the exception of the sample cured at 11.5%, it appears that the $T_{1\rho H}$ decreases rapidly from dry to 7.6% and then remains relatively constant at the higher moisture contents. Ordinarily, a change in the $T_{1\rho H}$ as such would indicate a

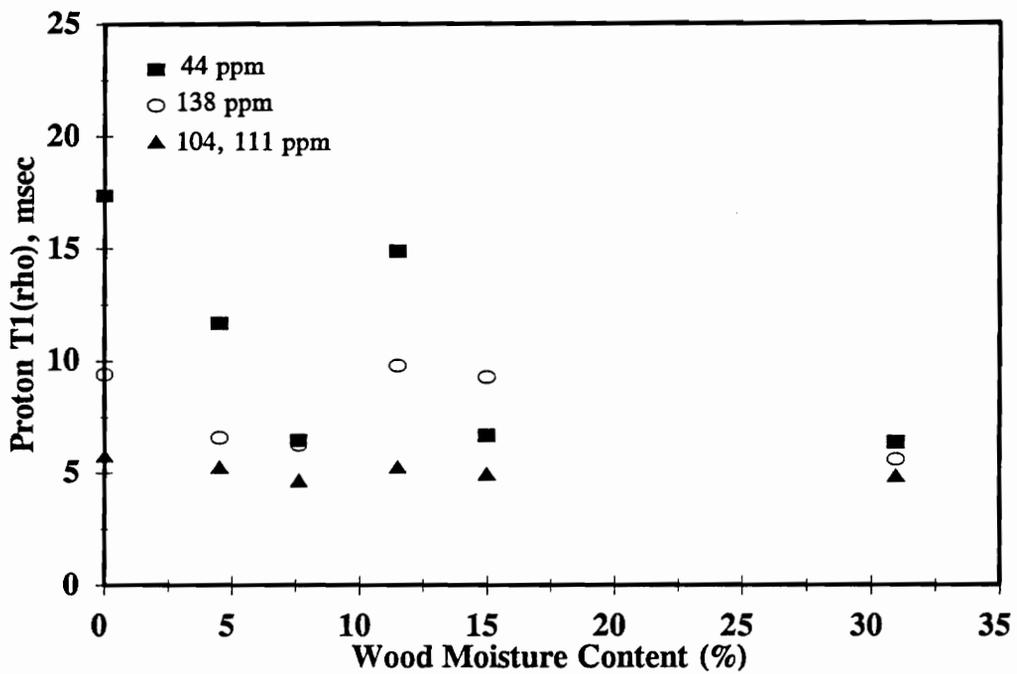


Figure 15: $T_{1\rho H}$ values calculated from cross-polarization variable contact time experiments for chemical moieties present in the bondline of wood/ ^{15}N -pMDI composites. versus wood precure moisture. Mean error for these values is $\pm 16\%$.

change in the kHz frequency molecular motions over this moisture range. In addition, the wide range in $T_{1\rho H}$ values observed for the different moieties in most of the composites would typically be evidence of phase separation. This behavior is particularly noticeable in the composites that were cured dry and at 11.5% moisture. However, recall from the discussion in Chapter 6 that this is not likely the true character of the resin since variable contact time experiments produce artificially high values of $T_{1\rho H}$ for nonprotonated nitrogens.

The interaction of cross-polarization and rotating-frame relaxation processes (responsible for the artificial inflation of nonprotonated $T_{1\rho H}$ values) can be avoided by altering the pulse sequence to include a variable spin lock period prior to the fixed contact time. Table 5 shows the $T_{1\rho H}$ values measured from variable spin lock experiments for the composites that were cured dry and at 31% moisture. These two composites were chosen because they represent the extreme values in $T_{1\rho H}$ obtained for the isocyanate peak by variable contact time experiments. Time prevented the analysis of all composites, but this will be the subject of future work. The data in Table 5 show that all nitrogen species in both composites are relaxing very rapidly with similar $T_{1\rho H}$ values. The conclusions drawn from these experiments are that the cured resin is probably not phase separated and that the molecular motion of residual isocyanate does not change over the range in moisture.

Table 5: $T_{1\rho H}$ Values Measured Using a Variable Spin Lock Period Prior to a Fixed Contact Time^a for Several Wood/¹⁵N-pMDI Composites.

Precure Moisture Content	¹⁵ N Resonance ^b		
	44 ppm	104/111 ppm	138 ppm
Dry ^c	3.7 ^d	4.1 (111 ppm)	4.0
31%	3.4	3.3 (104 ppm)	3.5

^a A contact time of 5 msec was used for these experiments.

^b Chemical shifts of ¹⁵N resonances referenced to glycine at 31 ppm.

^c Composites were cured at 17 wt. % resin, 120°C, and 50 psi platen pressure for 60 minutes.

^d All $T_{1\rho H}$ measurements are listed in msec. Mean error of these values is $\pm 5\%$.

7.2.3. Characterization Using FTIR

The wood/¹⁵N-pMDI composites were analyzed by FTIR. The surprising result is that the spectra are very similar to one another regardless of precure moisture content (Figure 16). In fact, there is not even a distinguishable difference between the composite that was cured dry and the one that was cured at 31% moisture. The only spectrum that is different from the others in any way is the composite cured at 7.6%, which has increased intensity for most of the major absorbances. The observation from FTIR that the cure chemistry does not significantly change beyond 4.5% is in agreement with the ¹⁵N CP/MAS results, but it is interesting that the composite cured dry is not noticeably different. Certainly there must be differences in the isocyanate cure chemistry between a composite that is cured at saturation (31% MC) versus one that is cured dry.

The other observation is that there is no indication of urethane formation in any of the composites. Figure 17 displays the FTIR spectrum of the composite that was cured dry along with that of the model urethane product from reaction of ¹⁵N-pMDI with dry methanol. There is no distinguishable absorbance at 1701 cm⁻¹ in the spectrum of the composite cured dry that would correspond to the urethane carbonyl stretch. This confirms the results from ¹⁵N CP/MAS that urethane formation in these composites is likely minimal, if occurring at all.

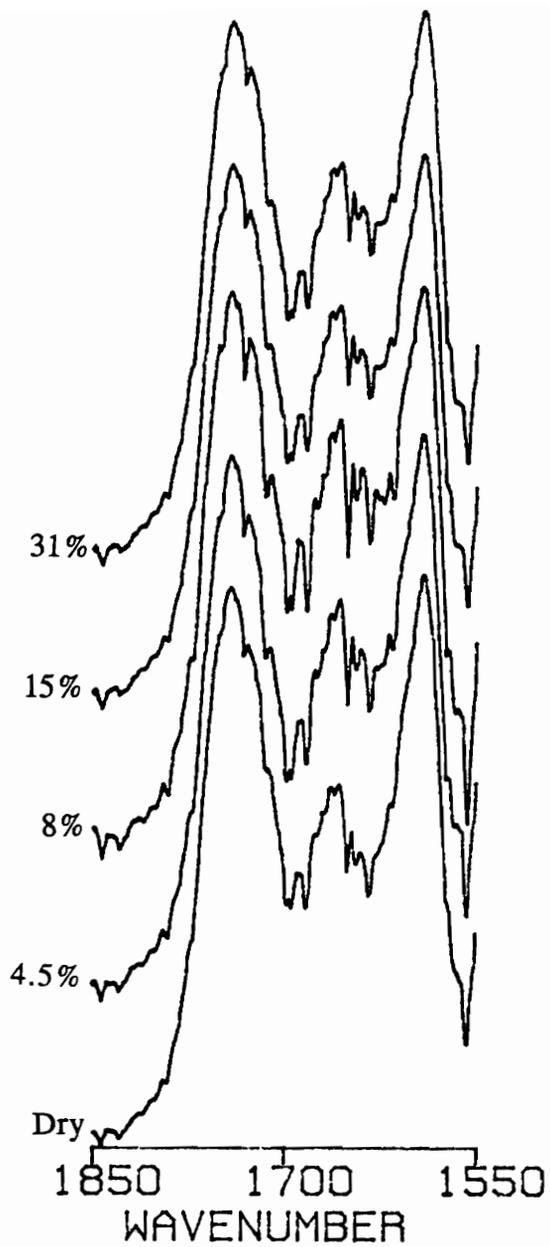


Figure 16: FTIR of wood/¹⁵N-pMDI composites cured as a function of wood precure moisture content, expanded to show carbonyl region.

