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Double labeled isocyanate resins for the solid-state NMR detection of urethane linkages to wood

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Abstract

Polymeric methylenebis(phenylisocyanate) resins prepared with ^{15}N and ^{13}C labeled functional groups allow the detection of urethane linkages to wood using solid-state NMR. Resins prepared with only ^{15}N do not reveal urethane formation because of urea and urethane nitrogen signal overlap. Likewise, resins having only ^{13}C suffer from overlapping carbonyl signals. However, in the case of the doubly labeled isocyanate group, ^{15}N causes narrowing that seems to provide partial resolution of the urethane and urea carbonyl carbons. Furthermore, the double label gives complimentary nitrogen and carbon spectra which are required for a complete interpretation. This method will be useful for the characterization of the adhesive mechanism in wood-based composites bonded with isocyanate resins. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Relentless population and economic pressures drive our need to improve the utilization efficiency of timber resources. The forest products industry is responding with tremendous investment in composite technologies for new wood-based materials. Composite technologies substantially improve wood use efficiency because low-quality logs or logs from underutilized tree species are reduced to particles with specific sizes and geometries; reconsolidation with thermosetting adhesives provides structural materials with excellent properties. Market forces naturally stimulate the desire to improve these materials. Consequently, research efforts become increasingly focused on the nature of the wood/adhesive interphase, and how properties of the interphase relate to performance, durability in particular.

Polymeric methylenebis(phenylisocyanate) is an important wood binder which is applied as the neat liquid in quantities of about 2–5% of the dry weight of wood. This adhesive, hereafter referred to as pMDI, is valued in the forest products industry for its rapid cure and excellent performance. For many years, the good performance of pMDI wood binders was attributed to urethane formation with the abundant wood hydroxyl groups. However, the significance of covalent attachment to wood has not been clearly revealed under conditions similar to industrial processes. Previous ^{15}N NMR studies have provided indirect evidence for urethane formation; this was in the form of cure dependent changes in molecular dynamics, and through the spectral manipulation of differential mobility [1]. This fact has compelled us to investigate the utility of ^{13}C labeling for direct urethane detection. Most thermosetting wood adhesives are thought to bond through adsorption, and not by covalent attachment. Consequently, there is great interest in revealing the incidence of urethane formation in hopes of promoting this more durable adhesive mechanism. A direct method of urethane detection in a simple one-dimensional NMR spectrum has a certain appeal, in spite of the extra synthetic effort. This work describes a method of isotopic labeling and solid-state NMR analysis that will shed light on this issue, and assist in the correlation of

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composite performance with the molecular properties of the adhesive interphase. The insertion of both ^{15}N and ^{13}C nuclei into the isocyanate functional group is the basis of the method.

2. Experimental section

2.1. Materials

Isotopically labeled materials, i.e., 99% carbon monoxide-^{13}C and 98% + aniline-^{15}N, were purchased from or donated by Cambridge Isotope Laboratories. Paraformaldehyde, aniline, 2-propanol, diethylamine, phenylmercuric acetate, anhydrous 1,2-dichlorobenzene and gaseous chlorine and carbon monoxide were purchased from Aldrich Chemical Company and used as received. 1,4-dioxane was dried over potassium pellets and distilled before use.

2.2. ^{13}C labeled phosgene

The extreme toxicity of phosgene gas is well known. The procedure described here provides phosgene dissolved in solution, which is much safer than using the gas. Nevertheless, the appropriate caution is required when handling this reagent. The procedure used here requires glassware designed for low to moderate pressures. The procedure of Masaki et al. was adapted [2] however trioctyl phosphine oxide had little impact on yield, so no catalysts were used. Chlorine gas (3.33 g, 46.9 mmol) was dissolved in anhydrous 1,2-dichlorobenzene (40 ml), and transferred to a 1 l pressure vessel pre-filled with ^{13}C labeled carbon monoxide (40.8 mmol). The flask was sealed and heated to 50°C for 24 h until the solution was nearly clear and colorless. The yield was 45%, as determined by quenching phosgene with excess aniline and triethylamine to form diphenylurea [2], or by an iodometric titration [3]. ^{13}C NMR for a 0.5 M solution ($CDCl_3$): δ143.2 (s, CO).

