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Elucidating How Wood Adhesives Bond to Wood Cell Walls using High-Resolution Solution-State NMR Spectroscopy

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Introduction

Some extensively used wood adhesives, such as pMDI (polymeric methylene diphenyl diisocyanate) and PF (phenol formaldehyde) have shown excellent adhesion properties with wood. However, distinguishing whether the strength is due to physical bonds (i.e., van der Waals, London, or hydrogen bond forces) or covalent bonds between the adherend and the adhesive is not fully understood. Previous studies, where pMDI model compounds were reacted with wood, showed that carbamate (urethane) formation with wood polymers is only possible when: 1. the number of moles of isocyanate is significantly higher than the moles of water molecules in the wood, 2. high temperatures are used, and 3. the isocyanate-based compound is of low molecular weight [1]. A complementary study confirmed that covalent bond formation between a pMDI adhesive and wood does not occur [2]. PF adhesive, like pMDI, has shown strong evidence for wood cell wall infiltration [3-8]. Thus, there is a definite need to discern how wood cell wall polymers interact with PF adhesive on a molecular and Ångstrom scale. This is especially important to understand when attempting to utilize lignin byproducts as PF resin substitutes.

The mechanism of alkaline catalyzed PF curing is a two stage reaction. The initial stage involves enolate formation with resonance stabilized ionization of the 2-, 4-, and 6-positions of the phenol followed by methylol formation via nucleophilic attack of the excess formaldehyde. During the second stage, the temperature is increased and the resols condense to form methylene bridges via a quinone methide intermediate (Figure 1). Methylene ether bridges (if formed) tend to revert to methylene bridges [9].

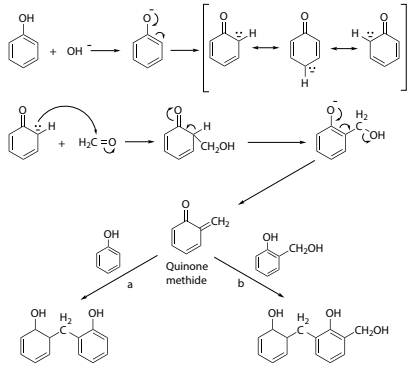

Figure 1. Alkaline catalyzed reaction of phenol with formaldehyde to form reactive methylols, which condense and polymerize to form PF resin.

Lignin, 25-30% of wood, is a phenolic polymer made up of branched phenylpropanoid units that are capable of reacting with other phenols during adhesive bonding. Model compound studies have shown that under alkaline conditions and ≥100 °C, β-aryl ether linkages release formaldehyde to give vinyl ether linkages (Figure 2a) [10]. Phenylcourmaran linkages release formaldehyde in a similar fashion to give stilbene linkages (Figure 2b) [10]. ^{13}C NMR spectroscopy showed that most of this released formaldehyde ends up as the methylene bridge between the 5-positions on guaiacyl units (Figure 2c) [11].

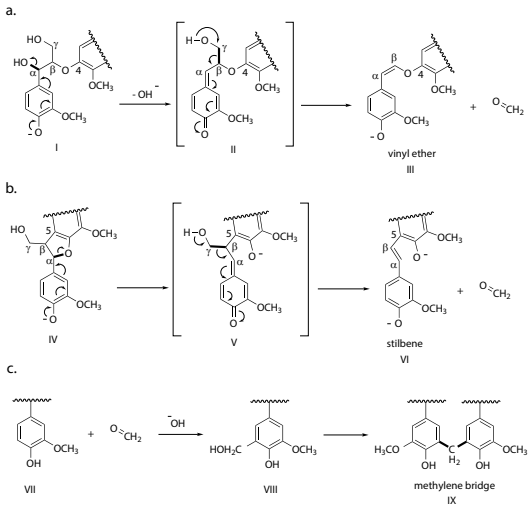

Figure 2. Lignin hydrolysis of β-aryl ether (a) and phenylcoumaran (b) linkages and methylene bridge formation (c) via condensation of formaldehyde with free-phenolic units.