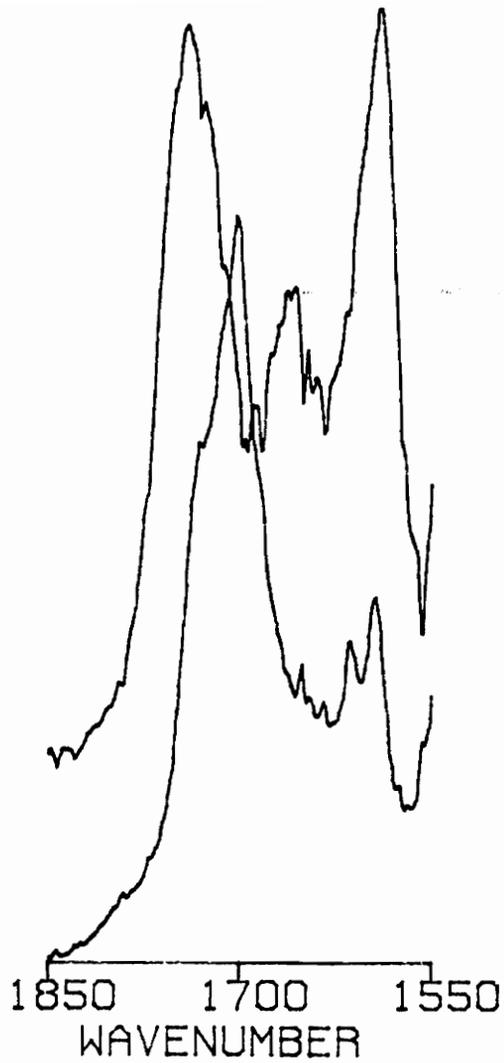


Figure 17: FTIR of a wood/¹⁵N-pMDI composite cured dry (top) and the urethane product from reaction of ¹⁵N-pMDI with dry methanol (bottom), expanded to show the carbonyl region.

7.3. CONCLUSIONS

A series of solid wood/¹⁵N-pMDI composites were cured as a function of the wood precure moisture content. The dominance of the isocyanate/water reaction on the cure chemistry is clearly demonstrated by ¹⁵N CP/MAS NMR. Unlike dry cellulose papers, dry wood flakes did bond together, although the ¹⁵N spectrum indicates that it was still water that dominated the cure reaction. The spectrum for this composite shows prominent amide (111 ppm) and imide (138 ppm) resonances, indicating that significant biuret formation took place. When the moisture content is increased to 4.5% or beyond, the chemistry becomes overwhelmingly polyurea type structures. There does not appear to be much change in the cure chemistry between 4.5% and 31% precure moisture content, even in the concentration of residual isocyanate. Also present in the ¹⁵N CP/MAS spectra is evidence of residual amine (52 ppm) and also the unknown resonance at 130 ppm.

It does not appear that urethane formation can be detected in wood/¹⁵N-pMDI composites using ¹⁵N CP/MAS NMR. The urethane resonance is located at 103 ppm according to a composite that was cured dry with 9.5% phenylmercuric acetate catalyst. This resonance is simply not well enough resolved from the urea resonance for it to be detected unless urethane is present in quantities similar to the urea.

Variable contact time experiments were once again demonstrated to produce artificially high $T_{1\rho H}$ values for nonprotonated nitrogens. A more direct measurement of the $T_{1\rho H}$ was obtained from variable spin lock experiments on the composites that were

cured dry and at 31% moisture. The results show very fast $T_{1\rho H}$ relaxation rates of about 3.5-4 msec for all nitrogens in both composites. This indicates that the cured resin is probably a homogeneous continuum and that the molecular mobility of the different chemical moieties likely remains unchanged over the moisture range studies here.

CHAPTER 8

WOOD/¹⁵N-pMDI COMPOSITES VS. CURE TEMPERATURE-----

8.1. INTRODUCTION

The cure temperature is an important press variable that contributes to the cure behavior of a wood adhesive. This temperature is typically controlled through the platen temperature of the press. Numerous studies have evaluated the mechanical and physical properties of pMDI-bonded wood composites with press temperature being a key variable [10-12,16]. Johns et al. [11] noted poor internal bond strengths for pMDI-bonded MDF when consolidated at 300°F with a fast press closing rate. However, increasing the press temperature to 330°F caused a significant increase in the internal bond strength. Since the internal bond is a good indication of adhesion, it was concluded that the low values at 300°F were due to insufficient cure. This chapter describes a set of experiments that were performed to characterize the pMDI/wood cure behavior as a function of the press temperature.

8.2. RESULTS AND DISCUSSION

8.2.1. Effect of Temperature on Cure Chemistry

A series of composites were made using five different press temperatures: 120°, 140°, 159°, 172°, and 185°C. These temperatures were chosen because they are similar to those reported by Chelak and Newman [13] for the commercial production of pMDI-

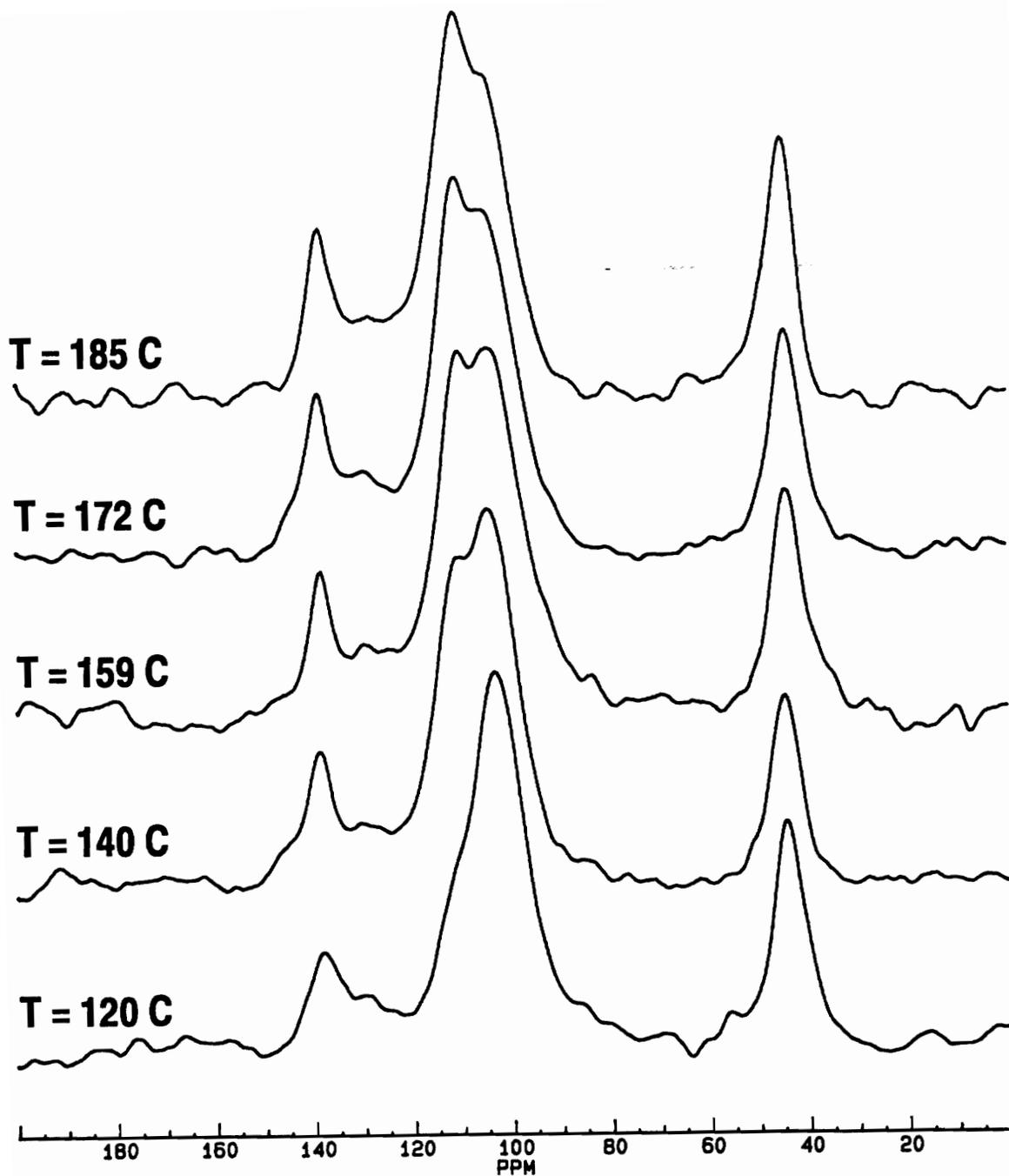


Figure 18: ^{15}N CP/MAS NMR spectra of wood/ ^{15}N -pMDI composites cured as a function of press temperature. Contact time is 2 msec and spectra are referenced to ^{15}N -glycine at 31 ppm.