2.3. Labeled pMDI, doubly and singly labeled (pMDI-^{13}C,^{15}N; pMDI-^{13}C)

The synthesis of pMDI begins with an acid catalyzed condensation of formaldehyde and aniline, followed by phosgenation [4]. The first step, preparation of the ^{15}N labeled polyamine, was conducted as described previously [1]. A solution of ^{15}N labeled polyamine precursor (2.0 g) in 1,2-dichlorobenzene (20 ml) was added dropwise to a round-bottom flask that was precharged with ^{13}C labeled phosgene solution (18 mmol); an insoluble carbamoyl chloride was formed immediately. The flask was sealed and heated to 180°C. The intermediate decomposed within 10 min to form a clear solution. After stirring for 0.5 h (180°C), pressure was released and the remaining insolubles were filtered. Removal of volatiles in vacuo (10^{-2} mmHg, 65°C) left pMDI-^{13}C,^{15}N resin as a brownish viscous liquid at a 89% yield (2.2 g). The singly labeled resin(pMDI-^{13}C) was prepared as above. A completely unlabeled resin was prepared in identical fashion for analysis; analytical results are assumed to represent the labeled resins. A portion of the unlabeled pMDI (0.2 g) was reacted with excess diethylamine (1.1 g, 15 mmol) in 2 ml $CHCl_3$ to form a urea derivative. After removal of volatiles, a yellow powder was isolated and dissolved in tetrahydrofuran (THF). The molecular weight distribution of the urea derivative was determined by gel permeation chromatography in THF. The number-average molecular weight and weight-average molecular weight of pMDI were determined, after correction for derivatization $M_n = 251$, $M_w = 271$. The isocyanate content of the resin was measured to be 31–32%, following a 1 in 10 scale version of ASTM Standard D 5155-91. The pMDI-^{13}C,^{15}N resin was further identified by solution ^{13}C and ^{15}N NMR(^{15}N NMR spectrum externally referenced to glycine-^{15}N at 31 ppm). In the ^{13}C NMR spectrum, the isocyanate signal shows up as a much stronger doublet (δ124.6) than the aromatic signals(δ129.9 doublet, 124.7 doublet) and bridging methylene groups (δ40.6). The oligomeric forms of pMDI can be found at 151.0 and 153.1 ppm as weak triplets. Doublets (δ47.6 for the strongest doublet) can also be observed in ^{15}N spectrum, and the one-bond coupling constant $^1J_{CN}$ between carbon-13 and nitrogen-15 is observed to be 47.3 Hz from both ^{13}C and ^{15}N spectra. The resin is mainly the 4,4′-isomer of MDI with some oligomers. Significant amounts of 2, 4′- and 2,2′-isomer were not detected.

2.4. Model compound preparation

Model compounds were prepared as described below. The compounds are identified by the general identity, urethane or urea, and by the reactants used in their synthesis.

Urethane: 2-propanol/pMDI-^{13}C,^{15}N (or pMDI-^{13}C). A solution of pMDI-^{13}C or pMDI-^{13}C,^{15}N (0.2 g) in 1,2-dichloroethane (2 ml) was added dropwise to 2-propanol (0.19 g, 3.2 mmol) in 1,2-dichloroethane (2 ml). After stirring (50°C, 24 h), volatiles were removed in vacuo to afford a yellowish solid in 98% yield (0.29 g). ^{13}C NMR (DMSO-d_6) for ^{13}C and ^{15}N labeled urethane: δ153.2 (d, CO); $^1J_{CN}$ 26.6. ^{15}N NMR (DMSO-d_6) for ^{13}C and ^{15}N labeled urethane: δ101.0 (d, NH).

