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Creep properties of micron-size domains in ethylene glycol modified wood across 4½ decades in strain rate

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ABSTRACT

The hardnesses of secondary cell wall laminae (SCWL) and compound corner middle lamellae (CCML) in wood were measured at indentation strain rates between approximately 7×10^{-4} s^{-1} and 20 s^{-1}, using a new method called broadband nanoindentation creep. The wood was subsequently modified with ethylene glycol (EG) and the properties were re-measured. The SCWL and CCML responded differently to this modification: in the SCWL, hardness decreased uniformly by a factor of 3.7 ± 0.3 across all strain rates, whereas in CCML, the modification had a similar effect at low strain rates. However, at high strain rates, hardness was only lowered by a factor of 1.8. The EG modification also lowered elastic modulus of the SCWL and CCML, swelled the SCWL and CCML, and caused previously placed indents to disappear (CCML) or partly disappear (SCWL).

INTRODUCTION

From an elementary viewpoint, wood cells are basically hollow tubes with walls composed of concentric laminae. In softwoods, the most abundant type of cells are axial tracheids and **Figure 1a** is a schematic of an axial tracheid with the primary (P) and secondary (S1, S2, and S3) laminae labeled. The S2 cell wall lamina (SCWL) is the thickest and largest contributor to the properties of the cell wall [1]. Cells are held together by the compound middle lamella, and at the junction of three or more cells, the compound middle lamella forms a region called the compound corner middle lamella (CCML) (**Figure 1**). The exact morphologies of SCWL and CCML are not known, but knowledge of their basic compositions and composite structures aid in understanding their properties. The SCWL consist of about 35% highly oriented semi-crystalline cellulose microfibrils (~16 nm in cross section) embedded in a matrix of amorphous cellulose (20%), hemicellulose (30%), and lignin (15%) [2]. Within the matrix, amorphous cellulose is closely associated with hemicellulose. The formation of distinct hemicellulose and lignin domains in cell walls is supported by the presence of separate thermal transitions attributable to the hemicellulose and lignin domains [3] and solubility parameter considerations [4]. The dimensions of the matrix domains are in the range of 5-10 nm [5]. Cellulose is a linear polymer and hemicellulose is mainly a branched polymer. Structural integrity of cellulose and hemicellulose domains is largely maintained by inter- and intramolecular hydrogen bonding. Hydrogen bonding plays less of a role in lignin, a cross-linked aromatic polymer. In contrast to SCWL, CCML is comprised of about 80% lignin [2]. The remainder consists of an irregular, interconnecting network of hemicellulose embedded in the lignin phase. The individual "limbs" within this network have diameters of about 6 nm [6].