bonded OSB. These authors made 4 ft. × 8 ft. OSB panels using a platen temperature of 365°F (185°C) and a target core temperature of 240°F (116°C). Since the composites made in this study consist of only two very thin flakes, heat transfer through the composite is not a consideration. The desired cure temperature for the resin is therefore dictated easily by the press temperature. In addition, a more realistic cure time of 140 seconds was used to make these composites [13]. A precure moisture content of 4.5-5% was used because that was the EMC at room conditions, making replication easy with little variability. It is reasonable to assume, then, that the results of this experiment could provide a cure chemistry profile throughout the thickness of a 100% pMDI-bonded OSB panel.

The ¹⁵N CP/MAS spectra for these composites indicate that the effect of press temperature on pMDI cure chemistry is quite significant (Figure 18). At low cure temperatures such as those characteristic of an OSB target core temperature (120°C), the cure is governed primarily by polyurea formation. There is some biuret formation at this temperature as evidenced by the small imide resonance and the amide nitrogen shoulder at 111 ppm. A very clear transition from polyurea to primarily biuret type structures occurs with increasing cure temperature. At 140°C the amide nitrogen resonance is a very discernible shoulder on the urea resonance, while increasing the cure temperature to 159°C results in a nearly equivalent concentration of urea and amide nitrogens. Temperatures greater than 159°C, which are characteristic in the face layers during the pressing of pMDI-bonded OSB, result in primarily biuret formation as evidenced by the

Table 6: Effect of Press Temperature on the Relaxation Parameters and Relative Intensity of Major Peaks for ¹⁵N-Enriched pMDI/Solid Wood Composites.^a

Cure Temp. (°C)	Peak ^b (ppm)	T _{NH} ^c (ms)	T _{1ρH} ^c (ms)	I*/I(4 ms)	Rel Int (I), %	
					uncorr	corr ^d
120	44	2.2	13.5	1.48	49.6	37.4
	104	0.12	4.2	2.85	31.1	47.5
	111	---	---	---	---	---
	138	2.2	8.5	1.41	19.2	15.2
140	44	2.9	15.5	1.27	41.2	36.8
	104	0.18	5.1	2.12	37.1	46.7
	111	---	---	---	---	---
	138	1.4	12.5	1.50	21.8	16.5
159	44	2.3	16.1	1.51	42.4	34.1
	104	0.10	4.3	2.31	33.8	45.2
	111	---	---	---	---	---
	138	2.1	8.7	1.39	23.7	20.7
172	44	2.7	13.8	1.56	43.4	34.7
	104	---	---	---	---	---
	111	0.11	4.3	2.65	31.6	44.5
	138	1.8	8.7	1.50	25.0	20.8
185	44	3.4	8.3	1.76	45.6	41.3
	104	---	---	---	---	---
	111	0.11	4.1	2.71	29.3	37.7
	138	2.2	6.2	1.91	25.1	20.9

^a Cured at ~5% wood moisture, 17 wt. % resin, 50 psi for 140 seconds.

^b Chemical shifts of ¹⁵N resonances referenced to glycine at 31 ppm.

^c The mean error is ±11% for both T_{NH} and T_{1ρH} values.

^d Calculated from the corrected peak intensities at a contact time of 4 msec.

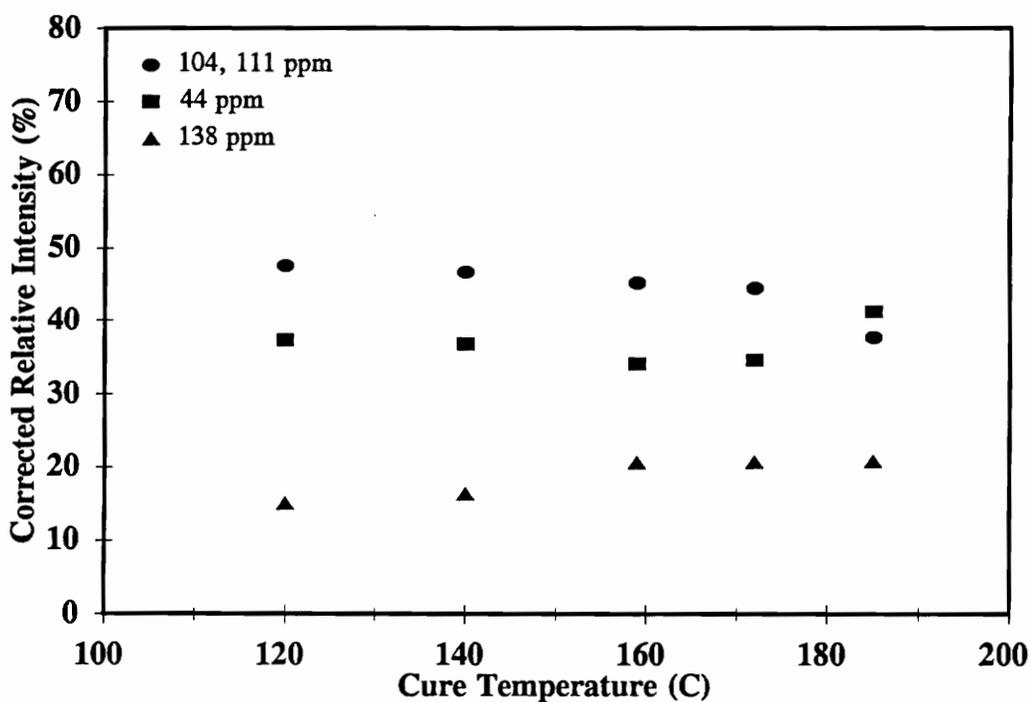


Figure 19: The corrected relative intensity, or percent composition, of the major chemical moieties present in the bondline of wood/¹⁵N-pMDI composites cured as a function of press temperature.

increased intensity of the imide and amide nitrogen resonances. These general trends in the cure chemistry are confirmed by the corrected relative intensity values (Table 6, Figure 19). With increasing cure temperature, a slight decrease in the combined urea/amide nitrogen concentration along with a corresponding increase in the imide concentration is noted. The concentration of residual isocyanate remains relatively constant over the temperature range. This is likely due to the large excess of isocyanate that was used (17 wt. % of the total composite weight) combined with the short press time. There does not appear to be significant residual amine in any of the composites. Note, however, that there is a small shoulder on the righthand side of the urea resonance in the composites that were cured at 159°C and 172°C. This could be an indication of urethane formation.

From this information, a cure chemistry profile can be obtained that may be applicable to the manufacture of OSB using pMDI resin. That profile would consist of primarily biuret type structures in the face layers where the temperature is highest, although a significant amount of polyurea would also remain. Some urethane formation might also be present in the outer layers. There appears to be a very uniform transition in the cure chemistry from the face layers to the core. That transition involves a reduction in the biuret formation, and instead, increasing amounts of residual polyurea. It appears that the lower core temperatures are not as conducive to the reaction of polyurea with residual isocyanate when using short press times. It may be that the higher temperatures are required to increase the isocyanate and/or polyurea reactivity.