Urethane: wood powder/pMDI-^{13}C,^{15}N (or pMDI-^{13}C). This model was prepared by a modified literature method [5]. In a two-neck round bottom flask, yellow-poplar(*Liriodendren tulipifera*) powder (60 mesh, 0.10 g) was dried overnight (10^{-2} mmHg, 100°C). The flask was charged with dry dioxane (10 ml) to produce a suspension which was then heated and stirred (50°C, 1 h). A mixture of pMDI-^{13}C or pMDI-^{13}C,^{15}N (0.30 g) and phenylmercuric acetate (0.015 g) in dry dioxane (5 ml) was added. After stirring (50°C, 1.5 d) under dry N_2 atmosphere, the wood powder was filtered, washed with acetone, dried in vacuo and weighed to be 0.18 g.

Urea: *p*-toluidine/pMDI-^{13}C,^{15}N (or pMDI-^{13}C). A solution of pMDI-^{13}C or pMDI-^{13}C,^{15}N (0.20 g) in 1,2-dichloroethane (2 ml) was slowly added to *p*-toluidine (0.34 g, 3.2 mmol) in 1,2-dichloroethane (2 ml). A white solid precipitated. After stirring (25°C, 12 h) and removal of volatiles in vacuo (10^{-2} mmHg, 65°C), a yellowish powder was isolated in 95% yield (0.35 g). ^{13}C NMR (DMSO-d_6) for ^{13}C and ^{15}N labeled urea: δ152.6 (d, CO); $^{1}J_{CN}$ 20.6. ^{15}N NMR (DMSO-d_6) for ^{13}C and ^{15}N labeled urea: δ103.6 (d, NH).

Urea: aniline/pMDI-^{13}C. A solution of pMDI-^{13}C (0.22 g) in 1,2-dichloroethane (2 ml) was dropwise added to aniline (0.32 g, 3.5 mmol) in 1,2-dichloroethane. A white precipitate formed. After stirring (25°C, 3 h) and removal of volatiles in vacuo, a yellowish solid was isolated in 95% yield (0.33 g). ^{13}C NMR (DMSO-d_6): δ152.6 (s, CO)

Urea: aniline-^{15}N/pMDI-^{13}C,^{15}N. Procedure was as above except pMDI-^{13}C,^{15}N and aniline-^{15}N were used. Product was a yellowish powder. Yield 94% (0.30 g). ^{13}C NMR (DMSO-d_6): δ152.6 (dd, CO); $^{1}J_{CN}$ 21.2, 21.3. ^{15}N NMR (DMSO-d_6): δ104.8 (dd, NH), 104.0 (dd, N'H); $^{2}J_{NN'}$ 5.8.

Urea: H_2O/pMDI-^{13}C,^{15}N (or pMDI-^{13}C). Excess distilled water (H_2O, 0.20 g) was added to a solution of pMDI-^{13}C,^{15}N or pMDI-^{13}C (0.37 g) in dioxane (4 ml). After stirring (25°C, 1 d; 50°C, 3 h) and removal of volatiles, a yellowish solid was isolated and found to be insoluble.

2.5. Preparation of pMDI/wood composite samples

A block of clear yellow-poplar sapwood was softened by soaking in distilled water overnight. Flakes with dimensions of 38 × 51 × 0.38 mm were sliced from the radial wood surface using a disk flaker. Flakes were dried at 105°C for 24 h to obtain dry weights, then conditioned to different moisture contents (flakes were equilibrated at ambient conditions to achieve a 6–7% moisture content, over saturated sodium sulfate aqueous solution for a 12% moisture content, or over distilled water for a 22% moisture content). Isotopically labeled pMDI resin (approximately 12% of total dry wood weight) was spread with a Teflon spatula onto one side of two flakes. The resin was sandwiched between the flakes by pressing in a Carver Laboratory Press at selected temperatures under 3.45 Mpa (500 psi). Samples were then stored in a desiccator loaded with Drierite until NMR spectra were recorded (within 24 h).

