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INVESTIGATING THE REACTIVITY OF PMDI WITH WOOD CELL WALLS USING HIGH-RESOLUTION SOLUTION-STATE NMR SPECTROSCOPY

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Introduction

Covalent bonds between an adhesive and wood are believed to improve bond durability. However, covalent bonds have never been unambiguously detected in an adhesive bondline. To determine whether an adhesive forms covalent bonds to wood, it must have the following characteristics: (1) be highly reactive with wood polymer hydroxyls, (2) be capable of permeating the cell wall, (3) exhibit strong wettability to wood, and (4) be amenable to study using a monofunctional model compound. Ideally the reaction between the monofunctional model compound and wood will produce distinct chemical shift differences between unreacted and reacted wood polymers in solution-state nuclear magnetic resonance (NMR) spectroscopy.

An adhesive that fits these characteristics is polymeric methylene diphenyl diisocyanate (pMDI). This adhesive may: (1) react with wood hydroxyls,[1] (2) permeate the cell wall,[2,3] (3) flow into microvoids if given access by a fracture,[4] (4) travel ~1 mm from the applied radial wood surface.[5]

Isocyanates undergo several competitive reactions. Polyurea is formed from the self-polymerization reaction of the diisocyanate with water. Wendler and Frazier found that when the wood is dry (moisture content <5%), pMDI reacts to form urethane and low molecular weight biuret structures.[6] As the wood moisture increased (>5%), they found polyurea formation to dominate,[6] thus optimizing penetration into wood. Urethane (i.e., covalent bond) formation with wood polymer hydroxyls may provide a secondary ‘anchoring’ mechanism within the cell wall at moisture contents >5%.

The difficulty in distinguishing between urea, biuret, and urethane structures in wood-pMDI bondlines are because of their structural similarities. Zhou and Frazier prepared pMDI with a double-isotopic label (i.e., ^{15}N & ^{13}C) in the isocyanate to enhance detection of urethane crosslinks in the cured wood-pMDI bondline using solid-state NMR spectroscopy.[1] However, urethane and polyurea signals displayed substantial overlap in the acquired spectra; therefore, covalent bonds couldn’t be identified unambiguously.

High-resolution solution-state NMR spectroscopy is a powerful tool for detecting covalent bonds between wood polymers and adhesives. Using non-degradative wood dissolution,[7] finely ground wood cell walls dissolve in a solvent system containing dimethylsulfoxide-d_6 and N-methylimidazole-d_6, keeping wood polymers in a non-derivatized state.[8] Two-dimensional (2D) NMR experiments, using ^{13}C–^{1}H one-bond Heteronuclear Single Quantum Correlation (HSQC) spectroscopy on whole cell walls reveal the major cell wall polymers. Previous work with a pMDI model compound (i.e., p-methylphenyl isocyanate) showed that HSQC spectroscopy can detect chemical shift changes upon reactions with wood cell wall polymers.[9] In this study, we investigate the reactivity between wood cell wall polymers and pMDI model compounds (i.e., phenyl isocyanate & 4-benzylphenyl isocyanate) to determine the exact site(s) of urethane formation (if reaction occurs) as well as quantification of the urethanes formed.

The objectives of this study are the following: (1) Use solution-state NMR to assign contours in HSQC spectra of the reaction products between pMDI model compounds and: (a) lignin model compounds, (b) milled-wood lignin, (c) ball-milled wood, (d) microtomed loblolly pine; (2) Determine where and to what degree urethane formation occurs with loblolly pine cell wall polymers at 0% and 5% moisture content (MC).

Experimental

Materials: All reagents were from Aldrich Chemical Company. Phenyl isocyanate and 4-benzylphenyl isocyanate and solvent N,N-dimethylacetamide were dried over 3Å molecular sieves. N-methylimidazole-d_6 was synthesized.[8] Ball-milled loblolly pine was prepared using a Retsch PM100 planetary ball-mill with ZrO_2 vessel and balls. Lignin models (β–O–4 & β–5) were prepared by standard methods.[10] Milled-wood lignin was prepared using the Björkman method.[11] Microtomed Loblolly pine (20 mm × 20 mm × 0.050 mm & 20 mm × 20 mm × 0.300 mm) tangentially sliced earlywood sections were

equilibrated at 0% and 5% MC prior to reactions with pMDI models.

Wood dissolution: 50 mg of ball-milled pine was dissolved directly in a 5 mm NMR tube with DMSO-d_6 and NMI-d_6 using sonication. NMR experiments (^{1}H, ^{13}C, HSQC) were run on 500 MHz Bruker instruments equipped with cryoprobe.