In this study, wood cell wall polymer reactivity is investigated when PF adhesive is bonded to earlywood and latewood of loblolly pine. Solution-state NMR spectroscopy of dissolved PF-wood sections are analyzed for changes in chemistry using a 2D ^{1}H-^{13}C-correlation experiment. If the wood polymers are modified during the bonding process, the chemical shifts of the native wood polymers will move accordingly, thus revealing which wood polymer structures are reacting with PF, and to what degree.

Experimental

Microtomed wood preparation

Loblolly pine cubes $(20\ mm)^3$ were selected that had tangential sides exactly perpendicular to the radial sides.

The cubes were placed in boiling distilled water for 10 min and then kept submerged for 24 h before sectioning. Microtomed wood was prepared using a sled microtome to give tangential earlywood and latewood sections (0.030 mm radial × 20 mm tangential × 20 mm longitudinal) and equilibrated to a moisture content of 10% using a chamber with a saturated salt solution (NaBr).

PF resin formulation and application

Phenol (10.0 g) and formaldehyde (17.9 g of 37% solution) were charged into a cooled round bottom flask (5 °C) with stirring. After heating to 25 °C, NaOH (1.1 g, 50%) was added dropwise. The mixture was then heated to 70 °C and held for 60 min. After the first cook stage, the second NaOH (0.6 g, 50%) was added quickly to the reaction flask and heated to 85 °C over 15 min. After 45 min the viscosity reached 3.7-4.0 stokes. The adhesive was cooled in an ice bath and refrigerated until use.

The reaction was monitored with thin-layer chromatography using model compounds and PF standards to follow the stages of polymer growth of the resin at about 30 min increments. At each increment, a 2 mL aliquot was removed from the reaction flask and refrigerated. The increments chosen were 60, 90, 120, and 150 min, with the 120 min time-point representing a typical PF adhesive for wood composite production (49% solids).

Each PF aliquot was weighed out onto the wood sections so that the weight of the resin solids was approximately twice the weight of the sections. The sections were then quickly joined together on a glass slide and secured between two glass slides. The assemblies were placed into a non-spouted beaker with a watch glass on top, sat at r.t. for 30 min, heated to 140 °C and held for 1 h.

NMR preparation and experiments

Ball-milling of the PF bonded earlywood and latewood assemblies and controls were prepared as previously described [1].

One sample (20 mg) from each milled assembly was directly placed into a 5 mm NMR tube, 500 µL of DMSO-d_6 was added and was sonicated at 30 °C for 1 h.

NMR spectra were acquired at the University of Wisconsin-Madison on a Bruker-Biospin (Rheinstetten, Germany) AVANCE 500 MHz spectrometer fitted with a cryogenically cooled TCI probe as previously described [1].

Results and Discussion

For simplicity, the 120 min cook-time assemblies are the only assemblies shown with NMR spectra in this paper. The 60, 90, and 150 min cook-time assemblies were also analyzed via NMR, but focused here on the 120 min since this resin gave the target viscosity.

Alkaline hydrolysis of major lignin linkages

Under alkaline conditions the β-aryl ether and the phenylcoumaran linkages are cleaved at the Cβ—Cγ bond, releasing formaldehyde via a quinone methide intermediate to give the vinyl ether and stilbene structures. This chemistry is only possible on linkages that have a free-phenolic group. Hydrolysis of a 4—O branch is likely to occur to some degree under these conditions, thus converting some etherified units to free phenolics.

Previous literature of a vinyl ether model compound showed NMR correlations to be 6.2/112.5 and 7.3/143.0 ppm (Hα/Cα and Hβ/Cβ, *cis*), and 5.6/109.5 and 7.3/145.2 ppm (Hα/Cα and Hβ/Cβ, *trans*), respectively [12, 13]. Figure 3 shows the NMR spectra of the aromatic region of both the earlywood and latewood assemblies that were bonded with a 120 min PF cook-time. From the earlywood-PF samples, the vinyl ether correlations are not visible. Whereas, with the NMR spectra of the latewood-PF samples, the vinyl ether correlations are visible in every cook-time assembly, increasing at the higher cook-times.

Stilbene model compounds have also been studied previously, which typically show correlations of 7.1-7.4/128.5 ppm for both Hα/Cα and Hβ/Cβ, but do tend to overlap with some other lignin aromatics [12]. Thus, these correlations were difficult to confirm with these HSQC experiments alone, but further exploration is underway.