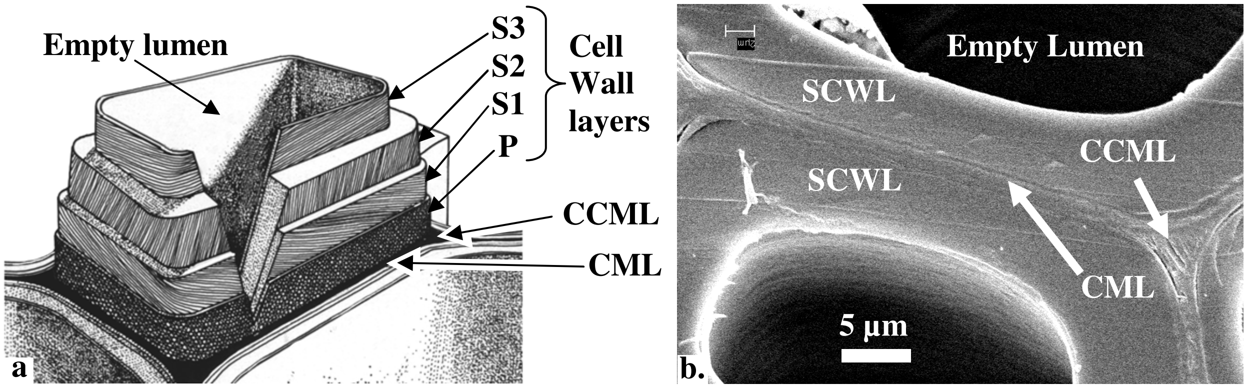

Figure 1. a) Illustration of the parts in a typical tracheid cell in softwood. b) Scanning electron microscope image of a cross section of tracheid walls in loblolly pine prepared for nanoindentation experiments. Indents are placed in the S2 cell wall lamina (SCWL) and compound corner middle lamella (CCML). The CCML is the continuation of the compound middle lamella (CML) into the junction between three or more cells.

With indents ~1 μm across, nanoindentation is capable of probing the properties of SCWL and CCML. One of the earliest works using nanoindentation in wood research showed differences in properties between the SCWL and CCML in unmodified spruce wood [7]. Wimmer and Lucas showed the Meyer's hardness was 340 MPa in the SCWL and 270 MPa in the CCML, and elastic modulus was 20 GPa in the SCWL and 7 GPa in the CCML. Numerous other studies (referenced in [8]) in wood research have since used nanoindentation to measure properties of the SCWL, including work finding that the Meyer's hardness and elastic modulus of SCWL in melamine-treated wood increased compared to unmodified wood [9], whereas in juvenile wood SCWL these properties decreased compared to mature wood SCWL [10].

Our work aims to build upon previous nanoindentation wood research by improving analysis methods to account for structural heterogeneity and developing a method to obtain creep data. Traditional nanoindentation analyses implicitly assume the material being tested is homogeneous and fills a half-space [11]. These assumptions are violated in wood, where the SCWL and CCML are affected by a range of heterogeneities including the lumina and cell wall laminae (**Figure 1**). These heterogeneities introduce artifacts into the nanoindentation data that are not accounted for in the traditional nanoindentation analyses. The artifacts can be removed using methods we have recently developed [8, 12]. In addition to the usual elastic modulus and Meyer's hardness, the creep properties of materials can be calculated from nanoindentation data [13]. Creep here refers to strain-rate-dependent plastic deformation, not the viscoelastic response often associated with creep in polymeric materials.

Probing the mechanical properties of the SCWL and CCML in unmodified wood and selectively modified wood can lead to greater fundamental understanding of wood properties. Modifications can be chosen to selectively modify different wood components (e.g., lignin or hemicellulose), and the modifications can be related to changes in properties of SCWL and CCML. In the present work, we investigate effects of ethylene glycol (EG) on the properties of the SCWL and CCML. EG is a simple, one-component modification that is known to swell wood and lower its mechanical properties [14]. EG is not expected to enter the crystalline regions of cellulose, but is expected to infiltrate the amorphous cellulose, hemicellulose, and lignin domains because of its small molecular volume (55.6 ml/mol) and hydrophilic nature. The EG likely disrupts hydrogen bonding in these domains. Because lignin is cross-linked and less dependent on hydrogen bonding for its structural integrity than amorphous cellulose and hemicellulose domains, the effect of EG is expected to be different for the lignin domain. Determining how the mechanical properties of the SCWL and CCML are affected by EG does not alone provide the information necessary for a greater fundamental understanding of wood properties. However, this work demonstrates the efficacy of our recently developed nanoindentation analyses to make property measurements. These results will be used in conjunction with future results from other modifications to better understand wood properties below the cellular level.