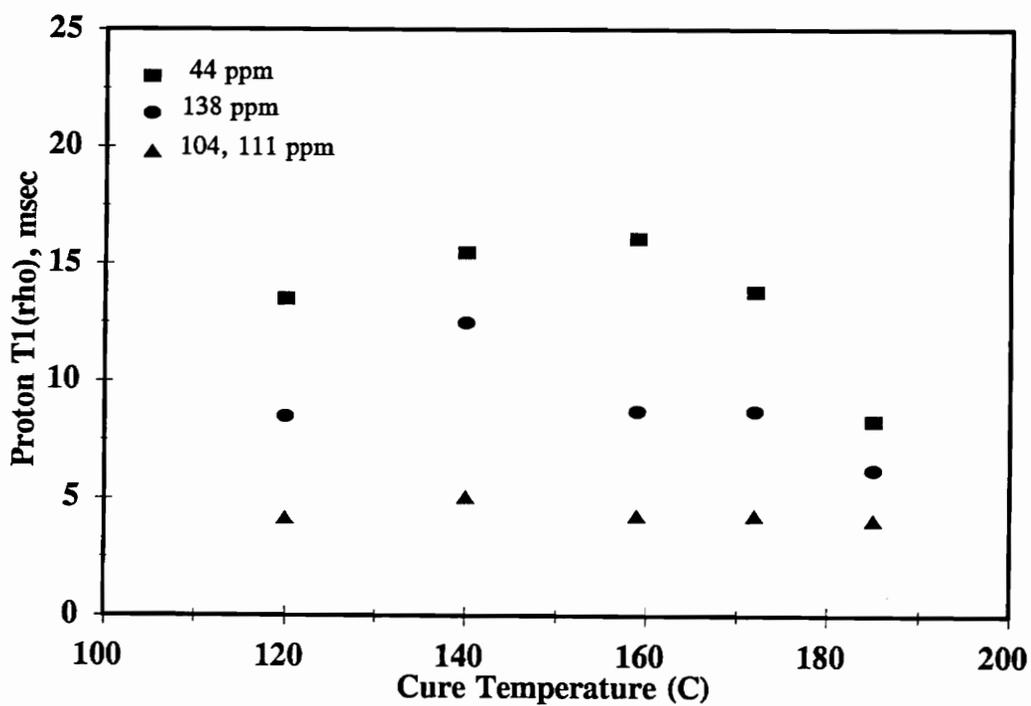


Figure 20: $T_{1\rho H}$ values calculated from cross-polarization variable contact time experiments for chemical moieties present in the bondline of wood/ ^{15}N -pMDI composites versus press temperature. Mean error for these values is $\pm 11\%$.

8.2.2. Effect of Temperature on Bondline Morphology

A measurement of the crosslink density could be obtained for the composites that were cured at 172°C and 185°C where the amide resonance is well resolved. The amide/imide nitrogen ratio was determined from the corrected relative intensities in Table 6 to be 2.14 at 172°C and 1.80 at 185°C. The ratio of 2.14 is actually greater than the theoretical upper limit of 2.0 for a perfect biuret system, but it is close enough to reasonably interpret it as 2.0. This indicates that the composite cured at 172°C is almost exclusively biuret in these regions with very little polyuret character. The composite cured at 185°C, on the other hand, may have slightly higher crosslink density through more extensive polyuret formation. Adding this information to the cure profile discussed above, it is possible that the crosslink density of the biuret type structures decreases from the high temperature outer face layers to the core.

Figure 20 displays the $T_{1\rho H}$ values obtained from cross-polarization variable contact time experiments as a function of the press temperature. Once again, conclusions cannot be made from these results because of the artificial inflation of nonprotonated nitrogen $T_{1\rho H}$ values. The composite amide/urea peak, which because of fast cross-polarization tends to be a good indication of the true relaxation rates, once again has fast and unchanging $T_{1\rho H}$ values over the temperature range. The data in Figure 20 would ordinarily be interpreted as a clear indication of phase separation into regions of isocyanate, urea, and biuret type structures. It would also provide interesting information regarding the molecular mobility of residual isocyanate as a function of temperature.

The parabolic shape of the $T_{1\rho H}$ values versus temperature would ordinarily be interpreted to mean that residual isocyanate has nearly the same molecular mobility in the face and the core, but that it changes throughout the intermediate temperatures. Imide nitrogens display a similar trend. However, it is very likely that these trends are simply the result of the artificially inflated $T_{1\rho H}$ values obtained from cross-polarization variable contact time experiments. Variable spin lock experiments have not been performed on these composites, but will be the subject of future work. Based on the previous results from cellulose and wood composites that were tested, as well as the amide/urea $T_{1\rho H}$ values in Figure 20, it is likely that the cured resin is a homogeneous continuum in these composites as well.

8.3. CONCLUSIONS

A series of solid wood/ ^{15}N -pMDI composites were cured using press variables characteristic of pMDI-bonded OSB manufacture as a function of cure temperature. The composites were cured at 4.5-5% moisture, 17 wt. % resin, and 50 psi platen pressure for 140 seconds. ^{15}N CP/MAS spectra indicate that at 120°C the cure chemistry is primarily polyurea type structures, with some biuret formation indicated by a small imide nitrogen resonance and the amide shoulder at 111 ppm. As the temperature is increased between 120°C and 185°C, a very clear transition occurs toward increasing amounts of biuret formation. At 159°C the urea and amide nitrogen concentration appears to be nearly equal, while at higher temperatures the amide peak is larger. There does not

appear to be significant residual amine in any of the composites, but there may be an indication of urethane formation in the composites cured at 159°C and 172°C. There is a very large amount of residual isocyanate in all of the composites, much of which will likely undergo postcure reactions with atmospheric moisture to form additional polyurea.

Variable spin lock experiments were not performed to more accurately determine the $T_{1\rho H}$ values of nonprotonated nitrogens. Based solely on the results from the previous two chapters, however, it is likely that the cured resin in these composites is also a homogeneous continuum.

CHAPTER 9

WOOD/¹⁵N-pMDI COMPOSITES VS. CURE TIME-----

9.1. INTRODUCTION

The length of time that an adhesive is allowed to cure will certainly affect the properties of the resultant bondline. In the manufacture of most wood composites, this cure time is usually the time that the composite panel remains in the press under elevated temperature and pressure. A balance must be met by the manufacturer between making a quality product (i.e., fully cured) and being cost effective. Certainly the goal is to make a high quality board in as short a press time as possible. pMDI has been shown to be capable of producing good board properties in relatively short press times compared to PF resins [2,10,13]. However, this does not mean that cure time is not an important consideration when using pMDI resins. Johns et al. [11] concluded that the difference between an uncured and a well cured bondline can be as little as 20 seconds for pMDI-bonded MDF.

This chapter details the results of two experiments that were performed to characterize the pMDI/wood cure behavior at different press times. Two composites were made at each cure time, one at a press temperature of 120°C and the other at 185°C. Both experiments were believed necessary since the cure behavior was found to be different at these two temperatures, as discussed in the previous chapter.

