NANOINDENTATION METHODS FOR WOOD–ADHESIVE BOND LINES

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Introduction

As an adherend, wood is structurally, chemically, and mechanically more complex than metals or plastics, and the largest source of this complexity is wood's chemical and mechanical inhomogeneities. Understanding and predicting the performance of adhesively bonded wood requires knowledge of the interactions occurring at length scales ranging from the macro down to the molecular level of chemical interactions. This work investigates such interactions occurring at and below the micrometer range using nanoindentation.

Observing a typical piece of softwood with the unaided eye reveals distinct light (earlywood) and dark (latewood) regions of wood, which are known as annual growth rings. Examination of the adherend under a light microscope reveals the cellular structure of wood. The primary difference between earlywood and latewood is the thickness of the cell walls, with latewood cells having substantially thicker walls than earlywood cells. Cell walls are composed of four layers (primary, S1, S2, and S3), of which S2 is the thickest (Figure 1). The cell wall layers are composed of a fiber-reinforced nanocomposite with cellulose microfibrils (~2–5 nm in diameter) embedded in a hemicellulose and lignin matrix. In addition to these three biopolymers, a fourth component of the cell wall, empty void spaces, must also be considered when considering the interactions between wood and adhesives. These void spaces offer potential avenues for adhesive components to diffuse into the cell wall and interact with its chemical constituents. Individual cells are held together by a lignin-rich middle lamella, and the lumen is the large opening in the middle of the cell.

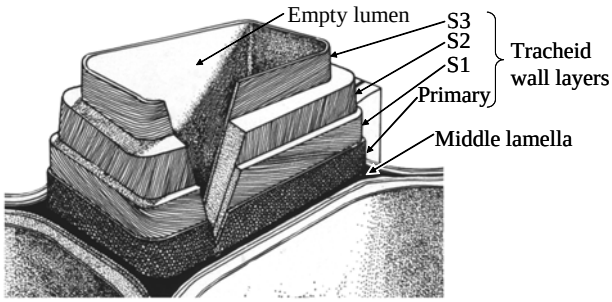

Figure 1. Illustration of a transverse cross-section of a typical cell, called a tracheid, in softwood.

An optical microscope image of a wood–adhesive bond line is displayed in Figure 2. Regions within the bond line are designated to facilitate its investigation. At the top and bottom of the image are the thin-walled bulk earlywood cells and thick-walled bulk latewood cells, respectively. These regions are presumed to be far enough from the bond line that the cells are unaltered by the adhesive and not mechanically damaged from the method used to prepare the bonding surface (e.g., planing) or the clamping pressure. The wood interphase regions are distinguished as the collections of cells that have been affected by some aspect of the bonding process, such as the aforementioned mechanical damage or adhesive penetration (filling the cell lumens or components of the adhesive diffusing into the cell wall). A heterophase interface, where adhesion occurs, is present between the wood and adhesive phases. Within the adhesive phase, two potential regions may be identified, the bulk adhesive and adhesive interphase. The bulk adhesive has not been affected by the presence of the wood, whereas the adhesive interphase is the region of the adhesive that has been affected by the presence of the wood. These final three regions are difficult to distinguish in Figure 2 and are included in the "interface and adhesive" region here.

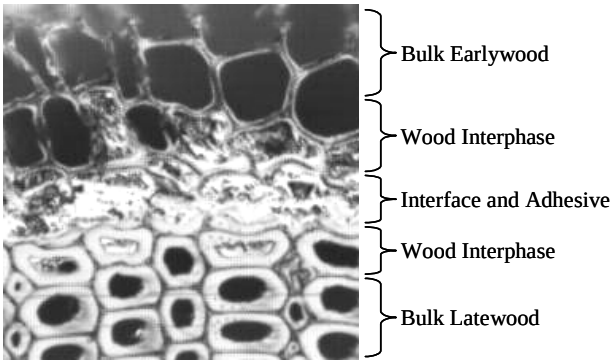

Figure 2. Optical image of PRF bond line. Image is approximately 0.15 mm on a side.

Nanoindentation allows researchers to probe the mechanical properties of the wood–adhesive bond line at the length scale of the cell walls' thickness. In nanoindentation experiments, a diamond tip is pressed into a specimen while continuously recording the load and depth during both loading and unloading. From the resulting load–depth data, values of hardness and elastic modulus are typically calculated using the standard Oliver and Pharr analysis [1]. However, this standard analysis assumes the specimen being indented is structurally rigid, semi-infinite, and homogeneous, assumptions that are violated when indents are placed in wood cells walls or adhesive in close proximity to a cell wall. To overcome these viola-

tions, we have developed an experimental method capable of accounting for and removing the effects of nearby structural heterogeneities, such as free edges or interfaces with materials of differing properties, from the calculations of hardness and elastic modulus [2]. In addition, this method can provide information about adhesion at the interface between the cell wall and adhesive.

