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Characterizing phenol–formaldehyde adhesive cure chemistry within the wood cell wall

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ABSTRACT

Adhesive bonding of wood using phenol–formaldehyde remains the industrial standard in wood product bond durability. Not only does this adhesive infiltrate the cell wall, it also is believed to form primary bonds with wood cell wall polymers, particularly guaiacyl lignin. However, the mechanism by which phenol–formaldehyde adhesive integrally interacts and bonds to lignin within the cell wall remains unclear. We used recently developed solubilization methodologies in conjunction with two-dimensional ^1H – ^{13}C solution-state NMR spectroscopy of ball-milled pine earlywood and latewood bonded assemblies to characterize the chemical modification of wood cell wall polymers after phenol–formaldehyde curing at various cooking times. The results showed that the highly alkaline resin at 140 °C decreased the frequency of the principal arylglycerol- β -aryl ether interunit linkage by eighty percent in earlywood and by twenty percent in latewood. The presence of newly formed diarylmethanes between guaiacyl lignin units and phenolic methylols was confirmed via NMR spectra of the aliphatic methylene and aromatic regions. The phenol–formaldehyde cure chemistry showed that *o*–*p* methylene bridges dominated in both earlywood and latewood cell walls, but the propensity of *p*–*p* substitution is higher in the latewood cell wall. Our results provide evidence for a simultaneous wood polymer degradation and guaiacyl unit C5 bond formation that occurs during phenol–formaldehyde curing. This competition may be necessary for developing good bond durability between the adhesive and wood.

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1. Introduction

Phenol–formaldehyde (PF) adhesive dates back to the mid-1930s when it was introduced as the first truly synthetic plywood adhesive. Its performance and durability has been unrivaled and remains a significant mainstay in the wood composite industry. Despite its ubiquitous use, elucidating its adhesion mechanisms with wood has been challenging. Research has confirmed that PF adhesive does indeed infiltrate the wood cell wall [1–7]; however, characterizing how the PF interacts with the cell wall polymers has not been well described. The energy of activation during curing of PF-based adhesives has been repeatedly shown to be lowered in the presence of wood [8–13]. These studies have led researchers to accredit strong primary intermolecular interactions (e.g., covalent linkages) between these adhesives and wood as a contributor to bond durability. The potential for covalent bond formation to occur between PF and wood has been demonstrated

[12,14], but evidence also suggests that its contribution may be small under standard thermosetting conditions, and that numerous secondary intermolecular forces between the substrate and PF oligomers may be solely responsible for substrate-induced activation of phenolic reactive sites [15]. However, what still remains quite mysterious is the structural chemistry of the wood cell wall following PF adhesive curing and a knowledge of the extent to which the wood has been chemically modified. With wood cell wall dissolution techniques in conjunction with two-dimensional solution-state NMR spectroscopy [16,17] some important aspects of wood adhesion mechanisms are now becoming evident [18]. Discerning chemical reactivity between adhesives and wood, and which cell wall polymers are involved, is not only important for understanding fundamental wood adhesion mechanisms, but is necessary to advance the field of wood adhesion towards new adhesive technologies, especially those that utilize lignin byproducts as PF resin substitutes.

The mechanism of alkali-catalyzed PF curing is considered by most to be a two-stage reaction. The initial stage consists of phenolate/enolate formation involving resonance-stabilized ions with significant negative charge density at the 2-, 4-, and 6-positions of

