Delineating pMDI model reactions with loblolly pine via solution-state NMR spectroscopy. Part 2. Non-catalyzed reactions with the wood cell wall

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Abstract

Solution-state NMR provides a powerful tool to observe the presence or absence of covalent bonds between wood and adhesives. Finely ground wood can be dissolved in an NMR-compatible solvent system containing dimethylsulfoxide-d_6 and N-methylimidazole-d_6, in which the wood polymers remain largely intact. High-resolution solution-state two-dimensional NMR correlation experiments, based on $^{13}C-^{1}H$ one-bond heteronuclear single quantum coherence, allow structural analysis of the major cell wall components. This technique was applied to loblolly pine that was treated with polymeric methylene diphenyl diisocyanate (pMDI) related model compounds under controlled moisture and temperature conditions. Chemical shifts of carbamates formed between the pMDI model compounds and loblolly pine were determined. The results show that: (a) under dry conditions and a high concentration of isocyanate, carbamates will form preferentially with side-chain hydroxyl groups on β-aryl ether and phenylcoumaran-linked lignin units in a swelling solvent; (b) phenyl isocyanate is more capable of derivatization in the cell wall than the bulkier 4-benzylphenyl isocyanate; (c) at 5% and 14% moisture content, detectable carbamates on lignin side-chains dramatically decrease; and (d) under typical conditions of industrial oriented strand-board production in a hot press at 5% and 14% moisture content, no carbamate formation was detected.

Keywords: β-aryl ether; 4-benzylphenyl isocyanate; carbamate; cell wall; heteronuclear single quantum coherence (HSQC); γ-hydroxyls; *Pinus taeda*; phenylcoumaran; phenyl isocyanate; polymeric methylene diphenyl diisocyanate (pMDI); solution-state NMR.

Introduction

Polymeric methylene diphenyl diisocyanate (pMDI) adhesive, applied in oriented strand-board (OSB), laminated strand-lumber and exterior particleboard production has been touted as the only adhesive that can chemically react with cell wall polymers since its introduction in the early 1970s (Deppe and Ernst 1971; Deppe 1977; Frisch et al. 1983). Indeed, isocyanate adhesives have been shown to create durable bonds with wood, thus withstanding swelling and shrinkage stresses at the bondline interface (Frazier 2003). To date, however, there is a lack in understanding of why these adhesives bond well to wood while others do not. Moreover, it is not clear whether covalent bonds are necessary for durable wood adhesion. To better formulate an adhesive with high bondline durability, the molecular characteristics of the interaction between the adhesive and wood should be better understood (Yelle 2009).

pMDI adhesion

In the industrial OSB manufacturing process, pMDI is typically used for the core layer adhesive, and phenol formaldehyde is often applied for the face layers. Bonding with pMDI tolerates higher moisture contents (MC > 6%) and relatively fast press cycles; this allows for continuous pressing where mats can be injected with steam to accelerate heat transfer and curing (Sellers 2001). Hence, a major objective is to form strong and durable bonds to wood.

Several studies have been devoted to exploring how pMDI cures and interacts with wood during adhesive application and hot pressing of OSB (Wendler and Frazier 1996a,b; Rosthauser et al. 1997; Frazier and Ni 1998; Harper et al. 2001; He and Yan 2005; Das et al. 2007; Riedlinger et al. 2007). In all these studies, cell wall moisture plays an important role. Bound water in the cell wall is ubiquitous and rapidly reacts with isocyanates to form urea- and biuret-type structures. Thus, this bound moisture has dramatic effects on cure (Wendler and Frazier 1996a; He and Yan 2005) and, in some cases, the wood species will also affect pMDI reaction kinetics (Das et al. 2007). In the absence of moisture, or under conditions where isocyanate molar equivalents exceed that of water, the possibility of carbamate and allophanate formation exists. This is because pMDI (1) wets lumina surfaces more effectively than aqueous resins (Dunky and Pizzi 2002); (2) flows into macrovoids if given access by a fracture

(Roll et al. 1990; Roll 1993); and (3) has the potential to infiltrate the cell wall (Marcinko et al. 1994; Frazier 2002).

Heterogeneous carbamylation of wood cell wall polymers

Isocyanate reactivity with wood and isolated cell wall polymers, through derivatization of the wood hydroxyls via heterogeneous carbamylation, has been the subject of considerable study. Based on thickness swelling data, it was concluded that isocyanate groups must form carbamate linkages with hydroxyl groups in lignin, hemicelluloses, and even to some extent with cellulose microfibrils in wood (Deppe and Ernst 1971). Methyl isocyanate was shown to derivatize southern pine wood blocks, which produced weight percent gains (WPGs) of up to 50% in the absence of catalysts at 120°C and 1.03 MPa (Rowell and Ellis 1979). The degree of substitution of carbamates on Klason lignin was found to be five times higher than that of holocellulose (Rowell 1980). Others found that brown rot lignin reacted approximately 10 times faster than holocellulose when *n*-butyl isocyanate was reacted with Scots pine, catalyzed with pyridine, at 100°C (West and Banks 1986). IR absorption bands characteristic of carbamate linkages in cellulosics were observed after various isocyanates were reacted under catalyzed (Weaver and Owen 1995) and non-catalyzed conditions (Steiner et al. 1980; Rensch and Riedl 1993; Gao et al. 2005).