EXPERIMENTAL WORK

The transverse plane of a latewood band in a plantation-grown loblolly pine (*Pinus taeda*) was prepared for nanoindentation using a diamond knife microtome without the aid of any embedment (**Figure 1b**) [8]. Nanoindentation experiments were performed with a Hysitron (Minneapolis, Minnesota, USA) Triboindenter equipped with a Berkovich tip. Indents were placed in the SCWL and CCML in unmodified wood. All residual indents were imaged with a Quesant (Agoura Hills, California, USA) atomic force microscope (AFM) incorporated in the Triboindenter. The AFM was operated in contact mode and calibrated using an Advanced Surface Microscopy, Inc. (Indianapolis, Indiana, USA) calibration standard with a pitch of 292 ± 0.5 nm. ImageJ (http://rsb.info.nih.gov/ij/) image analysis software was used to manually measure the projected contact areas of the indents [8]. After testing in the unmodified form, the specimen was submerged in ethylene glycol (EG) for 48 hours to modify it. After removal from the EG, the surface was blotted with a tissue paper and retested. In addition, the indent locations in the unmodified wood were imaged after EG modification to observe changes in residual indent impression and dimensional changes in the SCWL and CCML.

EXPERIMENTAL RESULTS

Figure 2a is a typical load-depth trace of an indent. The first six loading-unloading cycles were used to remove artifacts in the nanoindentation data arising from nearby structural heterogeneities by using the analyses of Jakes and coworkers [8, 12]. The Young's modulus (E_s) and Meyer's hardness (H) were then assessed in the usual way [8, 11, 12]. A Poisson's ratio of 0.45 was assumed in the calculation of E_s for the SCWL and CCML [8]. AFM images of residual indents are displayed in **Figure 3** and results for E_s and H are tabulated in **Table I**. For indents placed in unmodified SCWL, unmodified CCML, and EG-modified SCWL, the contact area used to assess E_s and H was determined from AFM images of the residual indents. With the EG-modified CCML, there were no residual indents and areas were calculated based on contact depth [11]. Dimensions represented by the double headed arrows on the unmodified SCWL (**Figure 3a**) and CCML (**Figure 3b**) increased from 5.1 to 6.5 μm and 3.6 to 4.4 μm, respectively, after EG modification. Observation of residual indents in the unmodified wood after EG modification revealed that residual indents placed in the SCWL partially recovered (compare **Figures 3a and 3c**) and residual indents in the CCML completely recovered (not shown). The creep segment in **Figure 2a** was analyzed using broadband nanoindentation creep (BNC) [15]. Data in **Figure 2b** show the increase in indentation depth during the creep segment collected over more than 4 decades of time. BNC is based on the creep analysis originally proposed by Stone and Yoder [13] and was recently validated using finite element analysis [16, 17]. Representative hardness versus indentation strain rate curves are plotted in **Figure 4**.