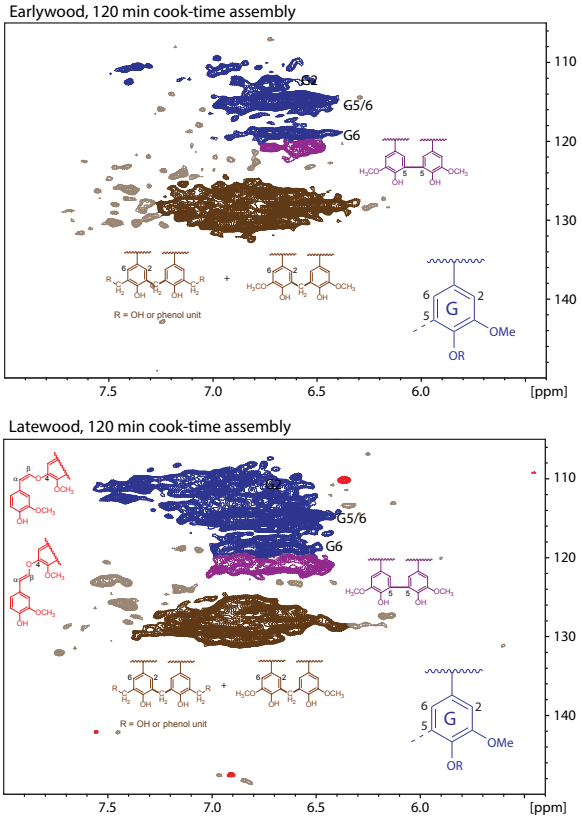

Figure 3. The aromatic region of NMR ^{1}H-^{13}C correlation spectra showing: the earlywood (top) and latewood (bottom) 120 minute cook-time assemblies. The native guaiacyl correlations are blue, the 5-5 (biphenyl) correlations are purple, and the methylene bridge correlations are brown. The vinyl ether correlations (red) are only seen in the latewood assemblies.

Aromatic condensed linkages

The formation of the methylene bridge (aryl—CH_2—aryl), as shown in Figure 1, is the most predominant link-

age formed between PF resins and guaiacyl units in lignin. Evidence for these types of linkages is the presence of correlations in the aromatic region between 6.5-7.5/126-132 ppm, which are shown in Figure 3. Further evidence is the presence of the three methylene correlations around 3.7-3.5/29-40 ppm, which were visible in all PF-wood assembly spectra, shown in Figure 4. The relatively large carbon chemical shift spread of these correlations suggests that these arise from not only the hydroxymethylated PF moieties condensing with phenols (i.e., at the 2, 4, and 6-positions), but the hydroxymethylated PF moieties condensing with the guaiacyl C5 of lignin as well. Other condensed structures are possible, such as the condensation of the primary hydroxyl at Cγ and the secondary hydroxyl at Cα of the β-aryl ether structure with phenols or even with guaiacyl C5's of adjacent lignin structures. Similarly, the primary hydroxyl at Cγ of the phenylcoumaran structure would be another likely condensation site. Thus, all these types of condensation products are likely to give chemical shifts of their methylene in the same vicinity as one another. Model compounds studies are currently underway to confirm these various structures.