Previous work on wood includes the investigation of wood–adhesive bond lines of four different adhesives using nanoindentation by Konnerth et al. [3,4]. Properties of earlywood cell walls in the wood interphase were compared to values obtained for earlywood cells in the bulk wood region. However, to aid in specimen preparation and support the cell structure during testing, specimens were first embedded with an epoxy that may have introduced an artifact by altering the properties of the cell walls. In addition, these researchers used the Oliver and Pharr method, and there is concern that the homogeneity assumption led to an artifact in their results because there is a direct correlation between the reported properties of the cell walls and stiffness of material occupying their lumens (epoxy or adhesive). To investigate the possible effects of these artifacts further, we performed a series of nanoindentation experiments on a wood–adhesive bond line prepared without an embedment material and analyzed the data using our nanoindentation methods capable of accounting for the inhomogeneities.

Experimental Work

The bond line investigated in this study was prepared from two ponderosa pine (*Pinus ponderosa*) adherends bonded with a phenol-resorcinol-formaldehyde (PRF) laminating resin. The assemblies were pressed in a screw press at a pressure of 1035 kPa (150 lb/in^2) for 24 h at room temperature. The indentation surfaces were prepared using a technique that required no embedment [2,5].

A Hysitron (Minneapolis, Minnesota, USA) Triboindenter® equipped with a diamond Berkovich tip was used in this study. All the experiments in this study employed multi-load indents in force control [2]. In nanoindentation, the Meyer hardness, H, is

$$H = \frac{L_{\max}}{A}, \tag{1}$$

where $L_{\max}$ is the maximum load of the final partial unloading segment and A is the projected area measured from an atomic force microscope (AFM) image. To calculate the elastic properties, the SYS correlation

$$C_t L_{\max}^{1/2} = (C_m + C_s) L_{\max}^{1/2} + J_0, \tag{2}$$

was used, where C_t is the total unloading compliance, C_m is the machine compliance, C_s is the structural compliance and $J_0 = H/E_{\text{eff}}^2$ in which E_{eff} is the effective modulus [2]. According to Equation 2, provided that there is no indentation size effect (i.e., J_0 is independent of size), $C_t L_{\max}^{1/2}$ plotted as a function of $L_{\max}^{1/2}$ forms a straight line of slope $C_m + C_s$. Machine compliance C_m is a property of the machine; for the indenter configuration used in this work, C_m = 3 µm/N. Structural compliance C_s behaves similar to C_m because it contributes additively to C_t and is independent of load. However, C_s will vary in our experiments depending on the proximity of the heterophase interfaces, such as free edges or elastic discontinuities between phases. In addition, the flexing of the open cellular structure of wood may also contribute to C_s. Therefore, C_s must be determined independently for each indent location by constructing a SYS plot from each indent location by determining the contact stiffness as a function of load using multi-load indents. From the measured area and corresponding SYS plot, E_{eff} may be calculated independent of nearby heterophase interfaces [2]. The Young's modulus of the material indented may be calculated from

$$\frac{1}{E_{\text{eff}}} = \frac{1}{\beta}\left(\frac{1-\nu_s^2}{E_s} + \frac{1-\nu_d^2}{E_d}\right), \tag{3}$$

where E_s and E_d are Young's moduli, ν_s and ν_d are Poisson's ratios of specimen and indenter, respectively and β is a correction factor that is taken to equal 1.23 [2]. To calculate E_s using Equation 3, E_d and ν_d for the diamond indenter were taken to be 1137 GPa and 0.07, respectively, and ν_s for the cell walls and PRF was assumed to be 0.45.

Results and Discussion

The indents placed in the earlywood and latewood interphase regions are displayed in Figures 3a–b. From these AFM images, deformed cell walls and PRF-filled lumens can easily be identified. Indents placed on the earlywood and latewood cell walls had maximum loads of 150 and 800 µN, respectively. A similar number of indents were placed in the cell walls of the bulk earlywood and latewood regions, and the resulting data are summarized in Table 1.

In the interphase regions, an increase in H was observed in both the earlywood and latewood, but an increase in E_s was observed only in the latewood. Even though the cell walls in the wood interphase regions underwent large deformations during the bonding process (Figures 3a–b), these results demonstrated that they maintained or even improved their H and E_s. The improvement was likely caused by diffusion of components of the adhesive into the cell walls, which has been previously reported for phenol-formaldehyde adhesives using UV spectroscopy by Gindl [6]. The mechanism by which the components of the PRF enhance the properties has not yet been elucidated, but possibilities include simply bulking the cell walls by filling the void spaces, forming an interpenetrating polymer network, or chemically reacting with the chemical constituents of the cell wall.

Our results are similar to those reported by Konnerth and Gindl [3], who used nanoindentation to probe earlywood cell walls in a bond line composed of spruce wood (*Picea abies*) and PRF. This agreement occurs despite the epoxy embedment and standard Oliver and Pharr analysis

employed by Konnerth and Gindl. However, one advantage of not embedding wood in epoxy is that the results in Table 1 can be used to directly determine the difference in properties of the cell walls caused by the PRF without the possibility of artifacts being introduced by the embedment. Also, the importance of our analysis to account for C_s is evident from the observation that not accounting for C_s = 15 ± 5 µm/N in the bulk earlywood cell walls would have led to the underestimation of E_s by nearly 2 GPa.

