WCTE 2016
World Conference on Timber Engineering
August 22-25, 2016 | Vienna, Austria

Simultaneous bond degradation and bond formation during phenol-formaldehyde curing with wood

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ABSTRACT: Bonding of wood using phenol–formaldehyde adhesive develops highly durable bonds. Phenol–formaldehyde is believed to form primary bonds with wood cell wall polymers (e.g., lignin). However, it is unclear how this adhesive interacts and bonds to lignin. Through wood solubilisation methodologies, earlywood and latewood bonded assemblies were characterized using two-dimensional ^{1}H–^{13}C solution-state nuclear magnetic resonance spectroscopy so that chemical modification of the wood cell wall polymers, after phenol–formaldehyde resol curing, could be elucidated. The results showed a marked depletion in native lignin and polysaccharide linkages via alkaline hydrolysis. What was also found was formation of methylene bridges between phenol–formaldehyde moieties and lignin, suggesting that bond degradation and bond formation occur at the same time during PF curing with wood.

KEYWORDS: Phenol–formaldehyde, wood cell wall, lignin, curing mechanism, nuclear magnetic resonance

1 INTRODUCTION

Phenol–formaldehyde (PF) adhesives have shown excellent adhesion properties to wood ever since its introduction in the mid-1930s. The mechanisms involved in this adhesion may take the form of physical bonds (i.e., van der Waals, London, or hydrogen bond forces) and chemical bonds between the wood and the adhesive. PF has shown a strong tendency to enter the cell wall micropore structure [1,2]. Therefore, molecular interaction between PF moieties and wood cell wall polymers must take place. Understanding this fundamental interaction has been a tremendous challenge, but is important for developing improved or new wood adhesives.

In this paper, wood cell wall polymer reactivity is delineated via structural characterization of earlywood and latewood of loblolly pine after curing with PF adhesive. Solution-state nuclear magnetic resonance (NMR) spectroscopy of dissolved PF-wood sections are analysed using a two-dimensional (2D) ^{1}H-^{13}C-correlation NMR experiment. The technique reveals which native wood polymers are modified during the curing process, and which wood polymer structures are reacting with PF to form methylene bridges.

2 LAYERED STRUCTURE OF THE WOOD CELL WALL

The wood cell wall is made up of three major polymeric components: cellulose, hemicelluloses, and lignin. Cellulose is the largest component, comprising 40-44%, while hemicelluloses comprise between 15-35%, depending on the wood species. Lignin, the second most abundant biopolymer on earth, comprises of approx. 18-35% of wood, depending on the species. The cell wall is made of several layers as shown in Figure 1 [3]. The layers include primary wall (P), the secondary wall (S1, S2, and S3), and in some species a warty layer (W). The secondary wall is the most unique to wood and the most substantial layer containing the most of the lignin in the cell wall, followed by the middle lamella. The middle lamella labelled "I" is an intercellular layer outside of the cell wall.

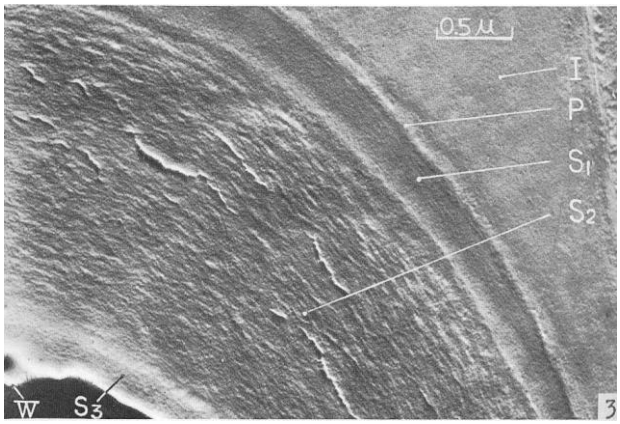

Figure 1: *An electron microscopic image of a latewood tracheid of Pinus densiflora in cross-section [3].*

Several models exist of how the secondary cell wall layers might be portrayed at the nanoscale. Figure 2 shows one of these models, first described by Kerr and Goring [4]. In

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this model, the cellulose microfibrils are placed adjacent to each other in groups, and surrounded by a layer of hemicelluloses and a lignin/hemicellulose matrix. The matrix is believed to allow for infiltration of certain sized molecules or compounds, of which include low molecular weight phenol formaldehyde moieties.