Characterizing pMDI reactivity with wood

To characterize specific linkages in the cured pMDI-wood bondline, solid-state NMR spectroscopy is a logical choice. A double-isotopically labeled (i.e., ^{15}N and ^{13}C) isocyanate permitted the application of one-dimensional solid-state NMR to detect carbamate crosslinks in the cured pMDI bondline (Zhou and Frazier 2001). However, carbamate and polyurea signals are not well resolved by solid-state NMR; therefore, covalent bonds could not be identified unambiguously in the aforementioned study. Two-dimensional solid-state ^{15}N–^1H correlation NMR experiments have also been conducted with wood and lignin powder treated with pMDI. Different urea-type structures, formed during the reaction of moisture in the wood, were characterized when the MCs of wood were 7% and 14%. Carbamate formation was suggested to occur with lignin powder, but this was not confirmed with model studies. Furthermore, the unfortunately poor peak dispersion and resolution did not allow unambiguous distinction of the urea ^{15}N–^1H correlation from that of the carbamate ^{15}N–^1H correlation (Bao et al. 2003).

High-resolution solution-state NMR spectroscopy is capable of characterizing detailed molecular structures of wood. With the development of larger NMR magnets, cryogenically cooled probes and sophisticated pulse programs, wood cell wall polymers are amenable to detailed investigation. Structural details of the major cell wall polymers have been revealed based on non-degradative (Lu and Ralph 2003) and non-derivatized (Yelle et al. 2008) wood dissolution combined with ^{13}C–^1H one-bond heteronuclear single quantum coherence (HSQC) spectroscopy. This technique has a high potential for answering the question whether and to what degree isocyanates have reacted with wood cell wall polymers.

Objective

The objective of this study was to determine the reactivity of pMDI model compounds with loblolly pine earlywood at different MCs. The working steps included: (1) derivatizing wood polymer hydroxyls with carbamates using phenyl isocyanate and 4-benzylphenyl isocyanate; (2) detection of carbamate formation with solution-state NMR and elucidating its regiochemistry, based on the dataset derived from model substrates as described by Yelle et al. (2011); (3) quantifying carbamate formation by two-dimensional volume integration of specific contours in HSQC spectra; and (4) determination of pMDI model compound reactivity with wood under conditions that mimic industrial OSB manufacturing.

Materials and methods

Chemicals

All reagents were from Aldrich Chemical Company (Milwaukee, WI, USA). Phenyl isocyanate and 4-benzylphenyl isocyanate (pMDI model compounds) and distilled *N,N*-dimethylacetamide (DMAc) were dried over 3 Å molecular sieves. *N*-Methylimidazole-d_6 was synthesized as described previously (Yelle et al. 2008).

Sample preparation and composition analysis

Loblolly pine (*Pinus taeda*) microtomed wood was prepared with a sled microtome (serial 3423) (Spencer Lens Company, Buffalo, NY, USA). Tangential earlywood sections (50 μm thick × 20 mm × 20 mm, and 300 μm thick × 20 mm × 20 mm) were cut. The sections were refluxed in acetone to remove any acetone extractables, dried and equilibrated at 0%, 5% and 14% MC (i.e., in chambers with P_2O_5, saturated $CaBr_2$ and saturated NaCl, respectively) prior to reactions with pMDI model compounds. The polysaccharide composition of the loblolly pine sapwood was analyzed by high pH anion-exchange chromatography (Davis 1998). Klason lignin was determined according to the standard acid-hydrolysis method (ASTM 1996). Results of these analyses are shown in Table 1.

Reactions with pMDI model compounds

For the reactions in DMAc, loblolly pine sections (50 μm thick) were removed from their respective humidity-controlled chambers and 8 sections per sample treatment were weighed (approx. 100 mg) and added to 5 ml of DMAc in a 50 ml round-bottom flask. Phenyl isocyanate or 4-benzylphenyl isocyanate was then added to the flask (1.88 mmol for a 2:1 NCO:OH molar ratio and 0.94 mmol for a

Table 1 Chemical composition of loblolly pine wood investigated in this study.

Klason lignin (%)	Glc (%)	Man (%)	Xyl (%)	Gal (%)	Ara (%)	Rha (%)	Extract. (%)
30.1	40.9	10.3	5.5	3.5	1.0	0.1	9

1:1 NCO:OH molar ratio). Reactions were carried out under a purge of N_2 at 160°C and refluxed for 2 h. After all reactions, dry methanol was added to quench the excess isocyanate. For the treatments in a miniature hot press, an automated bond evaluation system (Humphrey and Zavala 1989) was applied at 160°C for 10 min at approximately 10 bar to press-treat loblolly pine sections (300 μm thick) with 0.94 mmol of 4-benzylphenyl isocyanate. Then, the treated wood sections were refluxed in acetone to extract the byproducts (e.g., diphenyl urea and methyl carbamate) and the sections were dried at 45°C overnight under vacuum. The weight gains of reacted and press-treated wood, along with extracted byproducts, were measured to 0.01 mg accuracy (Mettler-Toledo, Columbus, OH, USA; model XS105 analytical balance). Separation and purification of methyl carbamate and diphenyl urea was performed as described previously (Yelle et al. 2011).

Preparation for NMR

Ball-milling of the isocyanate-reacted microtomed wood (approx. 200 mg) was prepared in a Retsch PM100 planetary ball-mill (Newtown, PA, USA) equipped with a 50 ml ZrO_2 jar. Initial milling was for 1 h under mild conditions (300 rpm, 10 min pause every 20 min, eight 10 mm plus three 20 mm ZrO_2 balls) and for 3 h (600 rpm, 10 min pause every 20 min, ten 10 mm ZrO_2 balls); the jar temperature remained at <50°C. Ball-milling of unreacted microtomed wood was prepared similarly.