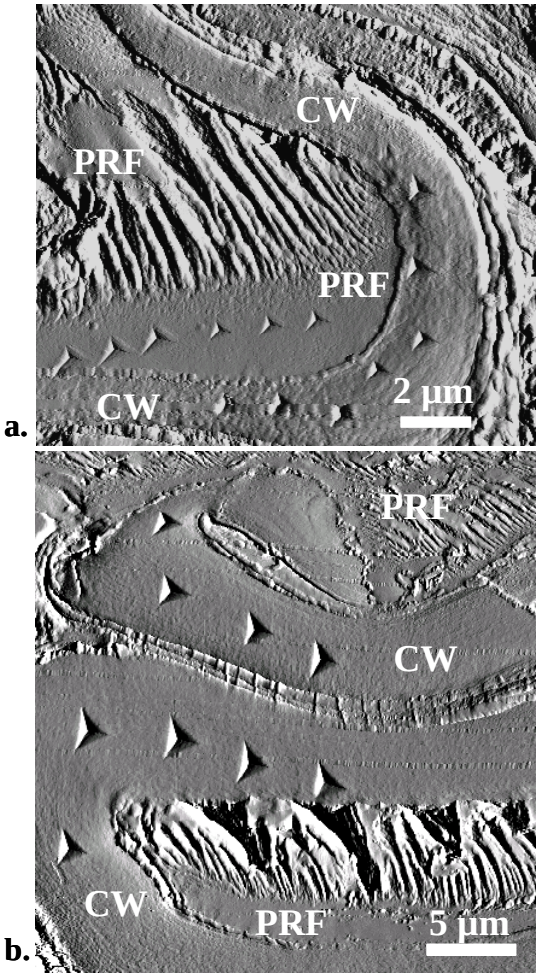

Figure 3. AFM images of indents placed on cell walls (CW) in the (a) earlywood and (b) latewood interphase regions.

Table 1. Results for indents placed on cell walls.

	C_m+C_s (µm/N)	$J_0^{1/2}$ (µm/N$^{1/2}$)	H (MPa)	E_s (GPa)
Bulk Earlywood	18 ± 5	1.12 ± 0.07	380 ± 20	12 ± 1
Interphase Earlywood	6 ± 1	1.18 ± 0.08	440 ± 20	12 ± 1
Bulk Latewood	3 ± 2	1.12 ± 0.07	380 ± 20	12 ± 1
Interphase Latewood	3 ± 2	0.97 ± 0.04	470 ± 20	15 ± 1

Note: ± one standard deviation.

In Figure 3, a series of indents were placed in the PRF adhesive at various distances from the interface between the PRF and cell wall phases to investigate the adhesion between the two phases. The three PRF indents to the right in Figure 3a had a maximum load of 150 µN, and the three to the left had a maximum load of 250 µN. Corresponding SYS plots and results are displayed in Figure 4. The increasingly negative slopes in Figure 4 as the indents in the PRF approach the stiffer cell wall phase indicates the two phases are well adhered at the interface [2]. Additionally, the consistent *y*-intercepts of the plots indicate the material properties do not dramatically change as the interface is approached.

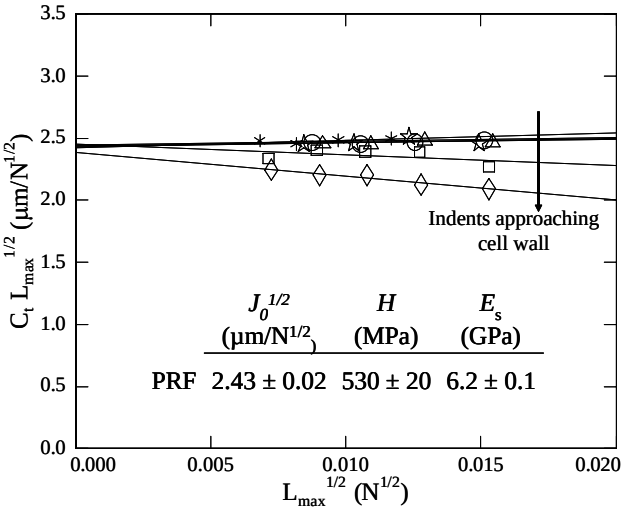

Figure 4. SYS plot for indents placed in the PRF in Figure 3a and summary of results.

Conclusions

Using our improved nanoindentation methods, we demonstrated that cell walls within the wood interphase region or a wood–PRF bond line have increased or similar values of H and E_s as compared to cell walls in the bulk wood region. The enhanced properties are attributed to components of the PRF diffusing into the cell walls. Also, good adhesion at the interface between PRF and cell wall was demonstrated by the negative values of C_s obtained as indents in the PRF approached the cell wall.

References

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