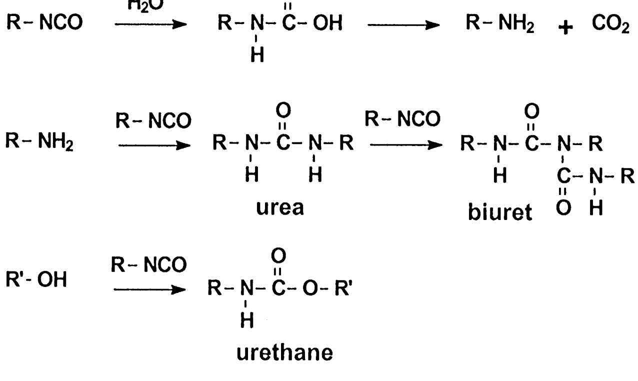
2.6. Solid state NMR measurements

^{13}C and ^{15}N CP/MAS NMR spectra were recorded on a Bruker MSL-300 MHz spectrometer, operating at 75.47 MHz for ^{13}C or at 30.43 MHz for ^{15}N nuclei using a variable contact time pulse at room temperature. The delay between scans was 3 and 6 sec for carbon and nitrogen, respectively. All ^{13}C spectra were referenced externally to adamantane, and all ^{15}N spectra to glycine-^{15}N at 31 ppm. Small discs were cut from the wood composite by using a paper hole puncher, and filled into a zirconium oxide rotor. The rotor was spun at 5.5 kHz for ^{13}C spectra or 4.0 kHz for ^{15}N spectra.

3. Results and discussion

Reactions pertinent to the cure of pMDI in wood-based composites are shown in Scheme 1. Most significant is that pMDI requires wood moisture for polymerization into a polyurea and biuret network. Covalent attachment is possible if the isocyanate forms urethanes by addition of carbohydrate alcohols or lignin phenols. It is also possible that nonstructural tree metabolites could react with pMDI, terpenoids and phenolic compounds for example.

Representative ^{15}N CP/MAS NMR spectra are shown in Fig. 1. The top spectrum is a composite wood sample (two wood flakes bonded with the doubly labeled resin). Chemical shifts are similar to published values where residual isocyanate is seen at 44 ppm; urea appears at 104 ppm; biuret amide and imide nitrogens are seen near 110 and 138 ppm, respectively [6]. The apparent weakness of the isocyanate and biuret imide signals results from the slow cross polarization of unprotonated nitrogens($T_{NH} \sim 2$–3 ms) [7,8], and that these spectra were acquired with a 2 ms contact time. The bottom spectrum in Fig. 1 is from a model urethane (wood powder/pMDI-^{13}C,^{15}N, δ102) made from the doubly labeled resin and wood powder under anhydrous



Scheme 1

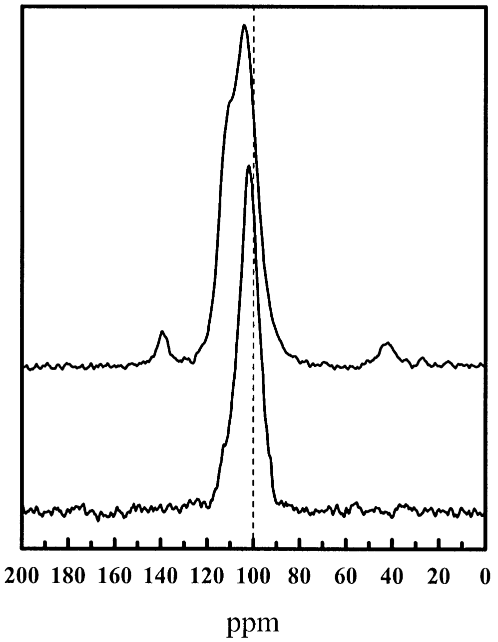


Fig. 1. Representative ^{15}N CP/MAS NMR spectra. Top: composite sample prepared from yellow-poplar wood flakes and pMDI-^{13}C,^{15}N. Bottom: model urethane prepared from yellow-poplar wood powder and pMDI-^{13}C,^{15}N under anhydrous conditions.

conditions. Fig. 1 demonstrates that urethane and urea signals are not resolved in the nitrogen spectrum, a well documented disappointment [1,5].

This investigation began with the synthesis of several model urethane and urea compounds from labeled pMDI. Table 1 lists some of the solid-state nitrogen and carbon chemical shifts for these models. Nitrogen chemical shifts are consistent with the assignments discussed for Fig. 1. However, the carbonyl chemical shifts do not correlate with the composite samples, as will be shown. The model compounds show solid-state urethane carbonyls at 154–155 ppm, and solid-state urea carbonyls at 156 ppm. Significant carbon line narrowing is provided by the ^{15}N nucleus in the solid-state spectra of these models. The carbonyl signals were narrowed by 66, 52 and 97 Hz, respectively for the models based on isopropanol, aniline and toluidine. This effect proves to be helpful for the detection of urethane in the following spectra.