Solution-state NMR

Approximately 50 mg of the ball-milled loblolly pine was dissolved directly in a 5-mm NMR tube with dimethylsulfoxide-d_6 (DMSO-d_6) and N-methylimidazole-d_6 (NMI-d_6) aided by sonication. NMR experiments (^{1}H, ^{13}C, HSQC) were acquired at 50°C on a Bruker DMX-500 instrument equipped with cryogenically cooled 5-mm TXI ^{1}H/^{13}C/^{15}N gradient probe with inverse geometry (proton coils closest to the sample). The central DMSO-d_6 solvent peak was taken as an internal reference (δ_C = 39.5 ppm, δ_H = 2.49 ppm). Adiabatic HSQC experiments (Bruker pulse program, hsqcetgpsisp2.2) (Kupče and Freeman 2007) had the following parameters: sweep width, 9.0–1.0 ppm in F_2 (^{1}H) (1698 data points, acquisition time, 170 ms) and 150–10 ppm in F_1 (^{13}C) (420 increments, F_1 ''acquisition time,'' 11.93 ms). The number of scans was 32 with a 1-s interscan delay, the d_{24} delay was set to 0.89 ms (approx. 0.125/J, where J is an average 145 Hz ^{13}C–^{1}H coupling constant) and the total acquisition time was 4 h 28 min. Processing included typical matched Gaussian apodization in F_2 and squared cosine-bell apodization in F_1. Volume integration of HSQC contours was performed on Bruker's TopSpin 2.1 software.

Results and discussion

The following assumptions are the basis of the present study: (1) the reactivity of the isocyanate group in the pMDI model compounds is identical to that of the isocyanate group in the pMDI adhesive. This was validated by choosing 4-benzylphenyl isocyanate, a model compound that mimics the 4,4′-MDI adhesive structure, less one NCO group. (2) The accessibility of cell wall polymers and steric mobility of the model compounds is similar to the low molecular weight fractions in pMDI adhesive. Because typical pMDI adhesive formulated for OSB contains approximately 50% MDI monomer (Frazier 2003), this assumption is realistic. (3) The

bound water in the cell wall has the same reactivity as the water in the cell lumen. In reactions where DMAc is used, bound water can be extracted out of the cell wall before reacting with isocyanate. However, this would not change the NCO:OH molar ratio in solution, thus maintaining the competition reaction in solution as found under neat conditions.

The reactivity of loblolly pine towards pMDI was then assessed. Previous literature suggests that, compared to wood polysaccharides, lignin is kinetically favored to react with isocyanates (Rowell 1980; West and Banks 1986). Lignin, a combinatorial and racemic biopolymer of phenylpropanoid subunits connected via ether and carbon-carbon bonds, and in which the cell wall polysaccharides are embedded, is mainly composed (in conifers) of β-aryl ether, phenylcoumaran, pinoresinol and dibenzodioxocin linkages (Boerjan et al. 2003). Table 2 shows the relative abundance of these linkages for loblolly pine as determined by contour integration in HSQC NMR spectra. Given that earlywood (EW) has more free-volume and higher lignin content than latewood (LW) in coniferous trees (Ritter and Fleck 1926; Wilson and Wellwood 1965; Larson 1966; Stamm and Sanders 1966; Wu and Wilson 1967; Fukazawa and Imagawa 1981) and that pMDI is thought to interact intimately with lignin and hemicelluloses in the cell wall (Marcinko et al. 1994, 1998; Frazier and Ni 1998), reacting pMDI with loblolly pine EW became the focus of this study. Microtoming the EW sections (tangentially) to 50 μm provides wood material that averages one-cell thickness, giving the isocyanate ample opportunity to react. Moreover, the DMAc, being an excellent wood swelling solvent (Mantanis et al. 1994), increases the free-volume between cell wall polymers. The reaction conditions for the microtomed wood are summarized in Table 3. Abbreviations in the sample codes are: Ph = phenyl isocyanate; BPh = 4-benzylphenyl isocyanate; numbers between slashes = first, molar ratio of NCO:OH and second, % moisture content (MC); DMAc = mixture reacted in N,N-dimethylacetamide; Press = mixture reacted in a miniature hot press. Note that NCO:OH is the molar ratio of the number of accessible isocyanate groups to the number of accessible OH groups in the wood cell wall polymers.
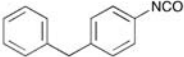
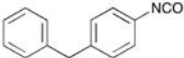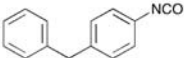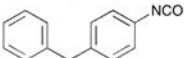### Reactions with phenyl isocyanate

The WPG of the reacted wood was determined after acetone extraction, leaving only wood carbamates. The highest WPG

Table 2 Relative abundance of lignin structures in acetylated cell walls of loblolly pine as determined by HSQC integration of their respective ^{13}Cα–^{1}Hα contours.

Structure	Relative integral	(%)[a]
β-aryl ether	1.00	64
Phenylcoumaran	0.45	29
Pinoresinol	0.06	4
Dibenzodioxocin	0.05	3

[a]Based on the sum of the integrals.

Table 3 Reaction conditions, weight percent gain (WPG) of derivatized microtomed wood and extractable products (MeC, methyl carbamate; DPU, diphenyl urea) recovered.

Sample codes (abbreviations)	pMDI model	Molar ratio NCO:OH[a]	MC (%)	DMAc[b] or hot press[c]	WPG of wood[d] (%)	Extractables (mmol)	
						MeC	DPU
Control			0	DMAc			
Ph/2:1/0% C/DMAc	NCO	2:1	0	DMAc	31.7	1.04	0.10
Ph/1:1/0% MC/DMAc	NCO	1:1	0	DMAc	14.8	0.32	0.08
Ph/1:1/5% MC/DMAc	NCO	1:1	5	DMAc	12.9	0.18	0.31
Ph/1:1/14% C/DMAc	NCO	1:1	14	DMAc	6.7	0.06	0.83
BPh/1:1/0% C/DMAc	NCO	1:1	0	DMAc	0.5	0.93	0.13
BPh/1:1/0% MC/Press	NCO	1:1	0	Press	3.9		
BPh/1:1/5% MC/Press	NCO	1:1	5	Press	0.1		
BPh/1:1/14% MC/Press	NCO	1:1	14	Press	-0.5		