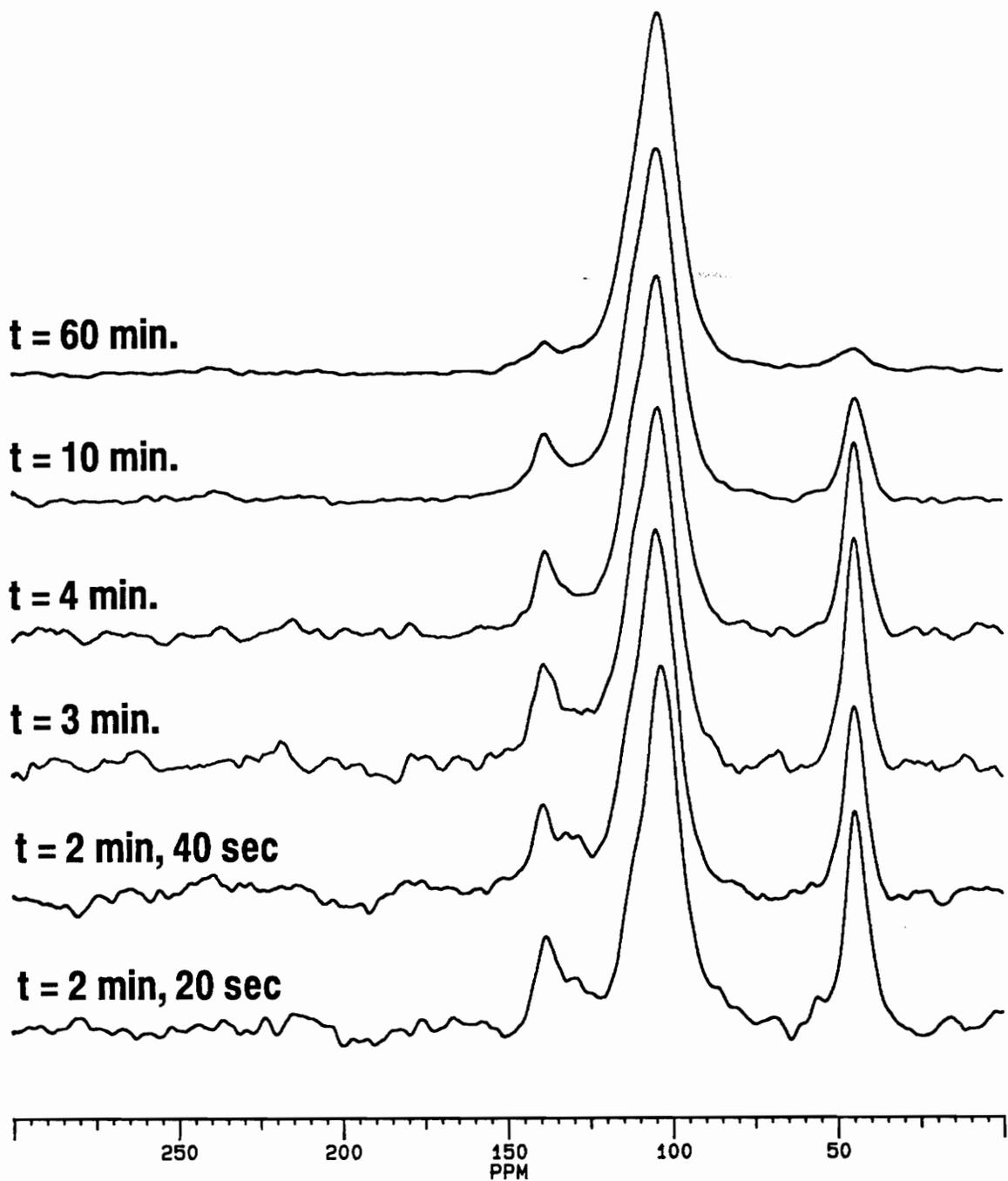


Figure 21: ^{15}N CP/MAS NMR spectra of wood/ ^{15}N -pMDI composites cured at 120°C as a function of press time. Contact time is 2 msec and spectra are referenced to ^{15}N -glycine at 31 ppm.

9.2. RESULTS AND DISCUSSION

9.2.1. Effect of Time on Cure Chemistry

Composites were made at six different press times: 140 sec., 160 sec., 3 min., 4 min., 10 min., and 60 minutes. The four fastest times were chosen since they are representative of those used for pressing various pMDI-bonded wood composites [1,6,12,13]. The longer two were chosen for comparison purposes. The cure time was taken as the length of time at which the composite remained under the full 50 psi of platen pressure.

The first set of composites was cured at 120°C. The ¹⁵N CP/MAS spectra of these composites show several clear trends in the cure chemistry, although most of the changes occur after the 4 minute press time (Figure 21). Very little change is noted for the composites cured between 140 seconds and 4 minutes. Each of these four composites has primarily polyurea formation, with lesser amounts of biuret type structures according to the intensity of the amide shoulder and the imide resonance. The amount of biuret formation does not appear to change very much over this range in time. They also have a very large amount of residual isocyanate which does not appear to significantly change over this range. The only noticeable difference in the chemistry of these four composites is seen in the unknown resonance at 130 ppm. This resonance appears most intense when cured for less than 3 minutes, then visibly decreases at each longer cure time. It is also clearly split into two resonances at the 160 second cure time. As mentioned earlier, this resonance displays a slow cross-polarization rate characteristic of

Table 7: Effect of Press Time on the Relaxation Parameters and Relative Intensity of Major Peaks for ¹⁵N-Enriched pMDI/Solid Wood Composites Cured at 120°C.^a

Press Time (min:sec)	Peak ^b (ppm)	T _{NH} ^c (ms)	T _{1ρH} ^c (ms)	I*/I(4 ms)	Rel Int (I), %	
					uncorr	corr ^d
2:20 ^e	44	2.2	13.5	1.48	49.6	37.4
	104	0.12	4.2	2.85	31.1	47.5
	111	---	---	---	---	---
	138	2.2	8.5	1.41	19.2	15.2
2:40	44	2.9	11.5	1.55	46.0	39.0
	104	0.15	4.4	2.62	36.4	48.0
	111	---	---	---	---	---
	138	1.7	11.1	1.60	17.6	13.0
3:00	44	2.9	11.9	1.45	46.0	40.7
	104	0.14	4.6	2.34	34.9	44.4
	111	---	---	---	---	---
	138	2.2	9.3	1.63	19.1	15.0
4:00	44	2.8	12.4	1.58	42.5	37.4
	104	0.16	5.1	2.14	41.3	48.6
	111	---	---	---	---	---
	138	2.2	9.9	1.60	16.2	14.0
10:00	44	3.3	10.4	1.44	29.5	28.0
	104	0.17	5.4	1.99	53.3	58.4
	111	---	---	---	---	---
	138	2.0	11.5	1.73	17.2	13.6
60:00	44	3.4	11.7	2.03	19.7	17.1
	104	0.11	5.3	2.05	62.8	64.9
	111	---	---	---	---	---
	138	3.7	6.6	1.72	17.5	17.9

^a Cured at ~5% wood moisture, 17 wt. % resin, 50 psi, and 120 °C.

^b Chemical shifts of ¹⁵N resonances referenced to glycine at 31 ppm.

^c The mean error is ±12% for both T_{NH} and T_{1ρH} values.

^d Calculated from the corrected peak intensities at a contact time of 4 msec.

^e Time the composite was exposed to the full 50 psi of pressure.

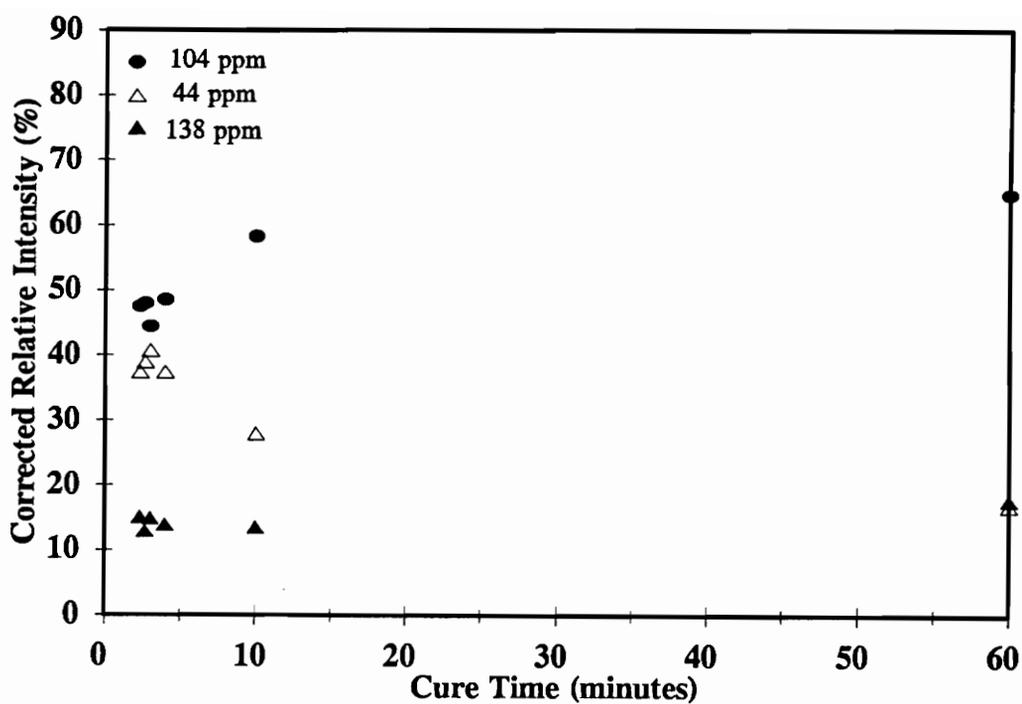


Figure 22: The corrected relative intensity, or percent composition, of the major chemical moieties present in the bondline of wood/¹⁵N-pMDI composites cured at 120°C as a function of press time.

