

TOOLS TO UNDERSTAND STRUCTURAL PROPERTY RELATIONSHIPS FOR WOOD CELL WALLS

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Abstract

Understanding structure-property relationships for wood cell walls has been hindered by the complex polymeric structures comprising these cell walls and the difficulty in assessing meaningful mechanical property measurements of individual cell walls. To help overcome these hindrances, we have developed two experimental methods: 1) two-dimensional solution state nuclear magnetic resonance (2D NMR) spectroscopy for chemical analysis of near-native state wood polymers, and 2) broadband nanoindentation spectroscopy (BNS) to more accurately assess mechanical properties of individual wood cell walls. Our approach to utilizing these two methods in the study of cell wall structure-property relationships is to first alter the cell wall through some type of modification, then use 2D NMR to determine what reactions took place in the cell wall polymers, and finally BNS to determine the changes in mechanical properties. These techniques have found utility in a wide range of wood science applications, including evaluating the validity of several theories on the bonding mechanism of isocyanate adhesives and determining changes of cell walls after acetylation.

Introduction

Wood is chemically, structurally, and mechanically complex, which makes it difficult to apply many of the standard materials characterization techniques used to study structure-property relationships in other materials. Therefore, to advance the understanding of the relationship between the chemistry of wood polymers and wood mechanics (specifically at the cell wall level), we developed 2D NMR and BNS methods to provide more detailed information about wood cell wall properties and the effects of wood modifications.

The 2D NMR method is based on that of Lu and Ralph [1], who showed that 2D NMR of wood can be accomplished by dissolving ball-milled wood via *in situ* chemical modification. Yelle and coworkers improved their technique by developing a method to eliminate the chemical modification step and to directly analyze the ball-milled wood [2], allowing chemical analysis of near-native state wood polymers. Using 2D NMR, researchers can determine which wood polymers and functional groups are altered during chemical, biological, or genetic modifications. 2D NMR is applicable in many areas of wood science research and has already been utilized to better understand brown rot decay [3] and wood-isocyanate adhesion [4].

Nanoindentation is capable of probing mechanical properties, typically hardness and elastic modulus, from small volumes of materials. In wood, nanoindentation can probe individual S2 cell wall lamina and compound corner middle lamella [5]. We have made many improvements to the conventional nanoindentation methodology. Typical surface preparation for wood specimens consists of first embedding the wood in epoxy. To remove the possibility of epoxy components infiltrating the cell walls and inadvertently affecting the mechanical properties, we developed a surface preparation for unembedded specimens [6]. Edges near nanoindents, such as the free edge existing with a cell wall and an empty lumen, can produce artifacts in the nanoindentation results. Therefore, we developed the first experimental method to assess and remove effects of edges from the measurements [6-8]. We have also developed broadband nanoindentation creep (BNC) to assess viscoplastic properties across 4-6 decades of strain rate [9-10] and broadband nanoindentation viscoelasticity (BNV) to assess viscoelastic properties across greater than eight decades of time scale [11]. Together, BNC and BNV comprise BNS. In addition to providing useful information about how mechanical properties change with time-scale, BNS results can also be used to identify the kinetic signatures of property-controlling mechanisms, which can provide additional insight into the cell wall structure-property relationships. Nanoindentation is applicable to

many areas of wood science research and has already been utilized to better understand the effects of ethylene glycol plasticized wood [12] and wood-isocyanate adhesion [13].

Our approach using 2D NMR and BNS to improve our understanding of structure-property relationships in wood cell walls is to first selectively modify wood, then seek out changes in polymer structure with 2D NMR, and finally assess changes in cell wall mechanical properties using nanoindentation. In the following sections, we first review our application of this approach to better understand the interactions of isocyanate adhesives with wood, and then we discuss our recent application of this approach to explore the effects of acetylation.

Wood-isocyanate adhesion

Adhesion of wood with polymeric methylene diphenyl diisocyanate (pMDI) creates durable bonds (especially in OSB panels) that withstand dimensional changes with moisture [14]. We wanted to evaluate the opposing hypotheses of whether the isocyanate reacts with wood under typical OSB bonding conditions or whether it doesn't because it reacts faster with water in the cell wall. We also wanted to determine whether the isocyanate might form an interpenetrating polymer network within the cell walls [15-16].