[a]See Yelle et al. (2011) for a description of determining NCO:OH ratio for these reactions.
[b]N,N-dimethylacetamide at 160°C.
[c]25 mm×25 mm, 160°C, approximately 10 bar (1.03 MPa).
[d]Based on dry weight of original wood.
Abbreviations in the sample codes: Ph, phenyl isocyanate; BPh, 4-benzylphenyl isocyanate; numbers between slashes, first, molar ratio of NCO:OH and second, % moisture content (MC); DMAc, mixture reacted in N,N-dimethylacetamide; Press, mixture reacted in a miniature hot press.

of all reacted microtomed wood samples (31.7%) was found with sample Ph/2:1/0% MC/DMAc. This is twice the WPG obtained by Ph/1:1/0% MC/DMAc, indicating that carbamylation is highly dependent on NCO concentration. When moisture is added, as with samples Ph/1:1/5% MC/DMAc and Ph/1:1/14% MC/DMAc, the WPG, i.e., the frequency of carbamylation, decreases. Clearly, the phenyl isocyanate reacts with water as demonstrated by the increase in extractable diphenyl urea along with the decrease in methyl carbamate (Table 3).

Figure 1 is a key to the structures found in all the HSQC spectra to follow. HSQC spectra from the phenyl isocyanate derivatized loblolly pine sections (samples Ph/2:1/0% MC/DMAc, Ph/1:1/0% MC/DMAc, Ph/1:1/5% MC/DMAc and Ph/1:1/14% MC/DMAc) are displayed in Figures 2–4; all spectra are scaled to give similar methoxyl peak intensities. Figure 2 depicts the aliphatic and anomeric region of the HSQC spectrum of Ph/2:1/0% MC/DMAc showing a high level of lignin derivatization along with some polysaccharide derivatization. For example, in the aliphatic region (Figure 2a) the β-aryl ether (structure A) and phenylcoumaran (structure B) γ-C/H side-chain chemical shifts of 4.33/63.05 ppm (C-Aγ) and 4.39/64.76 ppm (C-Bγ) are consistent with the derivatized milled-wood lignin (MWL) and derivatized structure A model compounds (Yelle et al. 2011). Also, the α-position of A structures prove reactivity; the α-C/H con-

tour of the derivatized structure A demonstrates that both the *erythro*- and *threo*-stereoisomers of the carbamate derivative are present (6.02/73.59 and 6.13/74.39 ppm, respectively), with a slight preference for the *erythro*-isomer. Hemicellulose reactivity is also evident from the spectra. For example, the H2/C2 (5.45/63.30 ppm) and H3/C3 (5.03/73.09 ppm) contours of carbamylated β-D-mannopyranosyl (C-Man) units are shown in the spectrum in purple, along with derivatized saccharides that are currently unassigned (yellow contours). In the anomeric region (Figure 2b), the internal β-D-mannopyranosyl (Man) units H1/C1 has a new correlation (4.92/100.10 ppm) downfield from its non-derivatized correlation (4.59/100.20), thus confirming H2/C2 and H3/C3 derivatization. Additionally, the terminal α-L-arabinofuranosyl (Ara) units H1/C1 correlation has shifted downfield slightly from its non-derivatized correlation (4.86/108.13 ppm) to 5.03/108.40 ppm, suggesting derivatization of C2, C3 or C5 hydroxyls. Incidentally, the anomeric region displays no internal β-D-galactopyranosyl (Gal) unit correlations; such components, particularly prominent in compression wood zones, are typically found at 4.33/105.4 ppm.

Figure 3 presents the HSQC spectra of Ph/1:1/0% MC/DMAc in both the aliphatic and anomeric regions. In the spectra, the decrease in NCO:OH concentration from 2:1 to 1:1 gives a dramatic decrease in structure A and structure B
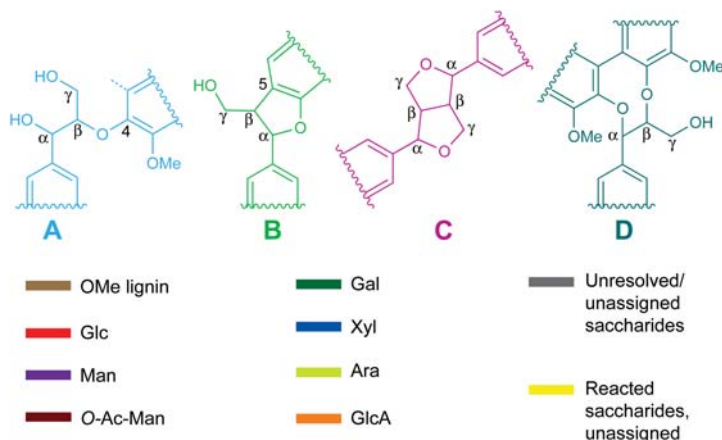
Figure 1 A key to the wood polymer structures found in the HSQC spectra for Figures 2, 3 and 4. All contour colors can be matched to their respective structure: (A) β-aryl ether, cyan; (B) phenylcoumaran, light green; (C) pinoresinol, raspberry; (D) dibenzodioxocin, sea green; (OMe) lignin methoxyls, brown; (Glc) β-D-glucopyranosyl units, red; (Man) β-D-mannopyranosyl units, purple; (O-Ac-Man) acetylated β-D-mannopyranosyl units at C2 and C3, maroon; (Gal) β-D-galactopyranosyl units, forest green; (Xyl) β-D-xylopyranosyl units, blue; (Ara) α-L-arabinofuranosyl units, chartreuse; (GlcA) 4-O-methyl-α-D-glucuronic acid, orange; unresolved or unassigned saccharides, gray; and reacted saccharides currently unassigned, yellow.

reactivity. The Man hydroxyls display no derivatization in this sample, but some hemicellulose derivatization is evident by the presence of the contours shown in yellow. The anomeric region (Figure 3b) shows a small terminal Ara H1/C1

correlation at 5.03/108.40 ppm, indicative of some Ara derivatization.