When considering CP/MAS carbon spectra of the composite samples, one must first address the overlap of resin and wood signals, as shown in Fig. 2. Wood signals appear near 152, 136 (lignin carbons), and 105 ppm(C1 carbohydrate, plus some underlying lignin). Two composite samples are shown; one was prepared with the singly labeled resin(pMDI–^{13}C), the other with the doubly labeled resin (pMDI-^{13}C,^{15}N). Residual isocyanate is seen at 124 ppm, and the cured resin carbonyls appear near 155 ppm. The labeled carbons provide strong signals, so strong that the overlap with wood is of little concern. Fig. 2 demonstrates that double labeling eliminates some carbon broadening and reveals structural detail that is absent in the singly labeled sample (Recall that ^{15}N substitution caused a 52–97 Hz narrowing in the model compounds. This amounts to a 0.7–1.3 ppm effect, which may be more significant in the case of overlapping signals, each becoming more narrow.) The doubly labeled sample exhibits a sharp maximum(δ 156) with a shoulder(δ 154). The assignments listed in Table 1 suggest that the downfield peak

Table 1
^{13}C and ^{15}N solid-state NMR chemical shifts for various urethane and urea model compounds as indicated. The model names indicate the reagents used for their preparation. The chemical shifts are of the carbon or nitrogen maxima arising from the isotopic label

	^{13}C chem shift (ppm)	^{15}N chem shift (ppm)
Urethanes		
2-propanol/pMDI-^{13}C	155	—
2-propanol/pMDI-^{13}C,^{15}N	155	101
Wood powder/pMDI-^{13}C,^{15}N	154	102
Ureas		
p-toluidine/pMDI-^{13}C	156	—
p-toluidine/pMDI-^{13}C,^{15}N	156	104
Aniline/pMDI-^{13}C	156	—
Aniline-^{15}N/pMDI-^{13}C,^{15}N	156	104
Water/pMDI-^{13}C,^{15}N	156	—

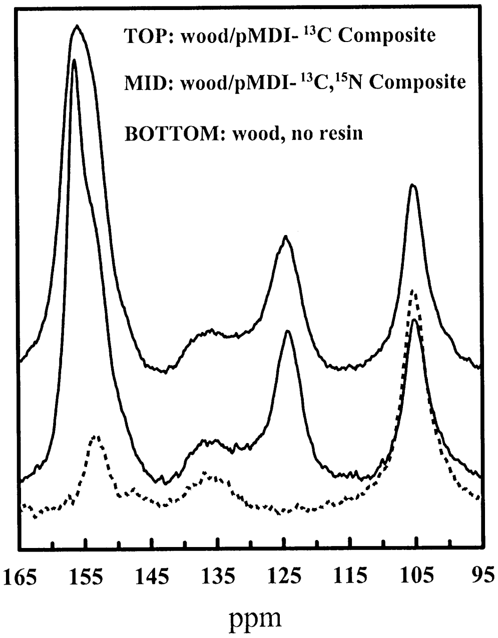


Fig. 2. Representative ^{13}C CP/MAS NMR spectra, showing the carbonyl region. Top: composite sample prepared from yellow-poplar wood flakes and pMDI-^{13}C. Middle: composite sample prepared from yellow-poplar wood flakes and pMDI-^{13}C,^{15}N. Bottom: yellow-poplar wood.

