Enhanced understanding of the relationship between chemical modification and mechanical properties of wood

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Abstract
Chemical additions to wood often change its bulk properties, which can be determined using conventional macroscopic mechanical tests. However, the controlling interactions between chemicals and wood take place at and below the scale of individual cells and cell walls. To better understand the effects of chemical additions to wood, we have adapted and extended two experimental methods for wood science research. The first method entails two-dimensional solution-state nuclear magnetic resonance spectroscopy of wood cell wall polymers after ball milling but without the usual chemical fractionation methods. This allows for detailed characterization of cell wall polymers and their reactions with chemicals that infiltrate the cell wall. The second method improves currently established nanoindentation analysis so the mechanical properties of wood cell walls can be determined free of artefacts arising from nearby structural heterogeneities including the lumen and various cell wall layers.

Introduction

Interactions between chemicals and wood are central to many areas of wood science and engineering, including the intentional chemical modification of wood (e.g., acetylation and heat treatment) and the incidental modification brought about by the contact of wood with adhesives, paints, coatings, and sealants. However, fundamental understanding of the interactions between chemicals and wood is greatly hindered by complexities arising from the many potential modes of interaction. The hierarchical architecture of wood makes measuring the effects of the interaction dependent on the scale of the experiment. For example, lumen-filling modifications typically increase the hardness of wood at the macroscopic scale, but at the microscopic scale, it is unknown if the hardness of the cell walls change. The chemical complexity of wood also renders interactions with chemicals difficult to assess. For instance, cured components of diisocyanate adhesives often infiltrate the cell wall and restrict cell wall polymer motions [1]. But it is unknown if these changes in molecular mobility are caused by components of the adhesive crosslinking cell wall polymers or self-polymerizing within the cell wall to create an interpenetrating polymer network.

This paper highlights our recent developments in applying two powerful techniques for wood science research: 1) using two-dimensional solution-state nuclear magnetic resonance (2D NMR) spectroscopy to determine interactions between chemicals and cell wall polymers [2] and 2) nanoindentation to determine the mechanical properties of wood at the microscopic cell wall level with a minimum of artefacts [3]. Using the collective information gained from these two techniques will improve fundamental understanding of interactions between chemicals and wood.

Wood–chemical interaction models

Two sets of schematics based on those developed by Norimoto [4] are employed to represent potential micron and molecular-scale wood–chemical interactions. To differentiate between wood–

chemical interactions at different scales, the term “infiltrate” means specifically that chemicals are entering the cell wall, and the term “flow” means chemicals are entering the micron-scale voids in wood structure, such as lumina and vessels. To refer to the unspecific case of chemicals entering the cell walls or micron-scale voids, the term “penetration” is used [5]. The first set of models representing the micron-scale schematic is shown in **Figure 1**. Model A1 shows the unmodified cell wall, A2 shows only chemicals infiltrating the cell wall, A3 shows chemicals infiltrating the cell wall and flowing into the lumen to partially fill it, A4 shows adhesive chemicals flowing to completely fill the lumen but not infiltrating the cell wall, and finally, A5 shows chemicals infiltrating the cell wall and flowing into the lumen to fill it. Model A5 was not included in Norimoto’s original schematic [4].

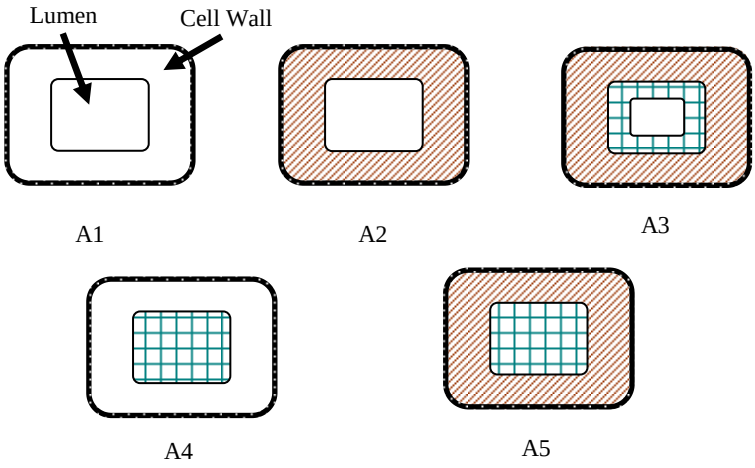

Figure 1. Models based on the schematic proposed by Norimoto [4] for micron-scale wood–chemical interactions. The inner rectangle represents the lumen and the outer one the cell wall. The diagonal lines in the cell wall indicate infiltration of the cell wall with chemicals and the cross-hatched area in the lumen represents partial or complete filling of the lumen.