To address the chemistry behind these hypotheses, we utilized the power of wood dissolution, synthesis of carbamylated wood model compounds, and 2D NMR experiments to fully characterize the reactivity of isocyanate with the major wood polymers. Firstly, the native wood polymer structures were characterized via solution-state 2D NMR. Dissolving ball-milled wood using non-degradative perdeuterated solvents enabled the characterization of natural acetates found in wood [2]. Moreover, this cell wall fingerprinting technique allows for detecting new bond formation or bond cleavage that can occur with chemical modifications. Secondly, wood was treated with pMDI model compounds at specific concentrations and moisture contents to determine cell wall reactivity. Lastly, wood model compounds were synthesized to establish an NMR chemical shift dataset of carbamylated wood polymers to assign new peaks that form during pMDI-wood reactions [17]. The results showed that under the typical OSB bonding conditions the pMDI adhesive does not react with wood polymers [4, 18].

The 2D NMR results only answer the question of whether or not the pMDI adhesive forms covalent bonds with the wood polymers. However, 2D NMR does not address whether or not the pMDI infiltrates the cell wall and if so, whether it forms an interpenetrating polymer network within the cell wall as previously proposed [15-16]. Components of the pMDI may still be infiltrating the cell wall and affecting the cell wall mechanical properties. Using nanoindentation we found that both the hardness and elastic modulus increased in wood cell walls after pMDI modification. This change in mechanical properties suggests pMDI is infiltrating the cell walls. The increase in mechanical properties also suggests a reinforcing effect caused by the formation of a polyurea interpenetrating polymer network within the cell wall polymers.

Acetylated wood

Acetylated wood is of interest because it is an emerging commercial wood product. During acetylation, hydroxyl groups in wood react and are converted to larger, less hydrophilic acetyl groups. The result is wood with increased dimensional stability with changing environmental conditions [19]. However, the effects of acetylation on the bulk mechanical properties of wood are poorly understood. Dreher and coworkers [20] found that compared to unmodified wood, the compressive strength and ball hardness increased, the elastic modulus measured from a bending test did not change, and the shear strength parallel to the grain decreased. Ramsden and coworkers [21] found the elastic modulus measured in tension decreased compared to the unmodified wood. Obataya and Yamauchi [22] found the compression modulus of acetylated wood decreased compared to unmodified wood. There are numerous other studies concerning the mechanical properties of acetylated wood (see references in [19]), but no firm conclusions can be drawn and the mechanisms affecting mechanical properties have thus far eluded researchers. However, all previous work has concerned the mechanical properties of bulk wood, which is of course a composite response. Here, we apply 2D NMR and nanoindentation to gain further insight into the effects of acetylation at polymer and cell wall levels in wood.

Matchstick-size (1 mm x 1 mm x 30 mm, with the 30-mm dimension in the longitudinal direction) specimens of loblolly pine (*Pinus taeda*) latewood were equilibrated to 14% moisture content. The wood was acetylated by submerging the specimen in acetic anhydride at 160°C for 2 hours. The control specimen was a similar matchstick specimen taken from the same growth ring and heat treated for 2 hrs under nitrogen at 160°C. These specimens were prepared and tested concurrently with our previously discussed work investigating wood-isocyanate adhesion and the same experimental procedures and analyses for 2D NMR and nanoindentation were performed on the acetylated and control specimens [4, 13].

Results from 2D NMR analysis confirmed acetylation of several wood polymer structures (Fig. 1). Specifically, partial acetylation of β -aryl ether (A) and β -5 (B) linkages in lignin was determined by the presence of acetylated A and B structures (labeled Ac-A and Ac-B). Galactoglucomannan, the predominant hemicellulose in softwoods, also displayed partial acetylation, as evidenced by the presence of newly acetylated 2-O-, 3-O-, and 6-O-mannan structures (labeled Ac-Man_{2,3,6}, Ac-Man_{3,2,6}, and Ac-Man_{6,2,3}). This newly acetylated mannan is different than the native acetates that already exist at the 2-O- and 3-O-positions in that it is a 2,3,6-triacetate. Hence, the presence of new chemical shifts for these mannan structures exists. Furthermore, 2D NMR revealed preferential acetylation of primary hydroxyl groups (on the lignin sidechains) over the secondary hydroxyl groups (on mannan)