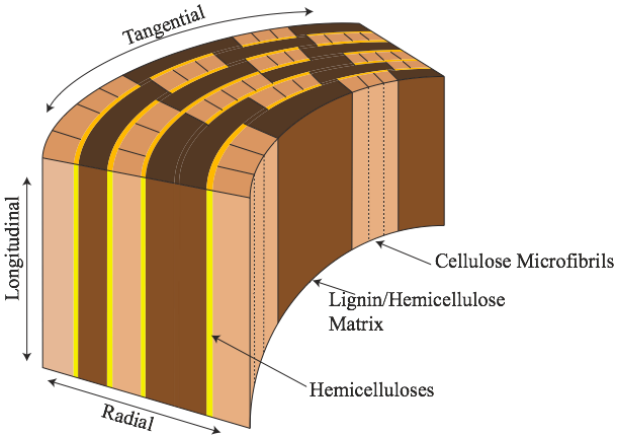


Figure 2: *A hypothetical model of the secondary cell wall as depicted by Kerr and Goring [4].*

3 WHY STUDY WOOD ADHESIVE BOND MECHANISMS?

Adhesives, like polymeric methylene diphenyl-diisocyanate (pMDI) and PF, are used extensively in the United States wood products industries. Distinguishing which mechanisms contribute to the overall bond strength (e.g., van Der Waals interactions, hydrogen bonds,covalent bonds, etc.) has been quite elusive. To formulate new adhesives for wood, we need unambiguous approaches that clearly demonstrate the existence or absence of covalent bonds between wood and adhesives. Figure 3 is an example of a common I-beam (cross-section) that requires three different adhesive systems to fabricate: pMDI for the oriented strand board (OSB), PF for the laminated veneer lumber (LVL), and emulsion polymer isocyanate (EPI) to bond the OSB to the LVL.

Figure 3: *A close-up of an I-beam in cross-section showing the various components of a single product (OSB, LVL, adhesives).*

4 THE PF CURING MECHANISM

The mechanism of alkaline catalysed PF curing (Figure 4) 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. Methylene ether bridges are also possible during the first stage, but with heat during the second stage these tend to revert to methylene bridges [5].

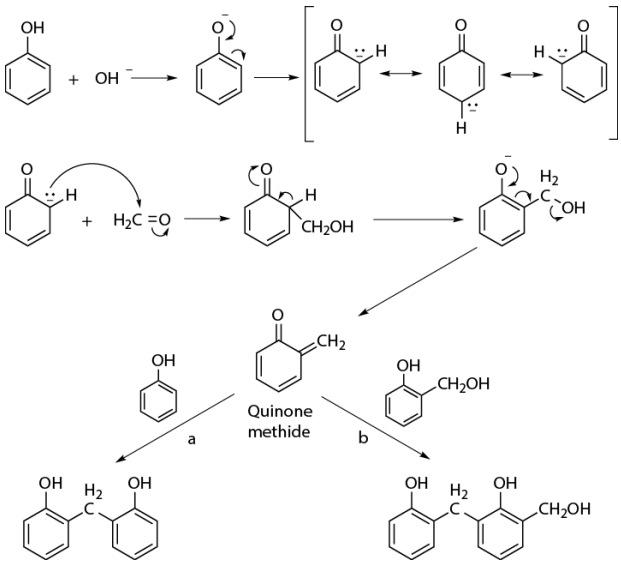


Figure 4: *A typical mechanism of alkaline PF catalysis.*

5 WOOD LIGNIN IN ALKALINE PF

Lignin is a phenolic polymer made up of mostly linear phenylpropanoid units that are capable of reacting with other phenols and hydroxymethylated phenols during adhesive bonding. Figure 5 shows a typical chemical structure of lignin in wood.