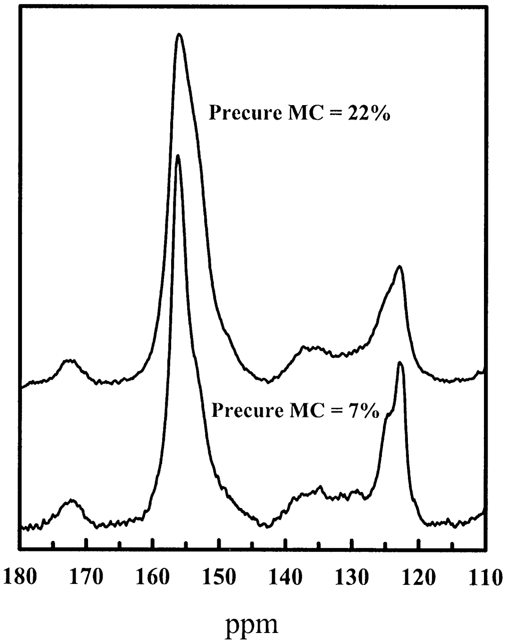


Fig. 3. ^{13}C CP/MAS NMR spectra demonstrating the effects of wood precure moisture content on the relative intensity of carbonyl carbon signals, cure conditions for both samples: 100°C, 500 psi, 3 min. Samples were prepared with yellow-poplar flakes and pMDI-^{13}C,^{15}N.

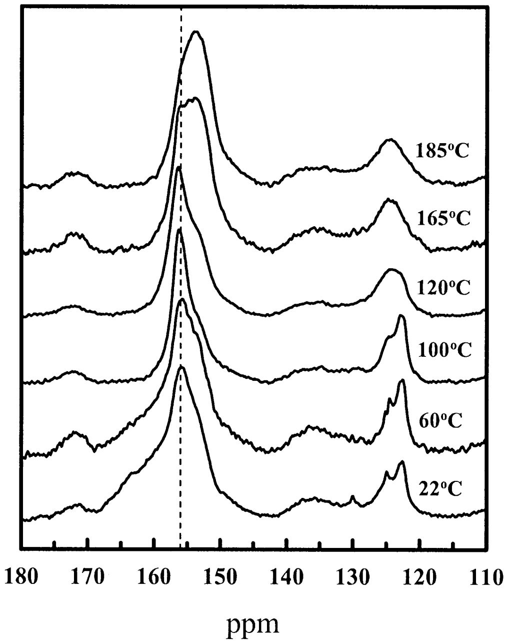


Fig. 4. ^{13}C CP/MAS NMR spectra demonstrating the effects of cure temperature as indicated. Samples were prepared with yellow-poplar flakes and pMDI-^{13}C,^{15}N.

may be urea, while the shoulder may correspond to urethane (biuret assignments will be discussed later). However, this is apparently not the case as indicated in Fig. 3; two composite samples are shown which differ only in the precure wood moisture content. The intensity of the 154 ppm shoulder displays a moisture dependence, as indicated by its relationship to the 156 ppm maximum. This suggests that the 154 ppm shoulder corresponds to urea.

Assignment of the carbonyl signals is further assisted by observing the temperature dependence of pMDI cure in the carbon (Fig. 4), and in the corresponding nitrogen spectra (Fig. 5). The carbon spectra show the putative urethane maximum at 156–157 ppm for cure temperatures of 22–120°C. A local maximum(δ 156) is also seen for the sample cured at 165°C, but not at 185°C presumably because of the well-known thermal decomposition of urethanes at higher temperatures. The shoulder(δ 154) generally grows with increasing cure temperature, becoming the dominant maximum at 185°C.

Let us now consider the corresponding nitrogen spectra, focusing on the sample prepared at 22°C, Fig. 5; the dominant nitrogen appears at 102 ppm, with a clear shoulder at 99 ppm. Nitrogen signals of 97–102 ppm are considered as urethane, according to the models (Table 1) and our previous work [1] (This is somewhat consistent with literature compilations of nitrogen assignments [9], but such compilations have limited utility because of the wide variation of sample specific nitrogen shieldings.) Consequently, curing at 22°C provides two urethanes(δ 99 & 102) in different environments or conformations, or possibly derived from different wood nucleophiles. The 99 ppm nitrogen shoulder becomes less distinct as the cure temperature