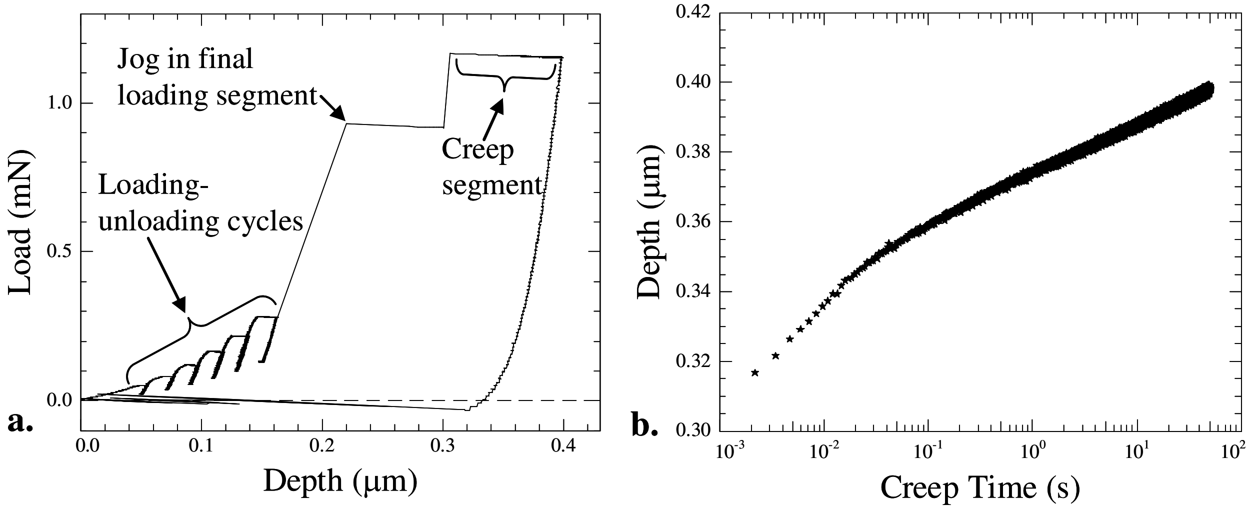

Figure 2. a. Load-depth trace for broadband nanoindentation creep multiload indent placed in an unmodified S2 cell wall laminae (SCWL). The jog in the final loading segment is from the finite loading resolution of the nanoindenter and does not affect the results. b. Increase of depth with creep time for the creep segment in a.

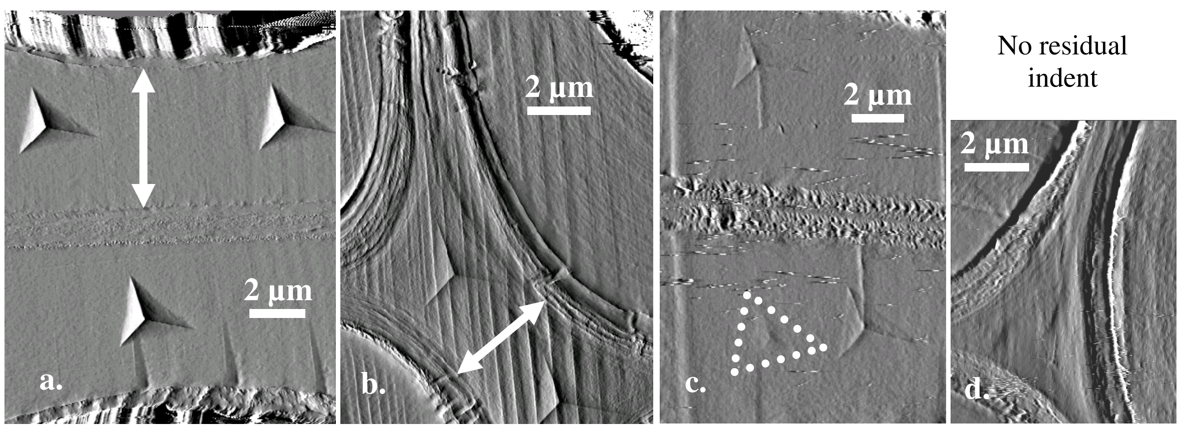

Figure 3. AFM images of indents placed in a. untreated S2 cell wall lamina (SCWL), b. untreated compound corner middle lamella (CCML), c. EG-modified SCWL, and d. EG-modified CCML. There was no residual indent in d. Double-headed arrows in a and b are referred to in the Experimental Results section to quantify swelling caused by the EG modification. The dashed triangle in c shows the bottom residual indent in a after the specimen was modified with EG. The CCML in b and d are not the same.

Table I. Summary of results for indents in unmodified and ethylene glycol- (EG-) modified loblolly pine. E_s is Young's modulus, H is Meyer's hardness, P_{max} is maximum load of indent, n is the number of indents performed, and uncertainties are one standard deviation.

		CCML		SCWL	
		Unmodified	EG-modified	Unmodified	EG-modified
E_s	(GPa)	6 ± 1	2 ± 1	21 ± 3	6 ± 4
H	(MPa)	340 ± 20	80 ± 40	380 ± 20	80 ± 10
P_{max}	(mN)	0.8	0.2	1.2	0.4
	n	6	5	21	18