Isolated lignin studies have shown that under alkaline conditions and ≥100 °C, phenolic β–O–4 linkages release formaldehyde to give styryl ether linkages [6]. Phenolic phenylcoumaran (β–5) linkages release formaldehyde in a similar fashion to give stilbene linkages [7]. ^{13}C NMR spectroscopy showed that most of this released formaldehyde ends up as the methylene bridge between the guaiacyl units to give methylene bridges [8]. Non-phenolic β–O–4 units, exposed to alkaline conditions and temperatures ≥100 °C, will cleave via an α-β- or β-γ-epoxide intermediate to result in arylglycerols [9]. Non-phenolic β–5 units exposed to alkaline conditions, and temperatures above 100 °C, will be stable for the most part [9]. Figure 6 shows reaction schemes for these potential lignin hydrolysis and condensation reactions.

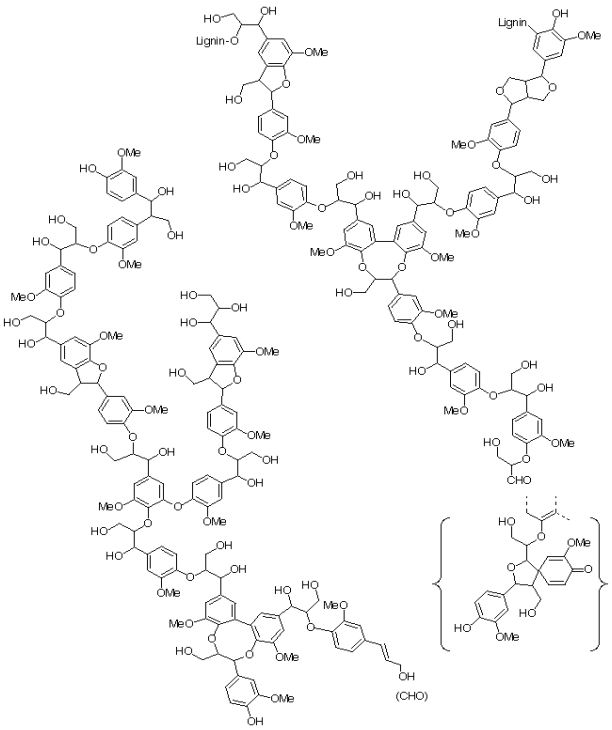


Figure 5: *A depiction of the structure of lignin in spruce [10].*

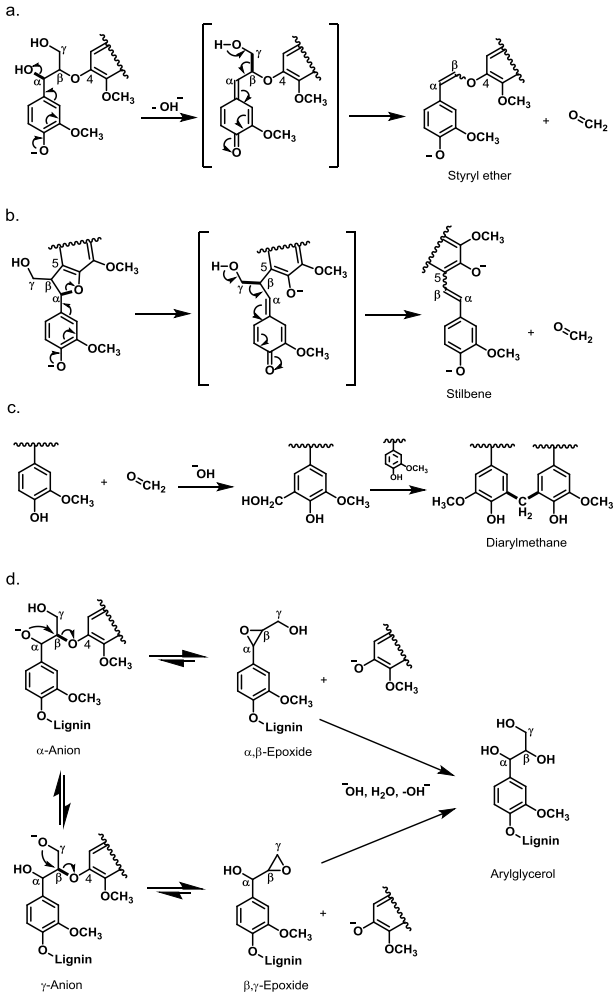


Figure 6: *Reaction schemes of phenolic lignin sub-units showing: phenolic β–O–4 units under alkaline conditions (a); phenolic β–5 units under alkaline condition (b); methylene bridge (diarylmethane) formation with guaiacyl lignin from released formaldehyde (c); and epoxide formation with non-phenolic β–O–4 units under alkaline conditions (d).*

6 EXPERIMENTAL

6.1 WOOD PREPARATION

Saturated loblolly pine cubes (20 mm)^3 were microtomed to give tangential earlywood and latewood sections (0.030 mm radial × 20 mm tangential × 20 mm longitudinal) and equilibrated to a M.C. of 10%.

6.2 PF RESOL RESIN

Table 1 shows how the PF was prepared. The cook was at 70 °C for 1 h, followed by 85 °C for 45 min to give final viscosity of 3.7-4.0 poise. The PF reaction was monitored every 30 min using thin-layer chromatography and aliquots were removed from the resin at the 60 min, 90 min, 120 min, and 150 min times during the cook.

Table 1: *PF Synthesis recipe*

PF Portion	Purity	Mass (g)	Solids (g)	Moles
Phenol	1.00	10.00	10.00	0.106
CH_2O	0.37	17.85	6.61	0.220
NaOH-1	0.50	1.12	0.56	0.014
NaOH-2	0.50	0.58	0.29	0.0072
Water*	1.00		2.97	

* This water is made from the condensation reaction.

6.2.1 GPC of the PF resins