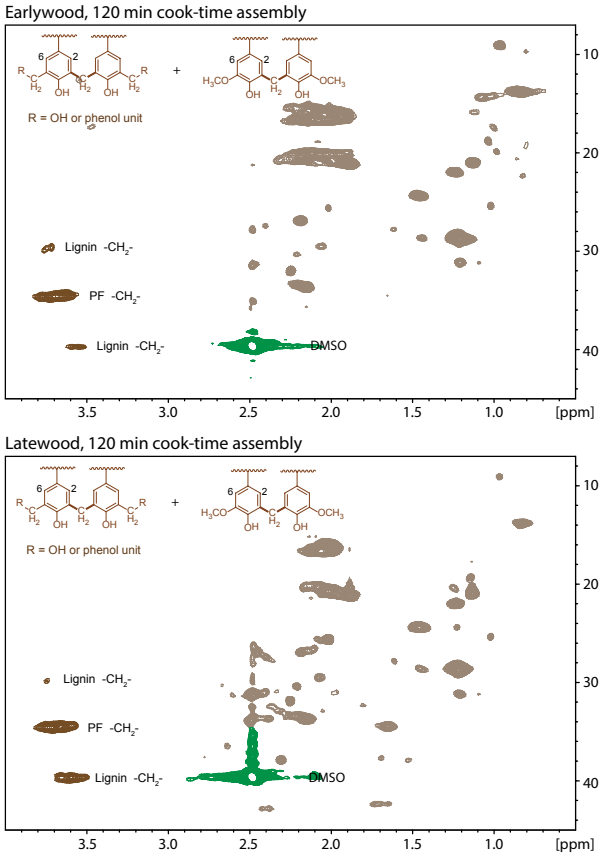

Figure 4. The aliphatic region of NMR ^{1}H-^{13}C correlation spectra showing: the earlywood (top) and latewood (bottom) 120 minute cook-time assemblies. The methylene bridge correlations are shown in brown. The PF methylene bridges were predominant.

Other new correlations in the aromatic region shown in Figure 3 may include those representing structures such as the 5-5 (biphenyl) and the 5-O-4 (aryl-O-aryl) linkages. For these linkages, their 6-position and 2-position H/C correlations tend to shift when the C5 position is condensed. For example, for a biphenyl the C6 correlations tend to shift from 119 ppm (uncondensed at C5) to 122 ppm (condensed at C5 with another C5 phenyl) (Figure 4). Similarly, for an aryl-O-aryl linkage the C2 correlations tend to shift from 111 ppm (uncondensed at C5) to 108-109 ppm (condensed at C5 with an O—4 linkage). The aryl-O-aryl correlations were not discernible in these PF-bonded spectra due to overlapping in these areas.

Depletion of native structures

Another complementary analysis of the NMR spectra is to look at how the chemistry of the original structures has changed. If a particular linkage from a native polymer is cleaved, we would see a depletion of this linkage. The cleaved linkage may become sequentially cleaved further to result in low molecular weight compounds, and/or it could be reacted with another polymer/molecule.

Native lignin linkages that I will mention here include: β-aryl ethers (**A**), phenylcoumarans (**B**), and pinoresinols (**C**). Figure 5 shows a typical spectrum of the sidechain region of earlywood and latewood cell walls with representative spectra after being PF-bonded. Figure 5 only shows the 120 minute cook-time assembly spectra, but it was evident that the most severe depletion of lignin was seen with the PF-bonded earlywood in the 60 min cook-time assembly; all of the **A**, **B**, and **C** structures were cleaved via alkaline hydrolysis due the increased susceptibility of the cell wall to infiltration of alkali. It was not until the 150 min cook-time assembly that some of structure **A** remained in the PF-bonded earlywood, showing that alkaline hydrolysis is lessened potentially due to less alkali present and a decreased chance for mobile compounds to enter the cell wall due to entrapment in the growing polymer. However, these spectra show that even though the higher molecular weight components of PF resin are filtered out of the cell wall, the alkali will infiltrate beyond the PF resin and continue to hydrolyze wood polymers to a certain degree. With the latewood, the depletion of the **A**, **B**, and **C** structures was lessened, showing that the higher polymer density most likely helped limit PF infiltration into the cell wall matrix. The yellow correlations (Figure 5) are tentatively assigned to methylene ether linkages. However, more research is needed to confirm the identity of these correlations.

Polysaccharides, although less reactive than the lignin polymer towards PF, also has the potential to react or become modified during the PF-bonding process. It was clear from the spectra in Figure 5 that the polysaccharides in the earlywood were more heavily degraded and modified than the latewood when bonded with PF, especially in the earlier cook-time assemblies. Complete removal of the native 2-*O*- and 3-*O*-acetyl sidechains along galactoglucomannan and removal of the 4-*O*-methyl-α-D-glucuronic acid sidechains along arabinoglucuronoxylan was evident for all PF-bonded assemblies analyzed.