Figure 4a and b show the HSQC spectra of samples Ph/1:1/5% MC/DMAc and Ph/1:1/14% MC/DMAc in only the
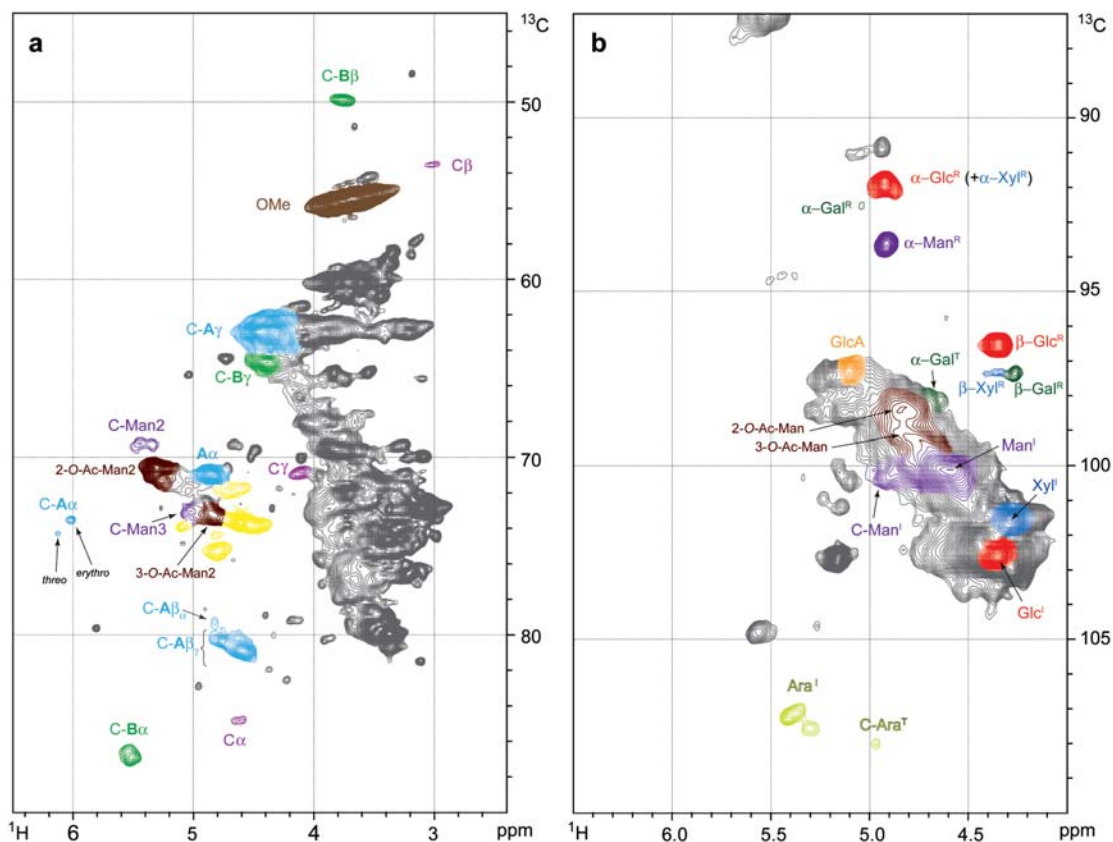

Figure 2 HSQC spectrum of sample Ph/2:1/0% MC/DMAc showing (a) aliphatic region and (b) anomeric region. Structures labeled with a ''C-'' represent carbamylation. In (a), the C-Aβ$_\alpha$ and C-Aβ$_\gamma$ refer to Aα- and Aγ-derivatization, respectively. In (b), the α- and β- refer to the two anomers found in a particular saccharide. The superscripts I, T and R refer to internal, terminal and reducing end-group units, respectively, for that particular saccharide. For a key to the structure codes see Figure 1.