Gel permeation chromatography (GPC) was used to characterize changes in molecular weight during the PF cook. The analysis used a HPLC model 1100 (Agilent, CA, USA) with refractive index and light scattering detectors (Wyatt Technology Corp., CA, USA). Dimethylformamide (DMF) was used with a Progel-TSK G2000 (Sigma-Aldrich, WI, USA) column. PF resin aliquots were dissolved in DMF and filtered through a 0.2 μm PTFE membrane before analysis. A 60-80 g/L solution of PF in DMF was injected (5 μL) and eluted at a flow rate of 0.500 mL/min.

6.2.2 Application

The PF resin 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, held at r.t. for 30 min (closed assembly time), and cured at 140 °C. A control PF resin with a 120 min cook time was cured alongside the bonded assemblies.

6.3 NMR EXPERIMENTS

Ball-milled PF-bonded earlywood and latewood assemblies were prepared as previously described [6]. 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. 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 probe as previously described [11]. Processing and peak integrations was conducted using Bruker-Biospin TopSpin software (Mac, v. 3.0). Volume integration of contours was based on the lignin methoxyl contour as the lignin methoxyl group is thought to be stable during alkaline PF curing [12].

7 RESULTS AND DISCUSSION

7.1 MOLECULAR WEIGHT DETERMINATION

Chromatograms of three PF resin aliquots (60 min, 90 min, and 120 min cook times) were determined. The data for the chromatograms (based on the refractive index data) are shown in Table 2. These data show two distinct molecular weight groupings: between 10 and 13 min (peak A) and between 14 and 18 min (peak B). At the 60 min cook time, most of the resin is made up of low molecular weight phenolic methylols, like dimers, trimers, and oligomers, giving an M_w of 0.5 kDa (peak B). At the later cook times, higher molecular weight condensed polymers dominate. For example, the 90 and 120 min cook time resins gave M_w values of 17.3 kDa and 187.3 kDa, respectively (peak A). From this data, it was found that the condensation reactions increased in number and rate once the 90 min cook time was reached, and molecular weight increased dramatically once the 120 min cook time was reached. For example, peak A showed that M_n and M_w increased four-fold and eleven-fold when the cook time was increased from 90 to 120 min, respectively.