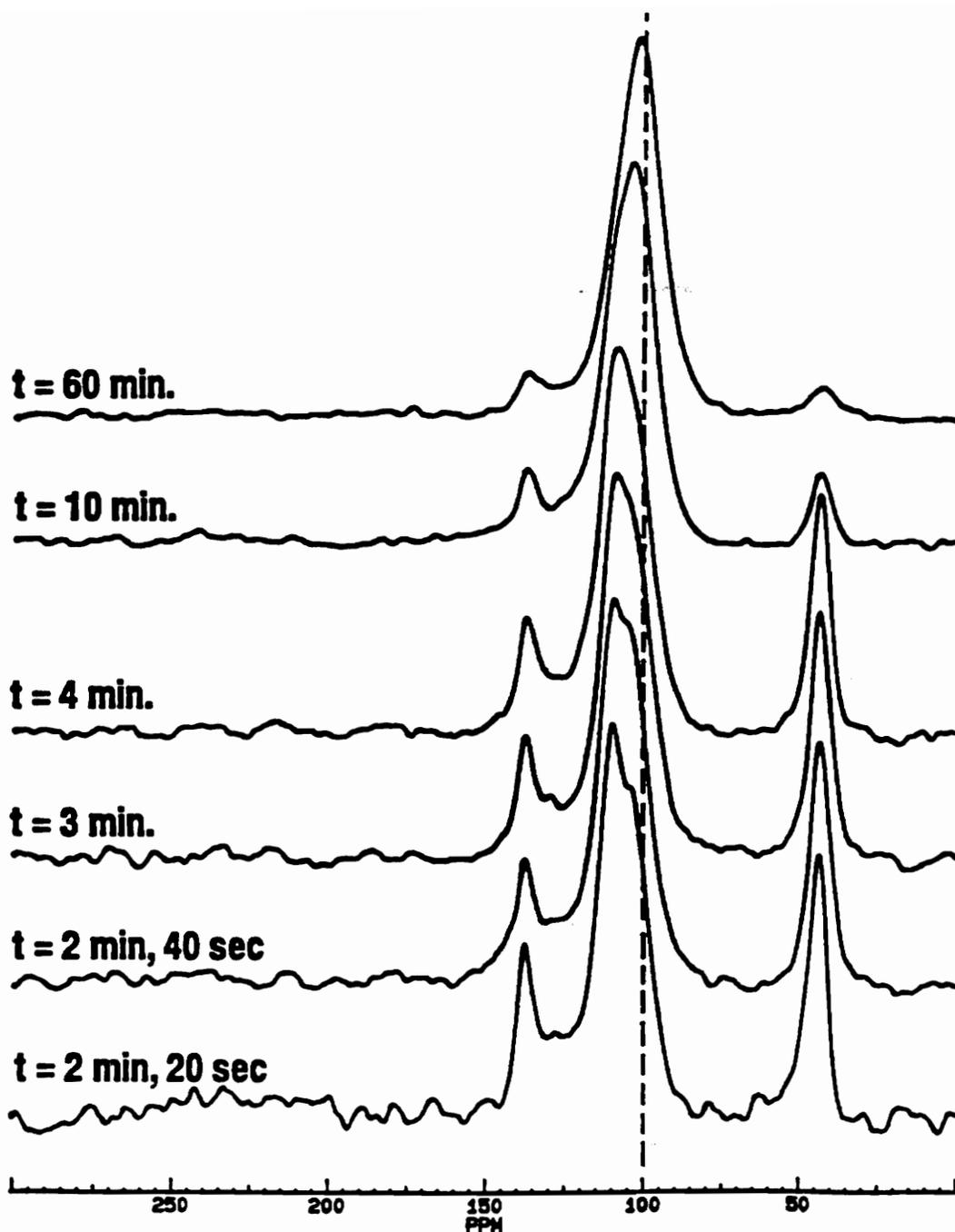


Figure 23: ^{15}N CP/MAS NMR spectra of wood/ ^{15}N -pMDI composites cured at 185°C as a function of press time. Contact time is 2 msec and spectra are referenced to ^{15}N -glycine at 31 ppm.

a nonprotonated species, but its identity has not been determined.

Other significant changes occur in the chemistry when cured for 10 min. and 60 minutes. The amide nitrogen resonance is visibly reduced, indicating that additional cure beyond 4 minutes seems to favor the formation of polyurea. It also appears from Figure 21 that there is a decrease in residual isocyanate and imide nitrogens after the longer cure times. However, note that the signal to noise ratio for these two spectra (10 and 60 minutes) is much greater than in the other spectra. As a result, direct comparisons of signal intensity cannot be made between them. Corrected relative intensity values support a reduction in residual isocyanate and a corresponding increase in polyurea, but indicate that the imide concentration is relatively unchanging (Table 7, Figure 22). Residual isocyanate makes up a large fraction of the cured resin composition up to 4 minutes of cure time, then reduces significantly after 10 minutes and again after 60 minutes. The imide nitrogen concentration remains relatively constant over the entire range of cure times examined, while polyurea increases after 4 minutes. This seems to indicate that the reduction in residual isocyanate at the longer cure times is primarily because of additional reaction with water rather than with polyurea which would form additional amide and imide nitrogens.

^{15}N CP/MAS of the composites that were cured at 185°C show the same general trends in the chemistry over press time as the composites cured at 120°C (Figure 23). The major difference between the two press temperatures is that at 185°C the cure is primarily biuret type structures at cure times of 4 minutes or less. Figure 23 shows a

Table 8: Effect of Press Time on the Relaxation Parameters and Relative Intensity of Major Peaks for ¹⁵N-Enriched pMDI/Solid Wood Composites Cured at 185°C.^a

Press Time (min:sec)	Peak ^b (ppm)	T _{NH} ^c (ms)	T _{1ρH} ^c (ms)	I*/I(4 ms)	Rel Int (I), %	
					uncorr	corr ^d
2:20 ^e	44	3.4	8.3	1.76	45.6	41.3
	104	---	---	---	---	---
	111	0.11	4.1	2.71	29.3	37.7
	138	2.2	6.2	1.91	25.1	20.9
2:40	44	2.5	11.3	1.76	43.0	37.6
	104	---	---	---	---	---
	111	0.14	5.4	1.98	36.1	41.1
	138	2.5	7.1	1.52	20.9	21.2
3:00	44	3.1	12.5	1.74	44.7	42.3
	104	---	---	---	---	---
	111	0.13	6.0	1.84	35.2	37.5
	138	2.9	8.3	1.64	20.1	20.2
4:00	44	3.0	13.4	1.78	43.8	41.6
	104	---	---	---	---	---
	111	0.16	6.6	1.75	37.0	38.2
	138	2.9	8.1	1.61	19.2	20.2
10:00	44	5.9	7.1	1.55	20.0	28.8
	104	0.15	6.4	1.76	61.4	56.1
	111	---	---	---	---	---
	138	2.1	10.0	2.78	18.6	15.0
60:00	44	2.9	16.9	1.72	8.3	8.1
	104	0.12	5.7	1.98	76.3	81.4
	111	---	---	---	---	---
	138	1.7	13.9	1.33	15.5	10.5

^a Cured at ~5% wood moisture, 17 wt. % resin, 50 psi, and 185 °C.

^b Chemical shifts of ¹⁵N resonances referenced to glycine at 31 ppm.

^c The mean error is ±13% for T_{NH} values and ±14% for T_{1ρH} values.

^d Calculated from the corrected peak intensities at a contact time of 4 msec.

^e Time the composite was exposed to the full 50 psi of pressure.