Figure 3 HSQC spectrum of sample Ph/1:1/0% MC/DMAc showing (a) aliphatic region and (b) anomeric region. Structures labeled with a ''C-'' represent carbamylation. In (a), the C-Aβ_γ refers to A$_\gamma$-derivatization. In (b), the α- and β- refer to the two anomers found in a particular saccharide. The superscripts I, T and R refer to internal, terminal and reducing end-group units, respectively, for that particular saccharide. For a key to the structure codes see Figure 1.
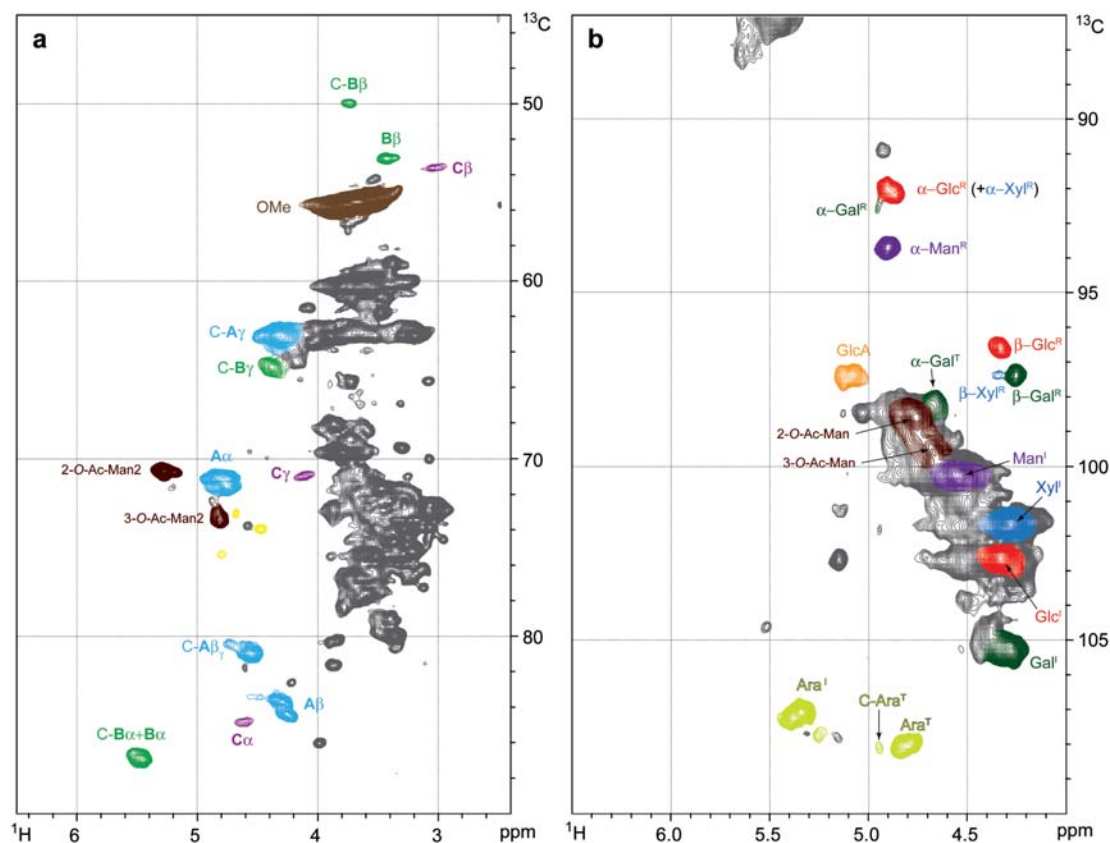
aliphatic region (Figure 4c and d will be discussed later). With Ph/1:1/5% MC/DMAc, the structure A and B γ-hydroxyls are partially derivatized (C-Aγ and C-Bγ), accompanied only by minor hemicellulose derivatization (not shown); all derivatization is much less evident here because of the competition of the water in the wood for the isocyanate. As the MC was increased to 14%, as in Ph/1:1/14% MC/DMAc, the derivatization of lignin side-chains decreased even further, demonstrating that even when a high concentration of isocyanate is present in solution, water is kinetically dominant and reaction of the isocyanate with water (and the subsequent aromatic amine) will be favored over reaction with the wood hydroxyls.

One of the many advantages of the adiabatic pulse sequence used during HSQC acquisition is its J-independence and its offset insensitivity over an essentially unlimited active bandwidth, allowing for quantitative measurements (Kupče and Freeman 2007; Koskela et al. 2010). For example, J-refocusing allows for making ^{13}C–^{1}H spin-spin couplings more uniformly distributed by matching the direction and sweep rate of the adiabatic pulse with the natural distribution of the $^{1}J_{C-H}$-couplings (Kupče 2001). Moreover, quantification errors caused by T_2 relaxations are eliminated by meeting the following criteria described by Zhang and Gellerstedt (2007): the selected internal standard contour and substrate contour should originate from the same type of polymer, have similar structural features, contain the same number of directly bound proton(s), have similar ^{13}C chemical shift values and similar $^{1}J_{C-H}$ values.

Quantification of carbamates on lignin side-chains, shown in Table 4, was performed using two-dimensional NMR volume integration of the Aα, Aβ and Bβ contours in HSQC spectra. The internal standards chosen were the contours representing the non-derivatized Aα and Aβ (Hα/Cα and Hβ/Cβ) and Bβ (Hβ/Cβ), whereas the substrate contours were represented by the derivatized Aα and Aβ (Hα/Cα and Hβ/Cβ) and Bβ (Hβ/Cβ). Because the γ-^{13}C–^{1}H correlations from structures A and B of carbamylated wood overlap with polysaccharide contours [e.g., C6/H6 of β-D-glucopyranosyl (Glc) units], direct integrations of the derivatized Aγ-C/H and Bγ-C/H contours are not possible. However, from the chemical shift data obtained on partially derivatized structures A and B model compounds (i.e., derivatized at the γ-position only), the β-position contours show distinct separation in the derivatized vs. the non-derivatized model compounds (Yelle et al. 2011). These β-contours were used for quantifying γ-reactivity of lignin side-chains. Because the contours of the α-hydroxyl of structure A were well dispersed, reactivity of the Aα position was quantified by direct integration of the Aα contours. Each contour integration was performed in triplicate on the same spectrum and the average value (along with standard deviation) is reported in Table 4.
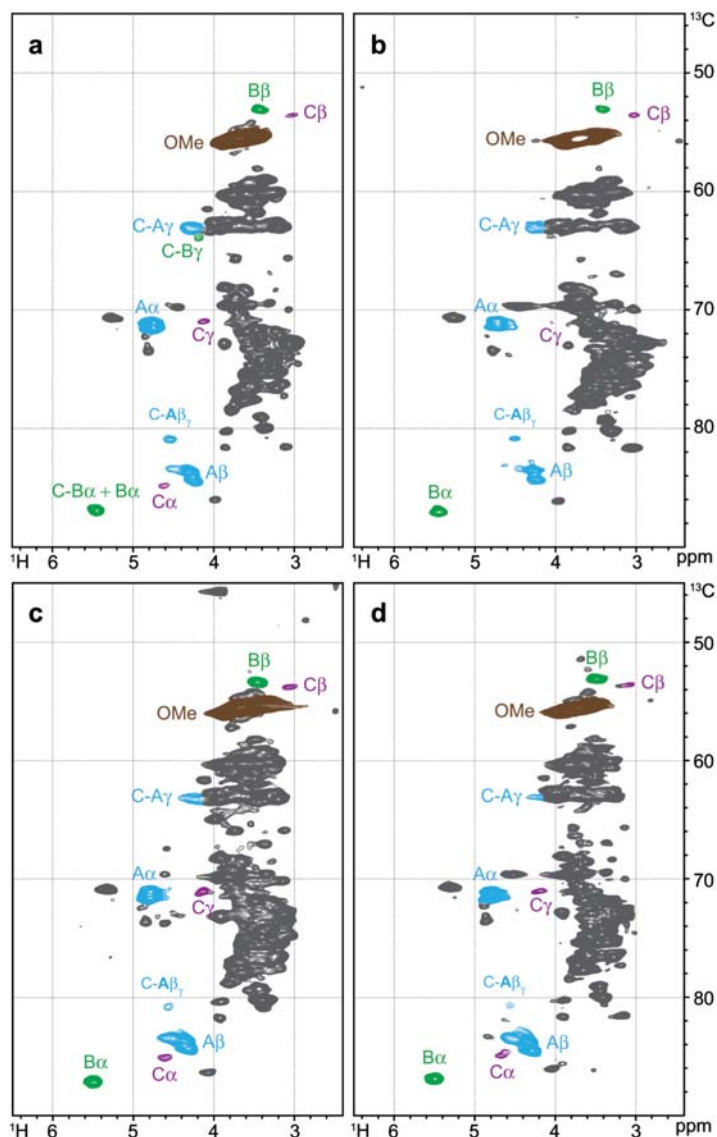
Figure 4 HSQC spectra of (a) sample Ph/1:1/5% MC/DMAc, (b) sample Ph/1:1/14% MC/DMAc, (c) sample BPh/1:1/0% MC/DMAc and (d) sample BPh/1:1/0% MC/Press, all showing the aliphatic regions. In all spectra, the C-Aβ_γ refers to A$_\gamma$-derivatization. Structures labeled with a ''C-'' represent carbamylation. For a key to the structure codes see Figure 1.