Lignin & Ball-milled wood reactions: Reactions between the lignin models (i.e., **A**, β–O–4- & **B**, β–5-models, **Figure 1**) and the pMDI models were carried out under N_2 in N,N-dimethylacetamide with 0.02 M dibutyltin dilaurate at 50 ºC. Reaction times varied from 2 h for lignin models to 12 h for ball-milled pine. Reaction products were precipitated in a MeOH/H_2O mixture (v/v = 5:1), filtered using a 0.2 μm nylon membrane, dried in a vacuum oven at 50 ºC, and analyzed using NMR in DMSO-d_6.

Microtomed loblolly pine reactions: Reactions between loblolly pine (0.050 mm thick) and pMDI models were carried out under N_2 in N,N-dimethylacetamide at 160 °C for 2 h. For testing normal bonding conditions, an Automated Bond Evaluation System (ABES) was used at 160 °C for 10 min. at 3.4 MPa to press loblolly pine (0.300 mm thick) entering the press at 0% and 5% MC. After all reactions, the remaining isocyanate and urea products were extracted in refluxing acetone.

Results and Discussion

The model wood compound study showed that the lignin models and the milled-wood lignin and can be reacted with the pMDI model compounds to give complete substitution **(Figures 2 & 3)**. The reacted β–O–4-model, β–5-model, and milled-wood lignin chemical shifts closely match those of reacted ball-milled loblolly pine whole cell wall **(Figure 4)**, confirming that these models are directly comparable to reacted loblolly pine.

The microtomed loblolly pine study results are summarized in **Table 1**. The loblolly pine reactions in N,N-dimethylacetamide displayed high lignin sidechain reactivity with phenyl isocyanate under 0% MC conditions. Quantification of urethanes on lignin sidechains was performed using 2D NMR volume integration of the Aβ and Bβ contours. With a 2:1 (NCO:OH) molar ratio the β–O–4- and β–5-γ–hydroxyls are >90% reacted at 0% MC. Some polysaccharide reaction was evident only with the 2:1 (NCO:OH) molar ratio, quite possibly at the primary hydroxyls and C2 hydroxyls of hemicelluloses. At a 1:1 (NCO:OH) molar ratio, the β–O–4- and β–5-γ–hydroxyls are 41% and 38% reacted at 0% MC. As the MC increased to 5%, a 1:1 (NCO:OH) molar ratio showed 9% and 7% of the β–O–4- and β–5-γ–hydroxyls had reacted. When microtomed loblolly pine in N,N-dimethylacetamide was reacted with 4-benzylphenyl isocyanate, reaction was substantially less effective, suggesting that the bulkier molecule has enough steric hindrance to block access to most lignin sidechains. Using 4-benzylphenyl isocyanate at a 1:1 (NCO:OH) molar ratio, the β–O–4-γ–hydroxyls are only ~1% reacted at 0% MC.

When microtomed sections of loblolly pine were bonded in the ABES press using 4-benzylphenyl isocyanate with a 1:1 (NCO:OH) molar ratio, <1% of the β–O–4-γ–hydroxyls reacted at 0% MC; no urethane formation was detected with 2D NMR using the ABES press at 5% MC.

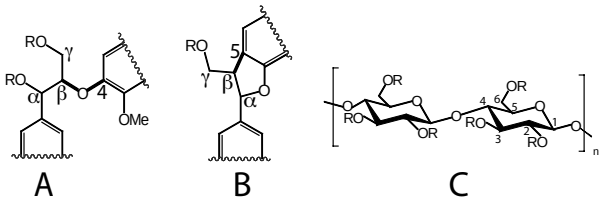

Figure 1. Key to the structures represented in Figures 2-4 below: **A**, β–O–4-linked units; **B**, β–5-linked units; **C**, repeat unit of cellulose. In the structures: R represents an H or carbamate (i.e., urethane); α, β, and γ designate the 1st, 2nd, and 3rd carbons from the aromatic ring.

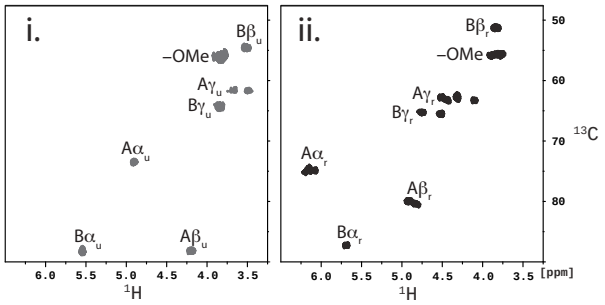

Figure 2. HSQC spectra of lignin model compounds: **i.** Unreacted models (dark gray contours); **ii.** Reacted models (black contours). Note the distinct differences between unreacted and reacted lignin model compound chemical shifts.