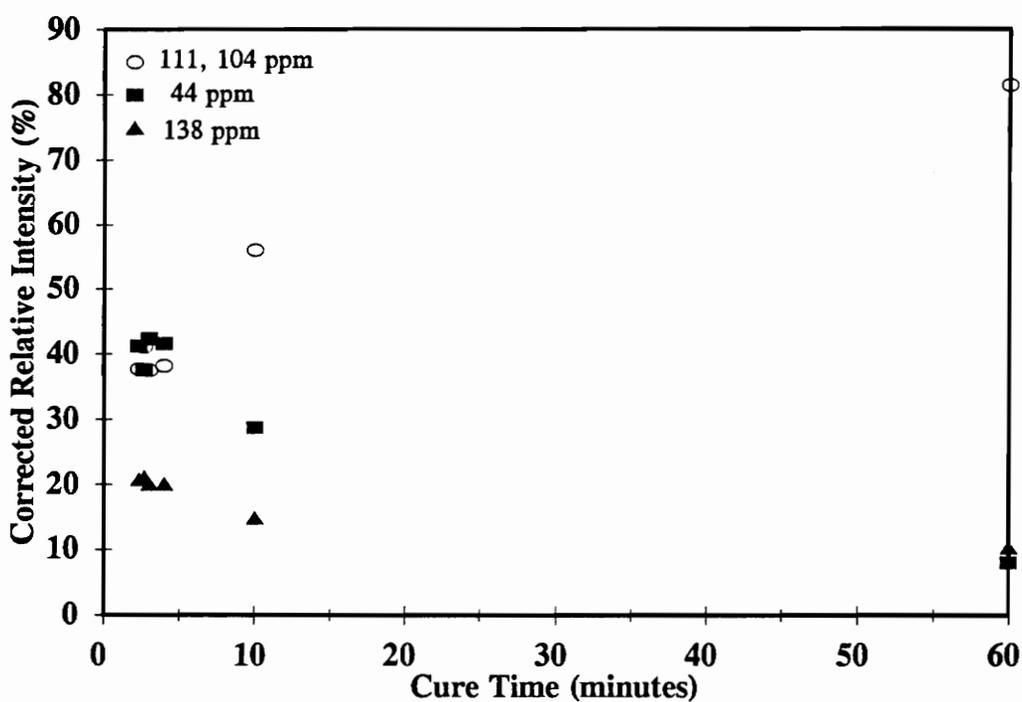


Figure 24: The corrected relative intensity, or percent composition, of the major chemical moieties present in the bondline of wood/¹⁵N-pMDI composites cured at 185°C as a function of press time.

very distinct transition in the cure chemistry from 140 seconds to 60 minutes. As the cure time is increased, polyurea formation becomes increasingly significant. Urea becomes the largest peak after 10 minutes of cure and is clearly dominant at 60 minutes. Additional biuret formation seems to be limited after 140 seconds, as evidenced by the decrease in the amide and imide nitrogen resonances. Residual isocyanate is relatively constant up to 4 minutes of cure, but then decreases significantly at longer cure times. Corrected relative intensity values indicate that residual isocyanate and amide nitrogens comprise nearly equal fractions of the cured resin when using cure times of 4 minutes or less (Table 8, Figure 24). Residual isocyanate then rapidly decreases to only a very small fraction after 60 minutes of cure. Corresponding to this loss of isocyanate groups is a large increase in the concentration of polyurea. Imide nitrogens, on the other hand, decrease only slightly in concentration after 4 minutes. Once again the reaction of residual isocyanate with water seems to be dominant after 4 minutes of cure, with only limited reaction of polyurea and isocyanate.

There might be an indication of urethane formation in the composite that was cured for 60 minutes at 185°C. The vertical line in Figure 23 corresponds to 100 ppm and was included as a measure of the base width of the 104 ppm resonance. Since the ¹⁵N urethane resonance would be present at 103 ppm, urethane formation might cause a broadening of the 104 ppm resonance. It appears that this may be happening in the composites that were cured for 10 and 60 minutes at 185°C, but particularly at the 60 minute cure time. The resonance centered at 104 ppm for these two composites is

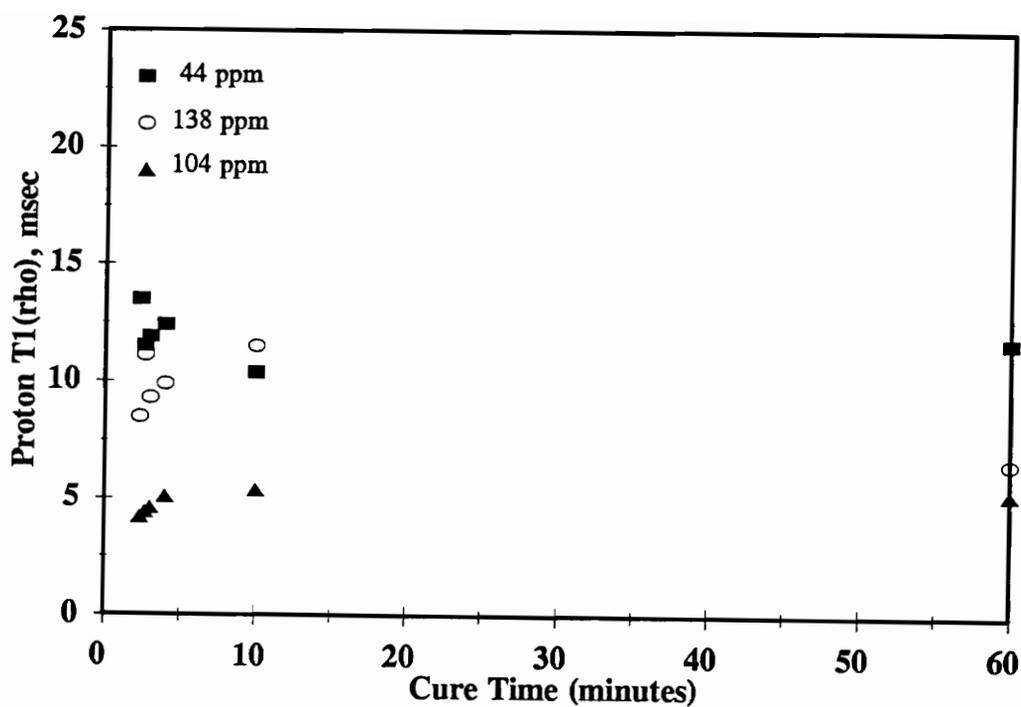


Figure 25: $T_{1\rho H}$ values calculated from cross-polarization variable contact time experiments for chemical moieties present in the bondline of wood/ ^{15}N -pMDI composites cured at 120°C as a function of press time. Mean error for these values is $\pm 12\%$.

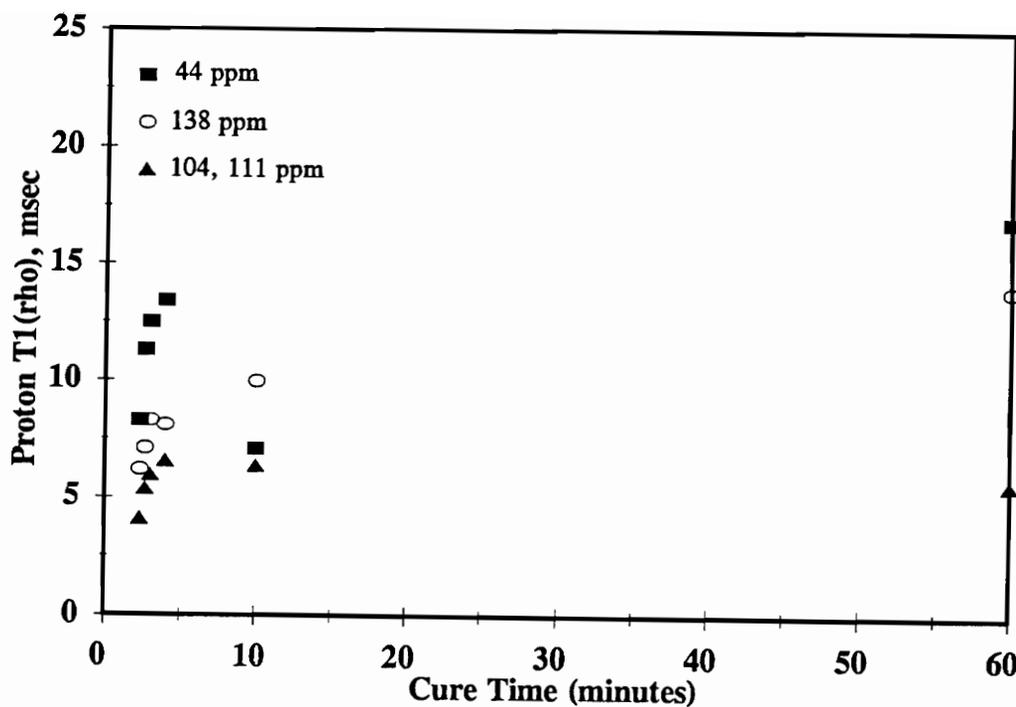


Figure 26: $T_{1\rho H}$ values calculated from cross-polarization variable contact time experiments for chemical moieties present in the bondline of wood/ ^{15}N -pMDI composites cured at 185°C as a function of press time. Mean error for these values is $\pm 14\%$.