The loblolly pine reactions in DMAc displayed high lignin side-chain reactivity with phenyl isocyanate under 0% MC conditions. Sample Ph/2:1/0% MC/DMAc gave 94% and 90% carbamylation of the Aγ- and Bγ-hydroxyls with 18% carbamylation of Aα-hydroxyls. Sample Ph/1:1/0% MC/DMAc revealed that the Aγ-, Bγ- and Aα-hydroxyls had reacted to 44%, 38% and 2%, respectively. As the MC increased to 5% (Ph/1:1/5% MC/DMAc), 14% of the Aγ- and 13% of the Bγ-hydroxyls had reacted along with 0.6% of the Aα-hydroxyls. At a MC of 14% (Ph/1:1/14% MC/DMAc), 9% of the Aγ- and 7% of the Bγ-hydroxyls had reacted.

Reactions with benzylphenyl isocyanate

When 4-benzylphenyl isocyanate was chosen as the pMDI model compound in DMAc (BPh/1:1/0% MC/DMAc),

approximately 14% of the obtainable WPG was lost compared to phenyl isocyanate (Ph/1:1/0% MC/DMAc, Table 3). Because the functionality is identical for the two pMDI models, this result is most probably caused by a size effect of the bulkier 4-benzylphenyl group compared to the phenyl group. For treatments that utilized the miniature hot press, only 4-benzylphenyl isocyanate was used because 160°C (press temperature) was too close to the boiling point of phenyl isocyanate. For BPh/1:1/0% MC/Press, the WPG was approximately 4%. This is an eight-fold increase in weight over that of BPh/1:1/0% MC/DMAc; however, this does not necessarily mean that carbamylation has increased; urea- or biuret-type structures could have been entrapped in the hot pressed wood cells, and these might not be fully extractable with acetone. No weight gains were detected for BPh/1:1/ 5% MC/Press (at 5% MC) and BPh/1:1/14% MC/Press (at 14% MC) after acetone extraction.

Table 4 Arithmetic mean and standard deviation for percent lignin side-chain derivatization in microtomed wood with pMDI model compounds as determined by contour integration in HSQC spectra.

Sample codes	Aγ		Aα		Bγ	
Ph/2:1/0% MC/DMAc	94.1	*0.3*	18.0	*0.5*	90.0	*0.1*
Ph/1:1/0% MC/DMAc	44.2	*0.5*	2.5	*0.1*	37.6	*0.5*
Ph/1:1/5% MC/DMAc	14.4	*0.4*	0.59	*0.09*	12.6	*0.3*
Ph/1:1/14% MC/DMAc	8.9	*0.1*	nd		6.8	*0.2*
BPh/1:1/0% MC/DMAc	4.6	*0.4*	nd		1.9	*0.04*
BPh/1:1/0% MC/Press	5.5	*0.5*	nd		nd	
BPh/1:1/5% MC/Press	nd		nd		nd	
BPh/1:1/14% MC/Press	nd		nd		nd	

Aγ, Aα and Bγ structures are shown in Figure 1.
Italic font denotes standard deviation.
nd, none detected.
For sample codes see Table 3.

HSQC spectra from the 4-benzylphenyl isocyanate derivatized loblolly pine sections (samples BPh/1:1/0% MC/DMAc and BPh/1:1/0% MC/Press) are presented in Figure 4c and d; samples BPh/1:1/5% MC/Press and BPh/1:1/14% MC/Press displayed no distinguishable changes in their HSQC spectra, and thus were identical to the control spectra (see Figure 5 in Yelle et al. 2011). Sample BPh/1:1/0% MC/DMAc displayed little derivatization of the Aγ and no derivatization of structure B or hemicelluloses. Sample BPh/1:1/0% MC/Press was hot pressed as in industrial applications, but again, little derivatization of the Aγ and no derivatization of structure B or hemicelluloses was found.