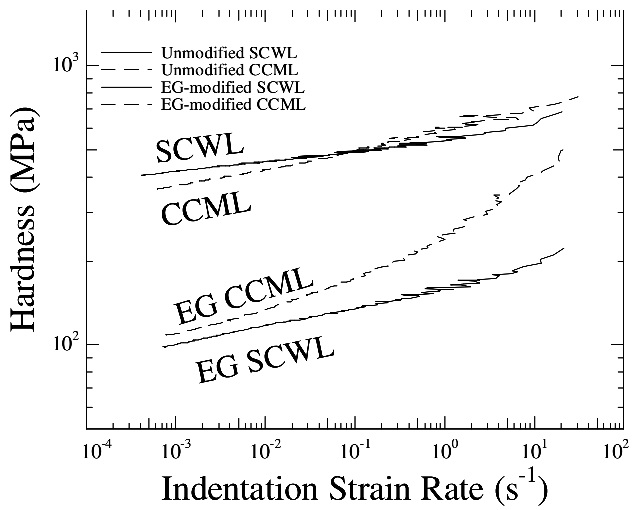

Figure 4. Broadband nanoindentation creep analysis for S2 cell wall lamina (SCWL) and compound corner middle lamella (CCML) of unmodified and EG-modified specimens. The leftmost data in the curves correspond to the *H* in **Table I**.

DISCUSSION

In our measurements, the E_s of unmodified SCWL is a factor of 3.5 higher than that of CCML. This difference is largely explained by the presence and orientation of stiff cellulose microfibrils in the SCWL. What seems odd, then, is that the *H* of SCWL and CCML are about the same not only at the lowest strain rates (where nanoindentation measurements are usually made) but across the 4½ decades of strain rate studied in our experiments (**Figure 4**). Hardness is a measure of yield strength, and it is not obvious from the structure of the SCWL and CCML how their yield strengths would remain the same across this broad range of strain rates, given the large differences in relative amounts of lignin and hemicellulose present in the two materials and the lack of crystalline cellulose fibrils in the CCML.

After EG modification, the E_s decrease by about 70% for both SCWL and CCML. For the curves in **Figure 4**, the *H* of the SCWL is lowered uniformly across all strain rates by a factor of 3.7 ± 0.3. The *H* of the CCML is lowered by a factor of 3.6 at the lowest strain rates but only 1.8 at the highest strain rates. The decrease in E_s and *H* along with the swelling of SCWL and CCML demonstrate that EG infiltrates both SCWL and CCML. It is not clear why the decrease in hardness is more uniform as a function of strain rate in SCWL than in CCML.

Residual indent recovery after EG modification is reminiscent of a shape memory effect [18] and provides additional insight to differences between SCWL and CCML. In a shape memory polymer, the permanent shape of the material is temporarily deformed (residual indent impression forms) and upon application of an external stimulus, the shape of the polymer returns to its permanent shape (impression disappears). The cross-linked structure of lignin more closely resembles known shape memory polymers [18] than cellulose or hemicellulose and is likely responsible for the shape memory effect. Complete recovery of the CCML supports that lignin is primarily responsible for the effect because CCML is composed of about 80% lignin. The external stimulus in our experiment causing the shape memory effect is EG modification. The EG-stimulated shape memory effect suggests the EG is modifying lignin domains.

CONCLUSIONS

Nanoindentation was used to measure effects of ethylene glycol (EG) on mechanical properties of the S2 cell wall lamina (SCWL) and compound corner middle lamellae (CCML) in latewood tracheids of loblolly pine. Dimensional and mechanical property changes in SCWL and CCML indicated that EG modified SCWL and CCML. Hardness and elastic modulus decreased after EG modification. The factor by which hardness decreased remained nearly constant over 4.5 decades of strain rate for the SCWL, but varied as a function of strain rate for the CCML, with a smaller effect at high strain rates than at low strain rates. This observation would not have been possible without our recently developed broadband nanoindentation creep techniques and methods to account for heterogeneities in nanoindentation experiments. Differences in mechanical properties (**Table I**), effect of EG modification (high strain rate data in **Figure 4**), and indent recovery after EG infiltration between SCWL and CCML demonstrate that these regions respond differently to EG modification.

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