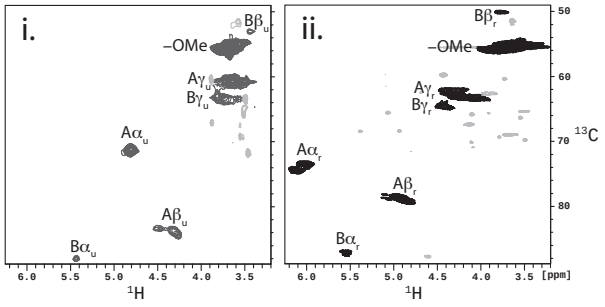

Figure 3. HSQC spectra of loblolly pine milled-wood lignin: **i.** Unreacted lignin polymers (dark gray contours); **ii.** Reacted lignin polymers (black contours). Note the distinct differences between unreacted and reacted lignin polymer chemical shifts.

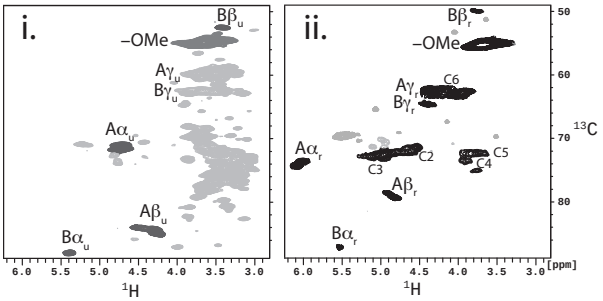

Figure 4. HSQC spectra of ball-milled loblolly pine whole cell wall: **i.** Unreacted wood polymers (dark gray contours); **ii.** Reacted wood polymers (black contours). Other contours (light gray) overlap or are not assigned here. Note the distinct differences between unreacted and reacted lignin polymer chemical shifts.

Table 1. Results from the microtomed loblolly pine reactions with pMDI models using HSQC volume integration of Aβ and Bβ contours.

pMDI Model	[1]Aβ$_r$	[2]Bβ$_r$	NCO:OH (moles)	%MC	[3]Solvent	Press (MPa)
Control	–	–	–	0	DMAc	–
	>90	>90	2:1	0	DMAc	–
	41	38	1:1	0	DMAc	–
	9	7	1:1	5	DMAc	–
	1	[4]nd	1:1	0	DMAc	–
	<1	[4]nd	1:1	0	–	3.4
	[4]nd	[4]nd	1:1	5	–	3.4

1. Aβ$_r$ is the percent β-O-4 sidechains that reacted with the pMDI model.
2. Bβ$_r$ is the percent β–5 sidechains that reacted with the pMDI model.
3. DMAc is N,N-dimethylacetamide, a good swelling solvent for wood
4. **nd** means none detected

Conclusions

This NMR method unambiguously answers the long-standing question of whether covalent bonds can form between wood cell wall polymers and wood adhesives. The data presented here showed that: (1) HSQC spectra of lignin model compounds (β–O–4, β–5 & milled-wood lignin) are directly comparable to spectra of ball-milled whole cell walls of loblolly pine; (2) HSQC spectra of the reacted microtomed loblolly pine, under dry conditions with high NCO:OH molar ratios in a swelling solvent, revealed that the only wood polymers reacted were lignin sidechain units; (3) as moisture increased from 0% to 5% MC and NCO:OH molar ratios decreased from 2:1 to 1:1, a dramatic decrease in lignin sidechain reactivity was observed; (4) under identical reaction conditions, phenyl isocyanate reacted with β–O–4-γ–hydroxyls ~40% more frequently than 4-benzylphenyl isocyanate, which shows that molecular size of the permeating pMDI model controls urethane formation to a large extent; (5) using an ABES press with microtomed loblolly pine and 4-benzylphenyl isocyanate at 5% MC, no urethane formation was detected, even under a high NCO:OH molar ratio. The results of this study suggest that, even though pMDI is highly reactive towards lignin sidechain hydroxyls at 0% MC, beyond 5% MC polyurea formation may be the predominant mechanism for adhesion between pMDI and loblolly pine.

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