Models A1–A5 are useful for understanding potential modes of interactions that occur between wood and different classes of adhesives. Wood adhesives can be divided into two classes: 1) *in-situ* polymerized adhesives that consist of monomers and oligomers that crosslink during curing to form rigid adhesives (*e.g.*, phenol formaldehyde, urea formaldehyde, epoxies, and isocyanates), and 2) pre-polymerized adhesives that consist of large, flexible molecules that are generally more ductile than *in-situ* polymerized adhesives when cured (*e.g.*, poly(vinyl acetate), emulsion polymer isocyanates, and proteins) [5, 6]. During bonding, both classes of adhesives flow into the lumina near the substrate surface (models A3–A5), but because the molecules in pre-polymerized adhesives are generally larger than molecules in the polymerized *in-situ* adhesives, they do not infiltrate the cell walls (model A4). However, the lower molecular weight monomers and oligomers of the *in-situ* polymerized adhesives can infiltrate the cell walls (models A3 and A5) [5, 6]. It is also plausible that *in-situ* polymerized adhesive components infiltrate cell walls deeper into the wood than the adhesive components flow into the wood lumina, resulting in model A2 cells. Finally, at a given distance from the bonding surface the cell walls will not be affected by the penetration of the adhesive (model A1).

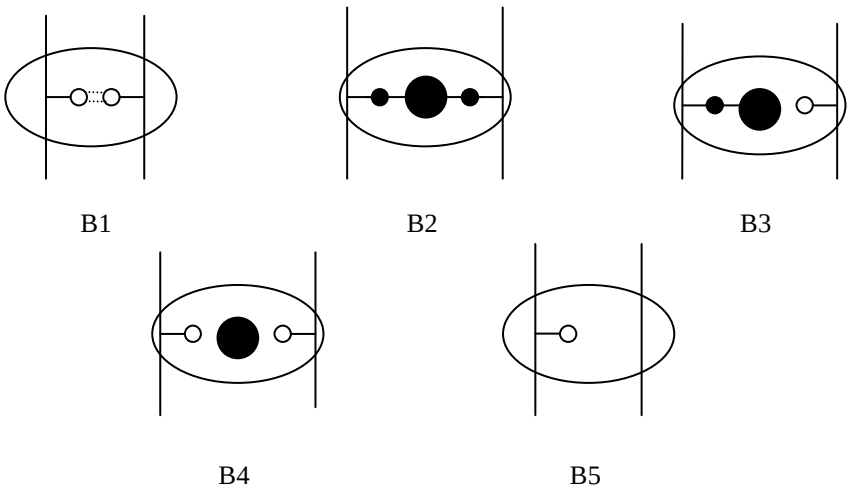

Figure 2. Models based on the schematic proposed by Norimoto [4] for molecular-scale wood–chemical interactions.

Norimoto's molecular-scale schematic [4], which addresses the potential molecular-scale wood–chemical interactions, is shown in **Figure 2**. Cell walls are a nanofibre-reinforced composite comprised of cellulose microfibrils embedded in a matrix of hemicellulose and lignin sub-domains [7]. The properties of the cell walls are largely influenced by hydrogen bonding within and between these three cell wall polymers. In this schematic, vertical lines represent lignocellulosic polymers, empty circles represent hydroxyl groups attached to the polymers, solid lines represent covalent bonds, dashed lines represent hydrogen bonds, small filled circles represent hydroxyl groups that were involved in the formation of covalent bonds, and the increase in horizontal distance between the vertical lines represents swelling.

Model B1 is the unmodified cell wall and potential molecular-scale wood–chemical interactions are illustrated by models B2, B3, and B4. A difunctional molecule, such as diisocyanate, may crosslink two hydroxyl groups (model B2) whereas an acetic anhydride molecule will only link to one hydroxyl group (model B3). An ethylene glycol molecule will not covalently bond with the hydroxyl groups (model B4). The molecules represented by the large filled circles in models B3 and B4 can also have hydrogen bonding capabilities. Another possible variation is the loss of a hydroxyl group (model B5) through condensation reactions, such as occur during heat treatments.