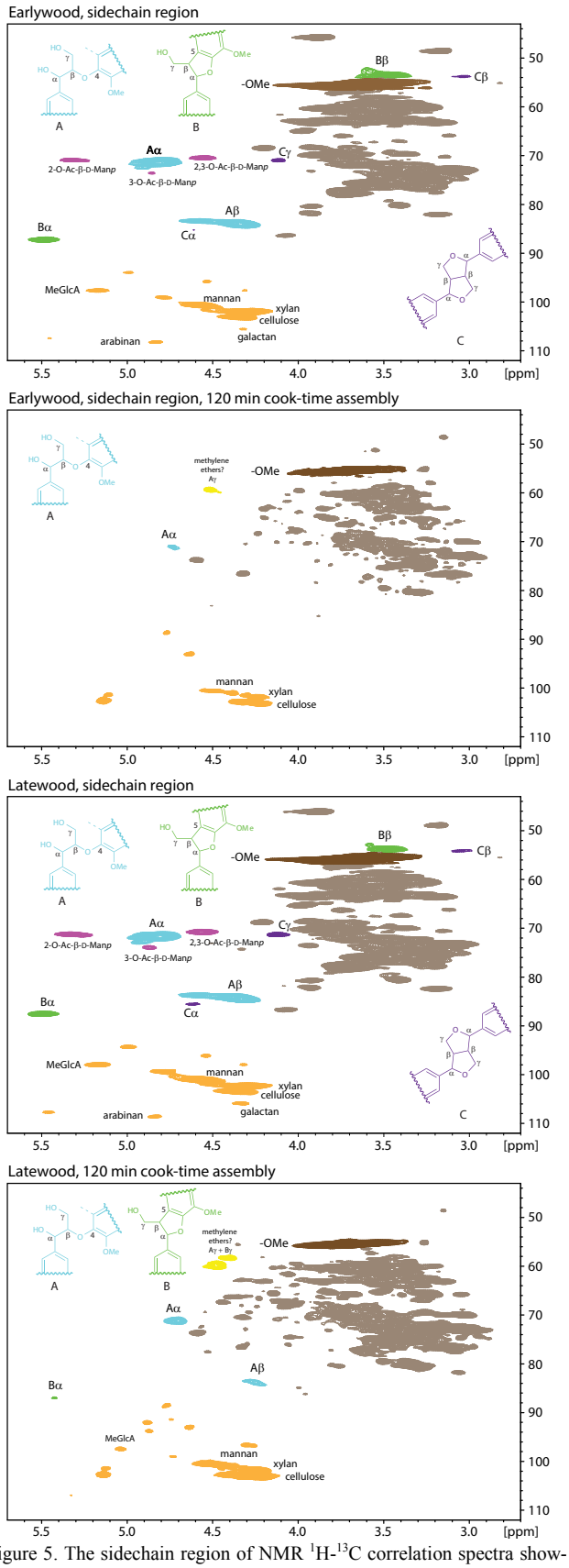

Figure 5. The sidechain region of NMR ^{1}H-^{13}C correlation spectra showing: earlywood without PF resin (top); bonded earlywood with PF resin (2nd from top); latewood without PF resin (3rd from top); and bonded latewood with PF resin (bottom).

Conclusions

Earlywood and latewood microtomed sections were bonded with alkaline PF resin using selected cook-time aliquots. The bonded assemblies were cured, milled, dissolved, and analyzed using solution-state NMR spectroscopy. 2D ^{1}H-^{13}C-correlation (HSQC) experiments revealed the following: 1. Alkaline hydrolysis of the β-aryl ether linkages in lignin gave vinyl ethers with release of formaldehyde; 2. Cleavage of the β-aryl ether and phenylcoumaran linkages were severe in earlywood and in the earlier cook-time assemblies in general; 3. Condensed structures were found not only between hydroxymethylated phenols, but also between α-hydroxyls and γ-hydroxyls of β-aryl ethers; 4. New guaiacyl C5 linkages were evident from the broadened H6/C6 correlations in the aromatic region; 5. Some hemicelluloses were degraded severely in the earlywood and earlier cook-time assemblies; 6. Complete removal of mannan acetates and xylan uronic acids was shown, regardless of growth ring and cook-time assembly. This research demonstrates that the several types of reactions occurring during PF bonding compete simultaneously, either via bond cleavage or bond formation. The lignin and hemicellulose linkages in wood are clearly being modified from their native state during PF bonding, and in some cases are no longer present after PF bonding.

Acknowledgements

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