Table 2: *GPC analysis results with various cook times.*

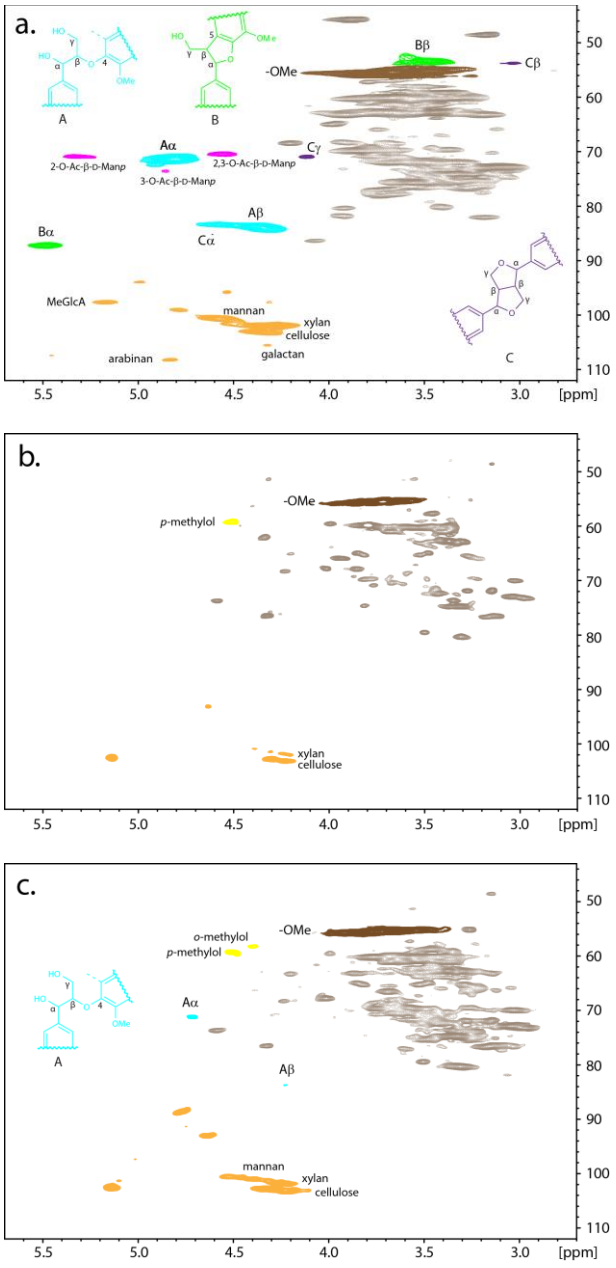
Cook time (min)	Peak	Mass Fraction (%)	M_n (g/mol)	M_w (g/mol)	M_w/M_n
60	A	4.7	4,120	10,000	2.43
	B	95.3	410	480	1.17
90	A	16.8	12,580	17,340	1.38
	B	83.2	970	1,590	1.64
120	A	41.2	52,820	187,300	3.55
	B	58.8	3,310	6,210	1.88

Note: The 150 min cook time resin was too viscous for GPC.

7.2 DEGRADATION OF WOOD POLYMERS

Figure 7 shows the NMR spectra of the control earlywood and the PF-bonded earlywood, as well as the control latewood and PF-bonded latewood. The most frequent native lignin linkages are β–O–4 (**A**), β–5 (**B**), and β–β (**C**). From this study, it was evident that the most severe depletion of lignin was seen with the PF-bonded earlywood with all cook-time resins; all of the **B** and **C** structures were cleaved via alkaline hydrolysis due to the increased susceptibility of the cell wall to alkali, but some of structure **A** remained. With the PF-bonded latewood, there was clear depletion of the **A**, **B**, and **C** structures, but less than in the earlywood showing that the more constrained micropore structure in the latewood [13, 14] most likely limited PF mobility into the cell wall matrix.