noticeably wider on the righthand side than any of the other composites. This might be an indication of some urethane formation when cured under elevated temperature for extended periods of time, but it does not appear significant at the shorter cure times that are characteristic of industrial wood bonding practices.

9.2.2. Effect of Time on Bondline Morphology

The amide/imide nitrogen ratio provides additional qualitative evidence that the cure chemistry of the composites cured at 185°C is relatively unchanging between 140 seconds and 4 minutes of press time. The amide/imide ratios for these four composites are 1.80 (140 sec.), 1.94 (160 sec.), 1.86 (3 min.), and 1.89 (4 min.). It is likely that these values are identical within statistical error, indicating that the crosslink density of biuret type structures does not change over this range of cure time. It was not possible to calculate this ratio for the composites cured for lengths of 10 or 60 minutes, nor any of the composites cured at 120°C since the amide peak is not well resolved.

The $T_{1\rho H}$ values as a function of cure time for both the set of composites cured at 120°C (Figure 25) and the set cured at 185°C (Figure 26) show an interesting trend. As stated in Chapter 6, $T_{1\rho H}$ values obtained from cross-polarization variable contact time experiments for the composite urea/amide signal are quite accurate. Recall that it is excessively long cross-polarization rates which serve to artificially inflate $T_{1\rho H}$ values in these experiments due to the latent effects of long range cross-polarization. However, urea and amide nitrogens are characterized by fast cross-polarization rates since they

have directly attached protons. As a result, there is no inflation of the urea/amide $T_{1\rho H}$ values obtained from these experiments compared to those obtained by more direct measurements using a variable spin lock period prior to the fixed contact time. Indeed, experiments discussed in Chapter 6 (Table 3) for cellulose and in Chapter 7 (Table 5) for solid wood composites confirmed this hypothesis.

The importance of the previous discussion is that the proton $T_{1\rho H}$ values for each nitrogen species indicate similar trends over the range in cure time. For the first time in this study the trend includes the composite urea/amide signal, which is believed to be a true indication of the cured resin's properties. In other words, this trend is likely real. It also seems possible that the similar trends that are seen for residual isocyanate and imide nitrogens could also be real. The magnitude of their $T_{1\rho H}$ values are likely still inflated, but the observed trend as a function of cure time is so similar for both sets of composites that it raises doubt about being a mere coincidence.

The apparent trend for urea/amide nitrogens in the composites that were cured at 120°C (Table 7, Figure 25) is an increasing $T_{1\rho H}$ between 140 seconds and 4 minutes followed by unchanging behavior over longer cure times. Although some scatter exists in the data, the same general trend can be observed for both isocyanate and imide nitrogens. In fact, the imide $T_{1\rho H}$ appears to increase slightly between 4 and 10 minutes as well. If these trends are indeed real, an increase in the $T_{1\rho H}$ as such indicates a change in the kHz frequency molecular motions of these chemical moieties within this range of cure times. Furthermore, it is likely that it represents a decrease in the molecular

mobility. This hypothesis requires that the relaxation of these nitrogen species lie on the low frequency side of the $T_{1\rho H}$ minimum, an assumption that was proved true by an elevated temperature CP experiment [70]. It is also plausible that molecular mobility would decrease as the resin cures due to changes in crosslink density, molecular entanglements, secondary interactions, and other factors.

Very similar trends in the $T_{1\rho H}$ are noted in the composites that were cured at 185°C. In fact, the changes in $T_{1\rho H}$ are even more pronounced at this higher temperature, especially for the residual isocyanate and composite urea/amide signals. Once again, the urea/amide $T_{1\rho H}$ relaxation rate seems to become constant after a cure time of 4 minutes. Residual isocyanate and imide nitrogens, on the other hand, continue changing all the way up to 60 minutes. The source of the severe discontinuity at 10 minutes for residual isocyanate is not clear and may be attributable to random error. Based on the previous discussion, these results might indicate that greater change occurs in the various molecular mobilities as a function of cure time when consolidated at higher temperature. Once again, this observation seems plausible since higher temperatures result in more extensive cure for a given cure time. Regardless, the results of these experiments indicate the importance of cure time as a press variable for consolidating pMDI-bonded wood composites.

9.3. CONCLUSIONS

A series of wood/¹⁵N-pMDI composites were consolidated as a function of cure time

using press temperatures of 120°C and 185°C. All of the composites that were cured at 120°C show primarily polyurea type structures, with biuret formation becoming less significant at the longer cure times. Very little difference is noted in the ¹⁵N CP/MAS spectra of composites cured between 140 seconds and 4 minutes in duration. After 4 minutes of cure time, reductions are noted in the residual isocyanate and imide nitrogen concentration.

Composites that were cured at 185°C show a very clear transition toward increasing polyurea content with increasing cure time. Significant biuret formation is evident in the composites cured for 4 minutes or less, but after 10 minutes the cure chemistry becomes primarily polyurea. The exceptionally broad base on the resonance that is centered at 104 ppm in the spectrum of the composite cured for 60 minutes might be an indication of urethane formation.

For the first time in this study, changes are noted in the composite urea/amide $T_{1\rho H}$ relaxation rate. This is important since the cross-polarization variable contact time experiments used in this study provide an accurate measurement of the $T_{1\rho H}$ for protonated nitrogens. The $T_{1\rho H}$ values increase sharply between cure times of 140 seconds and 4 minutes, then become constant over longer cure times. Similar trends are noted for both residual isocyanate and imide nitrogens. These trends are observed in the composites cured at both cure temperatures, but are more pronounced at 185°C. A change in the $T_{1\rho H}$ as such is a likely indication of a decrease in the various molecular mobilities within this range of cure times.

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VITA

Steven L. Wendler was born June 2, 1970 in Fond du Lac, Wisconsin. Parents, Ronald and Dianne, exemplify the hard-working middle class of America. After graduating from high school, my father served several years in the U.S. Air Force stationed at Fort Bragg, North Carolina. He then returned to Fond du Lac and in 1965 married my mother. At that time he was working for a local carpenter, but soon formed his own private construction business which he still operates today. My mother began working as a legal secretary for a local law firm. She put her career aside to stay at home, however, while my older sister Sue and I were in our preschool years. I remain ever grateful to her for this sacrifice and show of love. Since then she has worked for a vast number of firms, performing temporary services for many of them. She seems to really enjoy the freedom and periodic changes of pace which these positions provide.

The high school which I attended was Winnebago Lutheran Academy from which I graduated with a class of 89 students in 1988. The following Fall I began study at Michigan Technological University in the Wood & Fiber Utilization program. After several changes of mind and direction, I determined that my primary interest was in wood-based composite products. I graduated Summa Cum Laude from Michigan Tech in 1992 and immediately enrolled in the M.S. Wood Science and Forest Products program at Virginia Tech. The choice of Virginia Tech was not an easy one as my roots were firmly established in the Upper Midwest, but I decided that it was in my best interests. I have not been disappointed.

A handwritten signature in cursive script that reads "Steven L. Wendler". The signature is written in black ink and is positioned in the bottom right corner of the page, overlapping the page number.