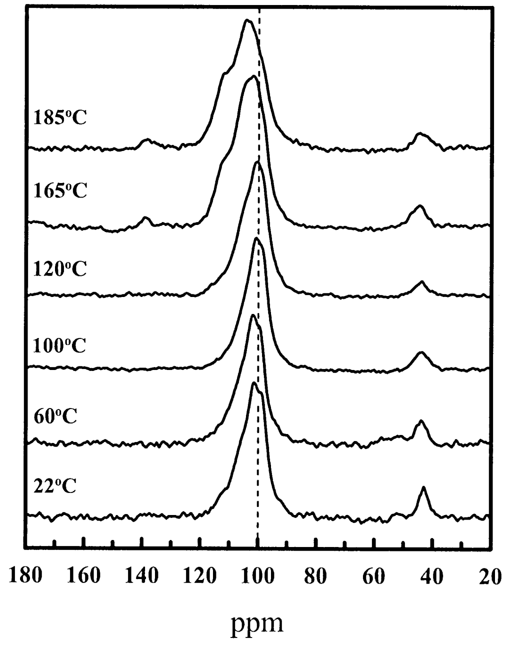


Fig. 5. ^{15}N CP/MAS NMR spectra (corresponding to spectra shown in Fig. 4) demonstrating the effects of cure temperature as indicated. Samples were prepared with yellow-poplar flakes and pMDI-^{13}C,^{15}N.

rises; the 101–102 ppm maximum remains up to a cure temperature of 165°C, but it is absent at 185°C. Once again, this suggests that the urethane decomposes near 185°C, leaving the more stable urea which appears at 104 ppm. Urea is apparent in all of the nitrogen spectra of Fig. 5; it becomes distinct at 120°C, and is finally dominant at the highest cure temperature as mentioned. Biuret nitrogens are only evident at the two highest cure temperatures, a fortunate event that simplifies the interpretation of the carbon spectra. In other words, interpretation of the carbon spectra is not complicated by biuret signals below cure temperatures of 165°C.

It is evident that the nitrogen peak shift from 102 to 104 ppm correlates with the shift from 156 to 154 ppm in the carbon spectra. This is consistent with earlier ^{15}N NMR studies, where a similar peak shift was accompanied by an abrupt change in proton rotating frame longitudinal relaxation [1]. We suggest that the peak shifts reflect the thermal cleavage of urethanes, where after ureas and biurets are left as the dominant spectral features. These observations, and those from previous efforts [1], lead us to assign the 156–157 ppm carbon signal to the urethane linkage. Likewise, the 154 ppm shoulder must arise from urea carbonyl carbons, and also biuret carbonyls at higher cure temperatures (Again, recall that this is contrary to the assignments made from model compounds, Table 1.) The cure temperature dependence shown here could have important industrial implications. Industrial processes typically employ platen temperatures of 185–200°C, and hotpress times are minimized so that panel core temperatures reach a target of 100–120°C. The findings here suggest that bondline chemistry and performance may vary through the thickness of composite panels.

These spectral assignments indicate that urethane formation is common in this system. However, additional studies are required before obtaining an accurate assessment of the adhesive mechanism for industrial materials. Industrial pMDI wood binders have a much higher proportion of polyisocyanate oligomers, and are somewhat less reactive than the highly monomeric resin used here. The carbon spectra in Fig. 4 provide additional opportunities for future study. Notice that at low cure temperatures at least three different isocyanate signals are apparent. These sharp signals probably arise from various types of free monomer or dangling endgroups. One will also notice a significant downfield broadening of the carbonyl signals at cure temperatures of 22°C and 60°C. The identity of this broad signal is currently unknown. Finally, the double label in these samples will be particularly useful for solid-state two-dimensional correlation techniques which are planned for the future.

4. Conclusions

Polymeric methylenebis(phenylisocyanate) resins prepared with ^{15}N and ^{13}C label in the isocyanate functional group reveal the formation of covalent urethane linkages to solid wood using solid-state NMR. Both isotopes are required because: (1) the ^{15}N isotope narrows the ^{13}C carbonyl signals, thereby aiding the partial resolution of urethane and urea carbonyls, and (2) the double label provides complimentary nitrogen and carbon spectra which assist with the spectral interpretation. This method will provide a more complete analysis of the adhesive mechanism in woods bonded with isocyanate resins, possibly promoting the development of more durable wood-based composite materials.

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