Chemical evaluation

Solid-state NMR has been used to investigate the polymeric structure of wood [8–11], but the results have been of limited utility because the signals tend to overlap and broaden because of short and multiple relaxation times. Lu and Ralph developed a method to perform solution-state NMR on wood, which provides more accurate and comprehensive data than solid-state NMR [12]. This method requires wood to be acetylated prior to dissolving, which prevents observation of naturally occurring acetates in the NMR data, and includes a precipitation step, which leads to the loss of unknown amounts of cell wall material. We performed a logical simplification of the Lu and Ralph method by eliminating acetylation and precipitation steps, allowing us to distinguish natural acetates and benzoates and preventing unknown loss of cell wall material. The simplified method involves dissolving ball-milled wood in a 4:1 (v:v) ratio of perdeuterated dimethylsulfoxide and perdeuterated 1-methylimidazole solvent [2]. This near-native state wood cell wall material is then characterized through solution-state NMR by using a heteronuclear single quantum coherence (HSQC) 1-bond ^{13}C-^{1}H correlation 2D NMR experiment. This technique gives excellent peak separation of aromatic, aliphatic correlations of the lignins and anomeric, aliphatic correlations of

the polysaccharides. Reaction of the wood hydroxyl groups on these polymeric components is determined through distinct downfield chemical shifts of the proton and carbon signals.

One area of controversy in the literature is whether covalent bonds form between components of isocyanate adhesives and wood hydroxyls. The data have generally supported the concept that isocyanates react faster with water than hydroxyl groups on the wood polymers under normal bonding conditions, but the data have not been conclusive because of the complex isocyanate reactions [13]. We detected under dry conditions that phenyl isocyanate molecules react extensively with lignin side-chain units and polysaccharides of ball-milled loblolly pine (*Pinus taeda*), which is a model B3 interaction (**Figure 2**). However, once water molecules are present, the phenyl isocyanate mainly reacted with the forming urea products, leading to model B4 interactions rather than the B3 reaction with the wood. **Figure 3** shows the 2D HSQC spectrums of unreacted and reacted ball-milled wood under dry conditions. Note that the reacted wood polymer hydroxyls display noticeable differences in chemical shift in both proton and carbon dimensions, allowing for determination of where and to what degree the phenyl isocyanate reacts in the cell wall polymers.

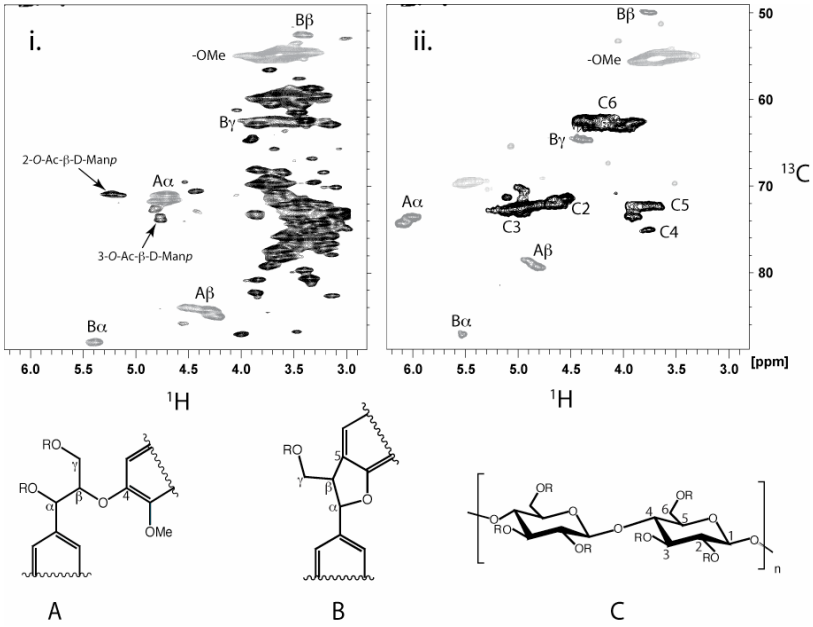

Figure 3. Aliphatic region of 2D HSQC spectra of i) near-native-state whole cell wall of loblolly pine, and ii) phenyl isocyanate, a model of diphenylmethane diisocyanate, reacted with ball-milled loblolly pine. The chemical structures at the bottom are A) β-aryl ether units, B) phenylcoumaran units, and C) cellulose repeat units. Greater detail on the technique and spectra of the unmodified pine are given by Yelle and others [2].

