PHENOL–FORMALDEHYDE REACTIVITY WITH LIGNIN IN THE WOOD CELL WALL

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MAIN CONCLUSION

Latewood from *Pinus taeda* was reacted with alkaline phenol–formaldehyde (PF) adhesive and characterised using two-dimensional $^{1}H–^{13}C$ solution-state nuclear magnetic resonance (NMR) spectroscopy so that chemical modification of the wood cell wall polymers, after PF resol curing, could be elucidated. The results showed depletion in native lignin linkages via alkaline hydrolysis along with confirmation of newly formed diarylmethanes (methylene bridges) between guaiacyl lignin units and phenolic methylols.

INTRODUCTION

Lignin, comprising 25–30% of wood, is a distinctive polymeric component of secondary cell walls and middle lamellae having a polyphenylpropanoid structure that is largely linear in nature. The three principal phenylpropanoids — *p*-coumaryl, coniferyl, and sinapyl alcohols — are linked through ether or carbon-carbon bonds via endwise free-radical coupling reactions. The majority of these linkages are at its sidechain β-position with a phenolic end of the growing polymer (i.e., β–O–4, β–5, and β–β), implanting tremendous complexity to the lignin structure [1]. These phenolic endgroups render lignin capable of reacting with phenols and hydroxymethylated phenols during the curing of PF adhesive.

Under alkaline conditions, and temperatures above 100 °C, free-phenolic β–O–4 units release formaldehyde to give styryl ethers [2]. The bulk of the released formaldehyde from styryl ether formation may give methylene bridges between the C5-positions on guaiacyl units (i.e., guaiacyl-guaiacyl diarylmethanes) [3]. Non-phenolic β–O–4 units exposed to alkaline conditions, and temperatures above 100 °C, will cleave the linkage via an α,β- or β,γ-epoxide intermediate [4].

This study used NMR spectroscopy to characterize the chemistry of lignin in *Pinus taeda* latewood after reacting with PF adhesive under alkaline conditions. NMR was key to identifying newly formed structures between PF moieties and native wood lignin, as well as revealing lignin degradation mechanisms within the wood cell wall.

MATERIALS AND METHODS

Pinus taeda cubes $(20\ mm)^3$ were microtomed to give tangential latewood sections (0.030 mm × 20 mm × 20 mm). PF resin was formulated to give a phenol:formaldehyde molar ratio of 1:2. The PF reaction was monitored by thin-layer chromatography to follow polymer

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growth and quenched once the viscosity reached 3.7-4.0 stokes. The PF resin (49% solids) was weighed onto two opposing wood sections so that the resin solid content was twice the weight of wood, and both sections joined between glass slides to make a 2-ply wood-PF assembly. The assemblies were heated to 140 °C and cured for 1 h. Then, the wood-PF assemblies were milled, dissolved, and NMR analysis performed as previously described [5].

RESULTS AND DISCUSSION

Figure 1 shows the aromatic region of the NMR spectrum of *Pinus taeda* latewood cured with PF. Alkaline hydrolysis of the β–O–4 linkages in lignin resulted in a minor amount of *cis*-styryl ethers as evidenced by *cis*-isomer correlations (SEα and SEβ) at 6.11/112.8 and 7.46/142.1 ppm. It is likely that degradation of styryl ethers occurred during the PF curing process, and the spectrum reflects an underrepresentation of their initial formation. Reactivity between PF moieties and lignin was evidenced via methylene bridges. The G5 correlation for free-phenolic guaiacyl lignin units in *Pinus taeda* is shown at 6.74/114.7 ppm, whereas its G6 correlation is at 6.82/119.2 ppm. The G5 correlation for free-phenolic lignin is overlapping with cured PF correlations, making this difficult to interpret. However, new contours have emerged centered around 6.62/120.9 ppm that are assigned to new guaiacyl unit A6/B6 correlations that have shifted upfield in response to the adjacent methylene bridge at A5/B5 [6]. This new contour gives evidence that free-phenolic lignin units react at their C5-positions to form methylene bridges between phenol, methylolated phenol, or another guaiacyl unit at C5. This study demonstrates that, during alkaline PF curing with wood, bond formation between PF moieties and lignin occurs concurrently with wood cell wall polymer degradation and that these mechanisms must compete.

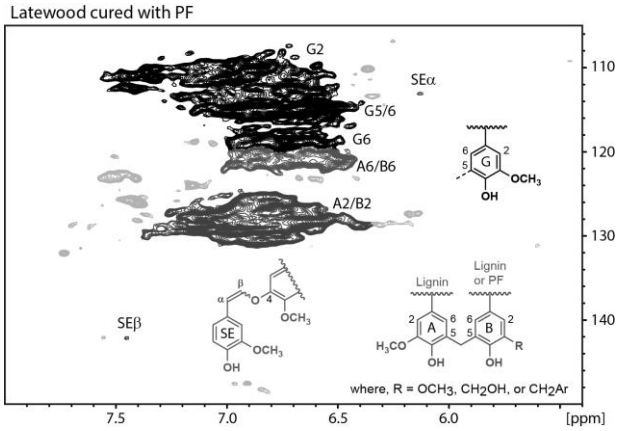

Figure 1. ^{1}H-^{13}C-correlation NMR spectrum of PF cured latewood showing native guaiacyl lignin, cleaved β–O–4 units, and condensed units from PF and lignin.

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ACKNOWLEDGMENT

JR was funded in part by the DOE Great Lakes Bioenergy Research Center (DOE Office of Science BER DE-FC02-07ER64494.

[Yelle, Daniel; Ralph, John 2016. Phenol-formaldehyde reactivity with lignin in the wood cell wall. Proceedings of the International Conference on Polyphenols, July 11-15, 2016, Vienna, Austria. Ed.: Krebs, Heinz A. Publisher: Book-of-Abstracts.com. pp. 170-171]