Polysaccharides, also have the potential to become modified during the PF-bonding process. The NMR spectra (Fig. 7) showed that the polysaccharides in the earlywood were more heavily degraded and modified than the latewood when bonded with PF. Complete removal of the native 2-*O*- and 3-*O*-acetyl sidechains along galactoglucomannan and partial removal of the 4-*O*-methyl-α-D-glucuronic acid sidechains along arabinoglucuronoxylan was evident for all PF-bonded assemblies analysed.



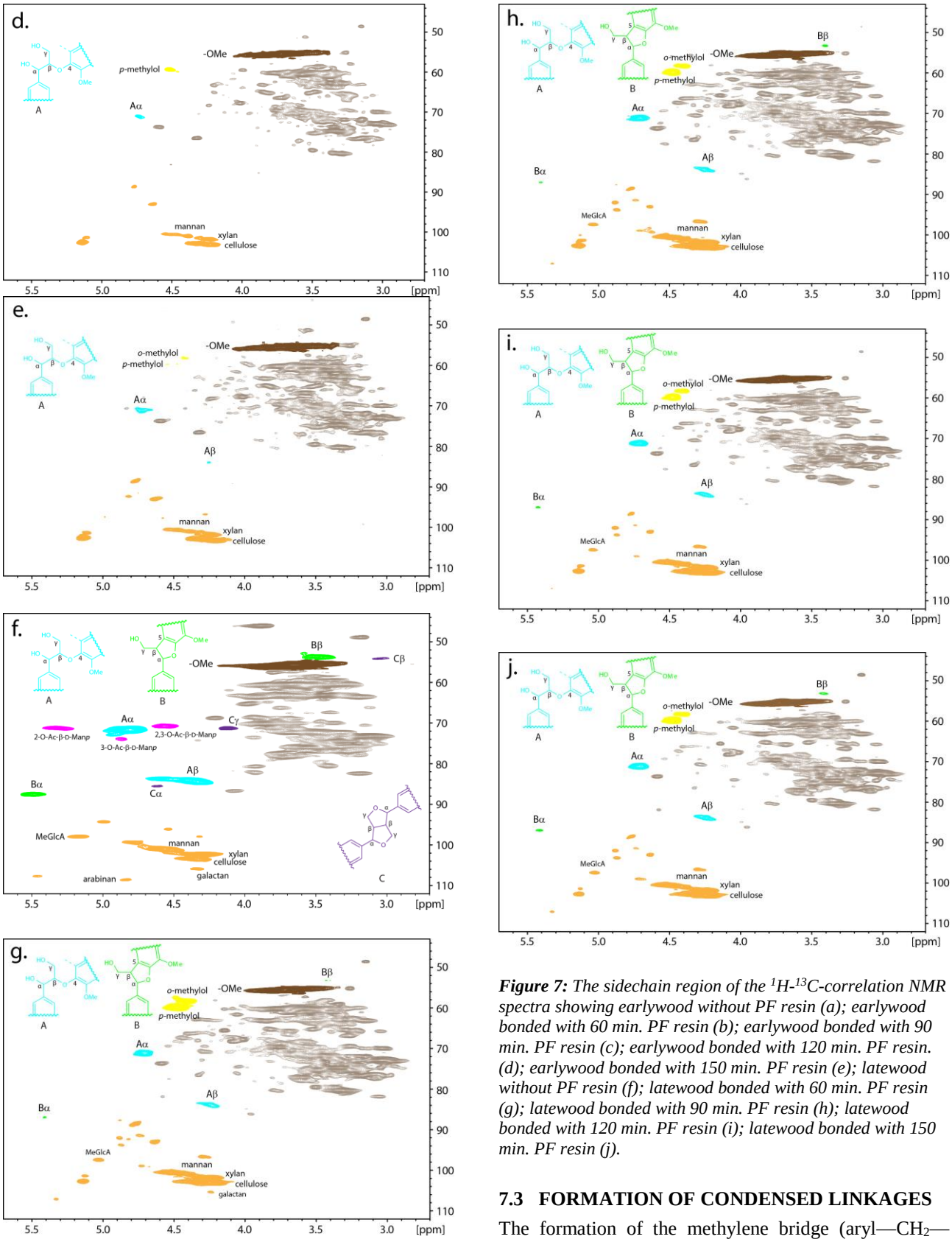


Figure 7: *The sidechain region of the ^{1}H-^{13}C-correlation NMR spectra showing earlywood without PF resin (a); earlywood bonded with 60 min. PF resin (b); earlywood bonded with 90 min. PF resin (c); earlywood bonded with 120 min. PF resin. (d); earlywood bonded with 150 min. PF resin (e); latewood without PF resin (f); latewood bonded with 60 min. PF resin (g); latewood bonded with 90 min. PF resin (h); latewood bonded with 120 min. PF resin (i); latewood bonded with 150 min. PF resin (j).*

7.3 FORMATION OF CONDENSED LINKAGES

The formation of the methylene bridge (aryl—CH_2—aryl), is the most predominant linkage formed between PF resins and methylolated phenolic moieties (i.e., phenols from PF and guaiacyl units). The C5 position on