In a similar experiment under dry conditions, 50-µm thick sections of loblolly pine (~ 1 cell wide) were reacted with phenyl isocyanate molecules, which favoured reaction with primary hydroxyls on lignin side-chain units (*e.g.*, β-aryl ethers and phenylcoumarans), giving model B3 interactions. As water molecules are incorporated into the wood, the lignin reactivity diminishes and urea products are formed again, leading to model B4 interactions.

Mechanical evaluation

Nanoindentation is capable of probing mechanical properties (elastic modulus, hardness, hardness strain rate sensitivity) of a wood cell wall, because the nanoindents are only about ~1 µm across compared to a typical wall thickness of 2–10 µm, (**Figure 4**).

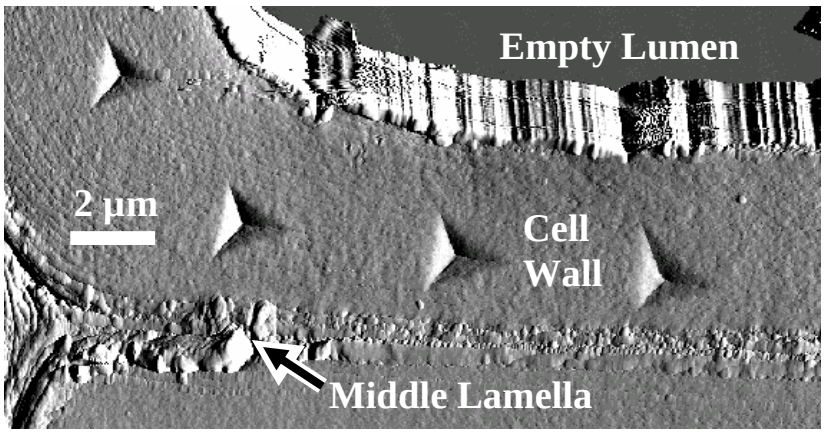

Figure 4. Atomic force microscope image of nanoindents placed on a ponderosa pine cell wall in close proximity to a cell wall-middle lamella interface and free edge with an empty lumen. Greater detail is given by Jakes and others [3, 17].

Gindl and co-workers [14–16] previously demonstrated that nanoindentation can detect changes in cell wall properties caused by chemical infiltration, but possible artefacts are present in their results because they first embedded their specimens with epoxy, and then analyzed their data using the standard nanoindentation analysis, which assumes the cell wall can be represented as a homogeneous half-space. To remove possible artefacts caused by the epoxy, we developed a specimen preparation procedure that does not require any embedment [3]. We also developed an experimental procedure to eliminate the half-space assumption used in the standard nanoindentation analysis. The method incorporates a structural compliance into the data analysis that accounts for nearby structural heterogeneities, such as the interface between the cell wall and lumen [3]. If the lumen is empty, then this interface is a free edge and contributes to a positive structural compliance. If the lumen is filled, then the interface is a heterophase interface and the structural compliance depends on the difference in material properties between the cell wall and material in the lumen. Typically, a polymer in the lumen is less stiff than the cell wall and the interface will contribute positively to the structural compliance of an indent in the cell wall, although the magnitude of the structural compliance will be less than if the lumen were empty. In the standard analysis, the structural compliance is not accounted for, which leads to an underestimation of hardness and elastic modulus when the structural compliance is positive [3, 17, 18].