Nanoindentation was performed in both the S2 cell wall laminae and compound corner middle lamellae. All mechanical properties assessed with nanoindentation decreased after acetylation. The elastic modulus of the S2 cell wall lamina decreased from 18 to 15 GPa after acetylation and in the compound corner middle lamellae decreased from 6 to 5 GPa. Broadband nanoindentation creep results are shown in Figure 2. In the S2 cell wall laminae, the hardness decreased about 10-20% across the strain rates tested in the acetylated specimen. The decrease in hardness in the compound corner middle

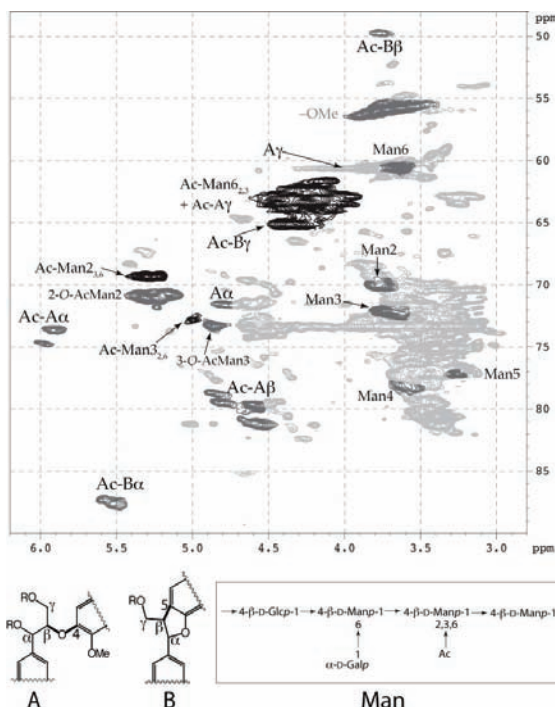


Figure 1. 2D NMR ^{13}C - ^1H correlation spectrum of partially acetylated loblolly pine matchsticks. Contour labels are as follows: A, β -aryl ether; B, β -5 (phenylcoumaran); Man, galactoglucomannan; -OMe, lignin methoxys; Ac-, acetylated structure. The labels correspond to the structures shown at the bottom. The light gray contours represent saccharides unassigned

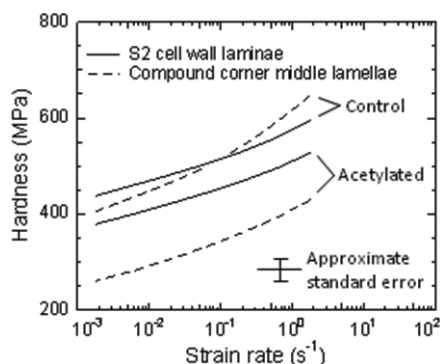


Figure 2. Broadband nanoindentation results for control and acetylated wood specimens.

lamellae after acetylation was greater, with an average decrease across all the strain rates of about 50%.

Conclusions

1. A methodology for better understanding of cell wall structure-property relationships can come from modifying wood selectively, then understanding the changes in the lignocellulosic polymers using 2D solution state NMR spectroscopy, and finally determining changes in mechanical properties of the cell wall and middle lamella by using broadband nanoindentation spectroscopy.
2. These methodologies have been used to show that polymeric methylene diphenyl diisocyanate (pMDI) does not react with the lignocellulosic polymers in wood under typical bonding temperature and wood moisture content. The nanoindentation data supports the formation of an interpenetrating polymer network rather than the hydrolyzed isocyanate just bulking the wood cell walls.
3. Both methodologies established that the acetylation procedure employed in this work partially acetylated the wood cell wall polymers, thereby significantly modifying its chemistry and mechanical properties. The 2D NMR spectra displayed evidence of marked lignin sidechain acetylation as well as acetylation of the major hemicellulose, galactoglucomannan.

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