Quantification of carbamates on the structure A side-chains, as previously described, was performed by means of two-dimensional NMR volume integration of the Aβ con-
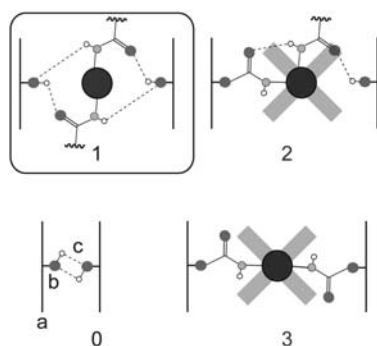

Figure 5 A hypothetical scheme showing how pMDI can interact with wood cell walls during OSB production at the macromolecular scale. Labels are as follows: a, hypothetical chain that is part of the cell wall; b, hydroxyl group; c, physical bond; dark gray dots, oxygen atoms; empty circles, hydrogen atoms; light gray dots, nitrogen atoms; and black circles represent bulky adhesive polymer. In the scheme, state 0 is the initial untreated state showing physical bonding between cell wall polymers, state 1 is the bulky adhesive polymer with physical bonding only, state 2 is bulky adhesive polymer covalently bonded to wood with physical bonding, and state 3 is bulky adhesive polymer covalently bonding across wood cell wall polymers to form a crosslink. Note that states 2 and 3 have been deemed non-contributors to pMDI adhesion. Models by Norimoto et al. (1992) were used as a starting point to derive this scheme.

tours (Table 4). When microtomed wood in DMAc was reacted with 4-benzylphenyl isocyanate (BPh/1:1/0% MC/DMAc), the Aγ- and Bγ-hydroxyl reactivity was only 5% and 2%, respectively. Compared to Ph/1:1/0% MC/DMAc, this is a drop of approximately 39% in Aγ-reactivity. This infers that the bulkier benzylphenyl isocyanate, as compared to the phenyl isocyanate, has limited access to most lignin side-chains. When microtomed wood (300 μm thick) was bonded in the hot press with a 1:1 NCO:OH molar ratio (BPh/1:1/0% MC/Press), 6% of the Aγ-hydroxyls reacted. No carbamate formation was detected with two-dimensional NMR using the hot press at 5% MC (BPh/1:1/5% MC/Press) or at 14% MC (BPh/1:1/14% MC/Press).

Hypothesis of pMDI macromolecular scale interactions

The results establish that at a MC ≥5% wood polymers do not react with pMDI under the industrial OSB conditions employed here. These results confirm previous research conducted on loblolly pine matchstick specimens treated with neat pMDI adhesive (Yelle et al. 2010). The long-hypothesized wood carbamate formation therefore appears to be negligible and cannot therefore be responsible for the bonding mechanism of pMDI. It is probable that nanoscale physical interactions are responsible for bond stability due to their resistance to hydrolysis. Even though several studies have not found conclusive evidence of pMDI cell wall infiltration (Frazier and Ni 1998; Buckley et al. 2002; Gindl et al. 2004), other studies suggest the opposite. For example, if pMDI adhesive is able to infiltrate the cell wall it is most likely to occur via low molecular weight components that diffuse (Marcinko et al. 1994) into the cell wall microvoids (Persson et al. 2004) causing minute swelling of the matrices (Frazier 2002). Then pMDI can react with bound water to form polyurea and possibly polyuret (Wendler and Frazier 1996b) to promote hydrogen bonding and van der Waals interactions. Once pMDI is absorbed into the polymer free-volumes within the hemicelluloses and lignin matrices, it can intimately interact with wood polymer chains giving pMDI the opportunity to alter the cell wall mechanical properties at the nanoscale (Jakes et al. 2010).

Figure 5 is an illustration of how pMDI can interact with wood at the macromolecular scale. States 2 and 3 represent improbable contributors to pMDI adhesion. The adhesion strength derived from the formation of hydrogen bonds and van der Waals interactions (state 1) is essential.

Conclusions

- HSQC spectra of the reacted microtomed wood can be interpreted in the following way: wood treated with pMDI model compounds having high NCO:OH molar ratios in a swelling solvent under dry conditions reacts mainly with the lignin components; the side-chains in β-aryl ether and phenylcoumaran linkages are the main reaction sites. The primary γ-hydroxyls react first and then the secondary

α-hydroxyls. Minor reactivity was observed with mannan (and possibly with arabinan) at their secondary hydroxyls (C2 and C3), and primary hydroxyls (C6 and C5).

- As MC was elevated from 0% to 5% and 14% and NCO:OH molar ratios diminished from 2:1 to 1:1, the reactivity of the OH groups attached on lignin side-chains decreased considerably.
- Under identical reaction conditions, phenyl isocyanate reacts with β-aryl ether γ-hydroxyls approximately 9 times more frequently than 4-benzylphenyl isocyanate. This finding is interpreted to signify that the molecular size of the infiltrating pMDI model compound controls carbamate formation to a large extent.
- If pressing parameters similar to those used in industrial OSB production are applied at 0% MC in conjunction with a high NCO:OH molar ratio, 6% of the β-aryl ether γ-hydroxyls are derivatized with carbamates.
- No carbamate formation was detected in microtomed wood pressed in a miniature hot press (conditions: 4-benzylphenyl isocyanate at 5% and 14% MC), even if a high NCO:OH molar ratio was applied.
- Based on the data presented here, covalent (i.e., wood carbamate) bond formation is not a probable mechanism for pMDI-wood bonding.
- This research demonstrates that pMDI model compounds can effectively probe the reactivity of hemicelluloses and lignin matrices at the nanoscale level.

Acknowledgements

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