We used our nanoindentation methods to account for structural compliances for determining hardness and elastic modulus of cell walls in a phenol-resorcinol-formaldehyde (PRF)–ponderosa pine (*Pinus ponderosa*) bondline [17]. Cell walls of earlywood and latewood within the bondline (cells with PRF-filled lumina) and outside the bondline (unmodified cell walls) were indented. We found that the cell wall hardness of cells with PRF-filled lumina increased from 380 to 470 MPa for the latewood cells and from 380 to 440 MPa for the earlywood cells as compared to the unmodified cell walls. The elastic modulus increased from 12 to 15 GPa for the latewood cells, but remained an unchanged 12 GPa for the earlywood cells [17]. The differences in cell wall mechanical properties between the unmodified and PRF-filled lumen cells supports model A5 for the PRF-filled lumen cells. However, the unchanged elastic modulus in the earlywood cell walls suggests the effect of PRF components in the cell wall may not be consistent for earlywood and latewood cells. To demonstrate the importance of accounting for the structural compliance, consider that the average structural compliance of indents in the cell walls of the unmodified earlywood cells was 15 µm/N. Not accounting for this structural compliance would have led to a 2 GPa underestimation in the elastic modulus.

Discussion

Techniques for determining the appropriate micron-scale models for chemical–wood interactions are more established [4, 5, 19] than techniques available for verifying molecular-scale models. Nevertheless, fluorescence microscopy, audioradiography, transmission electron microscopy, scanning electron microscopy with X-ray dispersive emission spectroscopy, dynamic mechanical analysis, and anti-shrink efficiency have been used to demonstrate that chemicals have infiltrated cell walls, and in some instances show that they have modified their properties [4, 5]. However, none of these methods provide the same chemical and mechanical information that we can obtain with our solution-state 2D NMR and nanoindentation methods.

Using 2D NMR and nanoindentation, we can gain further insight into how wood adhesives create durable bonds in the presence of water. Wood substrates and adhesives swell differentially in the presence of water, and the resulting displacement mismatch at their interface creates stress within the bondline. Frihart hypothesized pre-polymerized and *in-situ* polymerized adhesives create durable bonds by accommodating for the displacement mismatch in two different manners [5, 6]. Pre-polymerized adhesive components are not expected to infiltrate the cell walls and result in model A4 cells next to the bondline. The cell walls of model A4 are unmodified, which can be verified using 2D NMR and nanoindenation, and are expected to swell to a similar extent as model A1 cells near the bondline. Therefore, to create a durable bond, the resulting displacement mismatch at the substrate–adhesive interface must be accommodated by an elastic displacement in the adhesive. Pre-polymerized adhesives can accommodate this displacement because their long segments between crosslinks afford them flexibility and the stress can be more evenly distributed throughout the bondline [5, 6]. In contrast, *in-situ* polymerized adhesives are less deformable than pre-polymerized adhesives and are not capable of accommodating the displacements at the substrate–adhesive interface. However, *in-situ* polymerized adhesive components infiltrate and modify the cell walls near the bondline. Frihart suggested this modification diminishes the swelling of the cells as the bondline is approached, which decreases the displacement mismatch at the substrate-adhesive interface [5, 6]. 2D NMR and nanoindentation can be used to determine how *in-situ* polymerized adhesive components modify cell walls within the bondline to create durable bonds. For instance, consider the two potential interactions between isocyanates, which represent components of an *in-situ* polymerized isocyanate adhesive, and wood polymers discussed in the chemical interactions section. If the isocyanates react with wood polymer hydroxyl groups, model B3 is formed, and if the isocyanates react with water molecules in the cell wall, urea products are formed leading to model B4. The 2D NMR technique can distinguish between these model B3 and B4 interactions. Model B3 interactions likely bulk the cell wall and decrease its hydrogen bonding capabilities, preventing water from entering the cell walls near the bondline. Bulking of the cell wall and presence of fewer water molecules, which act as a cell wall plasticizer, likely causes the elastic modulus and hardness of the cell wall to increase and the hardness-strain rate sensitivity to decrease. Model B4 interactions may bulk the cell wall and affect the mechanical properties like model B3 interactions. It is possible that the urea products in the B4 interactions plasticize the cell walls causing the elastic modulus and hardness to decrease and the hardness strain rate sensitivity to increase. These potential relationships between wood–chemical interactions and mechanical properties of the cell wall can be investigated with our nanoindentation methods.

Conclusions

2D NMR and nanoindentation provide greater understanding of complex chemical interactions occurring in the cell walls of wood and the corresponding changes in mechanical properties of the cell wall. To aid in identifying and understanding potential wood–chemical interactions that occur at different scales, we use micron-scale and molecular-scale models based on those originally proposed by Norimoto [4]. The methods are applicable in many different areas of wood science

research, including chemical modification and interactions between wood and adhesives, coatings, paints, and sealants.

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