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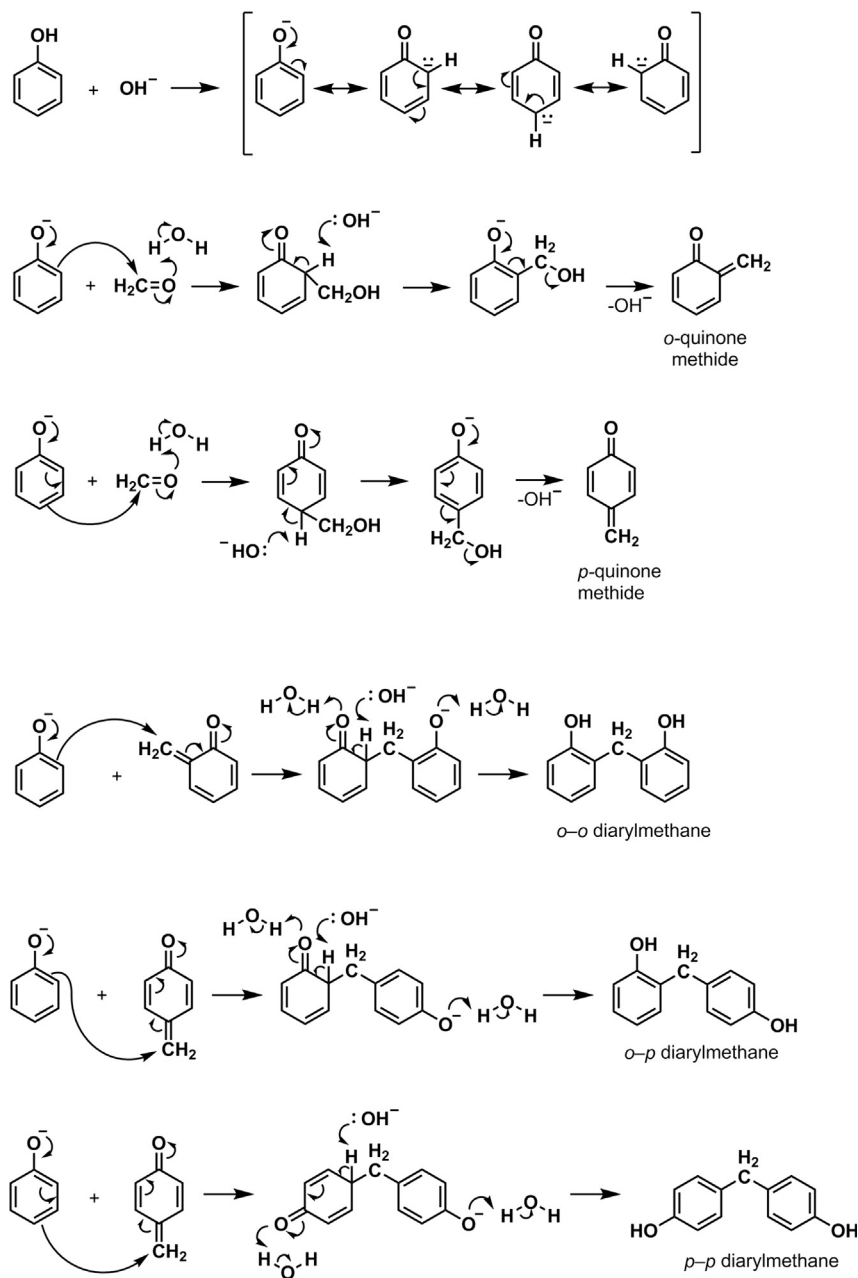


Fig. 1. Alkali-catalyzed reaction of phenol with formaldehyde to form reactive quinone methides that condense with phenol and polymerize to form PF resin.

the phenol followed by methylol formation via nucleophilic attack ($\text{S}_{\text{N}}2$) by the anion onto the formaldehyde carbonyl. During the second stage, the temperature is increased and the resols condense to form methylene bridges via a quinone methide intermediate (Fig. 1) [19].

Lignin, a largely linear polyphenylpropanoid comprising approximately 25–30% of wood polymers, has phenolic endgroups that render it compatible with some applications of phenol. It has the capability of reacting with other phenols and hydroxymethylated phenols during adhesive curing, for example [20].

Studies involving lignin model compounds [21–26] and isolated lignins [20,26–28] have shown that, under alkaline conditions at temperatures $\geq 100^\circ\text{C}$, free-phenolic β -aryl ether units release formaldehyde to give vinyl ethers (more appropriately termed styryl ethers, Fig. 2a) [20–25,27,28]. Similarly, free-phenolic phenylcoumaran units release formaldehyde to give stilbenes (Fig. 2b) [26,29–32]; α -ether linkages in phenolic structures can be selectively cleaved with

mild alkali treatments at room temperature [33]. Most of the released formaldehyde from styryl ether and stilbene formation may result in methylene bridges between the C5-positions of guaiacyl units (Fig. 2c) to give diarylmethane structures [20,34,35]. Studies by Capanema et al. [36] and Balakshin et al. [37] did not see evidence for guaiacyl-guaiacyl diarylmethanes from biogenic formaldehyde in their analyses of Kraft lignin and Kraft-AQ lignin. The lack of diarylmethanes in their studies may be explained by the fact that the addition of sodium sulfide [38] and anthraquinones [27] in pulping have been shown to dramatically increase the rate of delignification by β -aryl ether cleavage and this cleavage occurs prior to styryl ether formation [27]. Thus, the minor amounts of released formaldehyde during Kraft pulping would not have a chance to condense to form diarylmethanes.

Etherified (i.e., non-phenolic) β -aryl ether units exposed to alkaline conditions and temperatures $\geq 100^\circ\text{C}$ will result in cleavage of the β -aryl ether linkage via an α,β - or β,γ -epoxide intermediate (Fig. 2d)

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