a free-phenolic guaiacyl end-unit is the only position available in lignin for methylol formation under alkaline conditions. From the NMR spectra shown in Figure 8, the cured neat PF resin shows predominantly *o-p* and *p-p* methylenes at

3.75/34.3 and 3.70/39.8 ppm. In the PF cured earlywood and latewood, these *o-p* and *p-p* correlations are present as well, but two fairly strong *o-o* methylene signals are also seen around 3.75/29.8 and 3.71/29.7 ppm in the earlywood and 3.74/29.8 and 3.71/29.7 ppm in the latewood. These *o-o* correlations strongly suggest methylene bridges from a lignin guaiacyl unit. Moreover, the methylolated and condensed C5 positions on guaiacyl units from lignin would convert from a tertiary carbon to a quaternary carbon, which will affect the chemical shift of the H6/C6 position on the guaiacyl unit ring. From the NMR spectra shown in Figure 9 of the PF cured earlywood and latewood, these new signals (labelled A6/B6) have emerged being centered around 6.62/120.9 ppm that are assigned to new guaiacyl unit H6/C6 correlations. These contours give further evidence for C5 methylene bridges between guaiacyl units from lignin and other phenolic moieties.

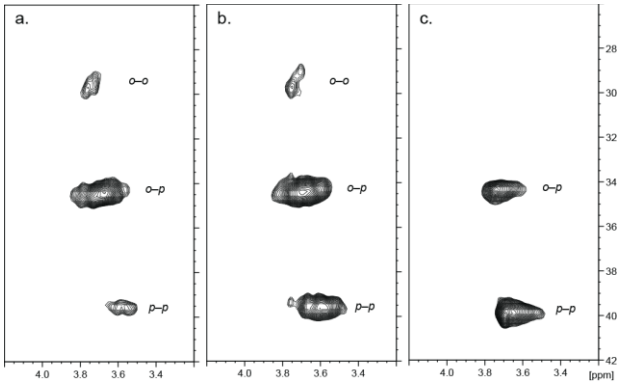
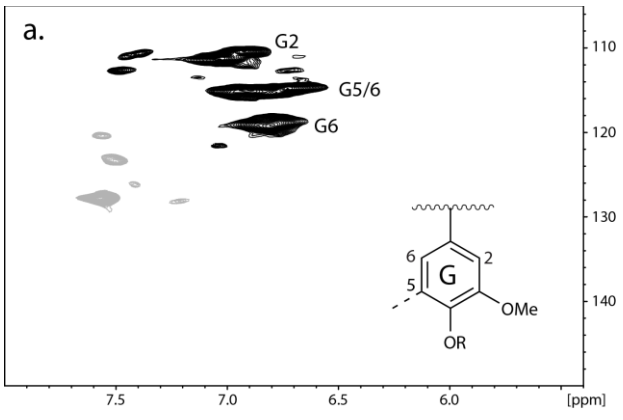


Figure 8: *The aliphatic region of the NMR spectra from the 120 min cook time PF cured with earlywood (a); 120 min cook time PF cured with latewood (b); and 120 min cook time PF (c). These spectra depict the ortho-ortho, ortho-para, and para-para methylene bridges.*



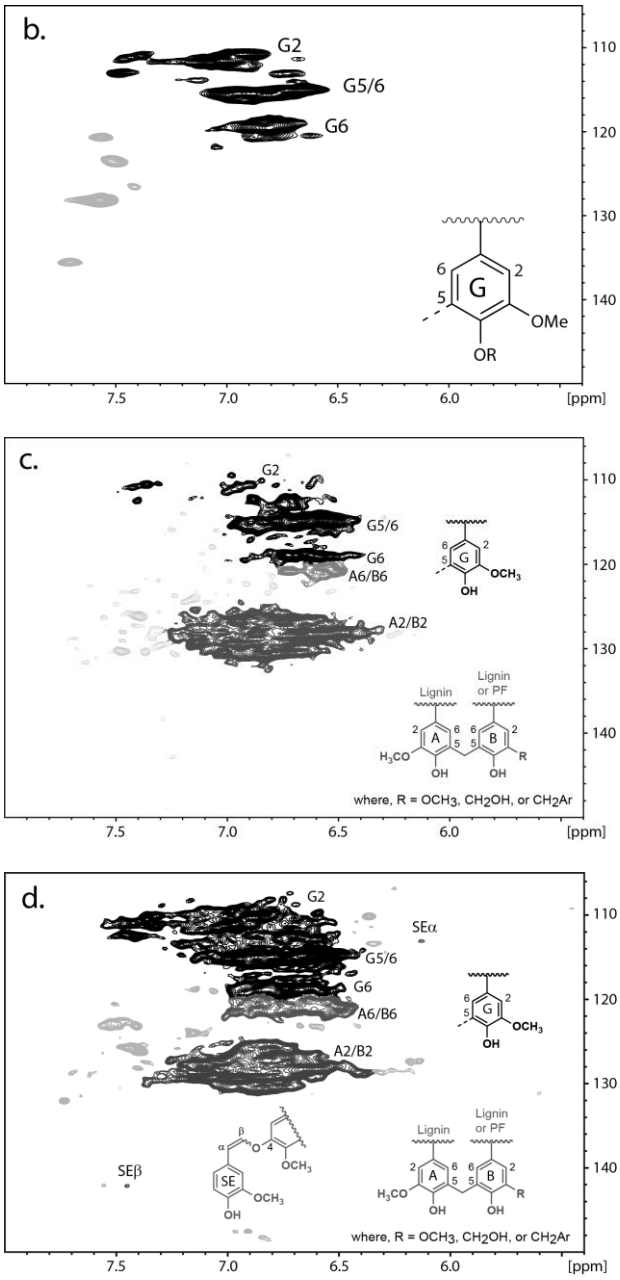


Figure 9: *The aromatic region of the NMR spectra showing: the earlywood (a); latewood (b); 120 min cook time PF cured with earlywood (c); and 120 min cook time PF cured with latewood (d). The PF cured assemblies display PF reactivity with itself as well as reactivity with lignin.*

8 CONCLUSIONS

Earlywood and latewood from loblolly pine were bonded with alkaline PF resol resin. The assemblies were cured, milled, dissolved, and analysed using solution-state NMR spectroscopy. The 2D ^{1}H-^{13}C-correlation experiments showed that: degradation of the β-aryl ether and phenylcoumaran linkages was more severe in earlywood than latewood; condensed methylene bridges were formed not only between methylolated phenols, but also between lignin guaiacyl units at C5; simultaneous bond degradation and bond formation may play a principal part in the PF-wood adhesion mechanism.

ACKNOWLEDGEMENT

The author thanks Chip Frazier for very insightful discussions and Linda Lorenz for the GPC analysis. JR was funded in part by the DOE Great Lakes Bioenergy Research Center (DOE Office of Science BER DE-FC02-07ER64494).

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