Nanoindentation creep properties of the S2 cell wall lamina and compound corner middle lamella

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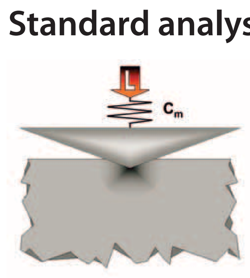
Abstract

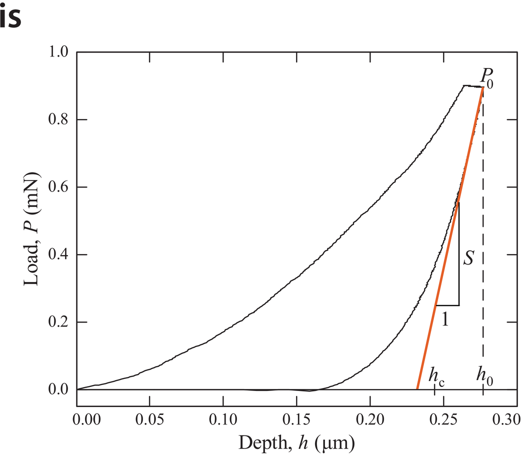
We are working to better understand the mechanical properties of wood and the effects of adhesives and chemical treatments on those properties. Our approach is to introduce a variety of chemicals to selectively interact with components in wood—lignin, cellulose, and hemicellose—thereby helping us to isolate the roles played by each of the components. We probe mechanical properties at the sub-cellular level by investigating the S2 cell wall lamina (SCWL) and compound corner middle lamella (CCML) with nanoindentation. We have invented a unique set of nanoindentation methods that isolate the viscoplastic creep properties across 4 to 5 orders of magnitude of strain rate in µm-scale regions. Unlike most nanoindentation methods that purport to map out spatially varying viscoelastic or viscoplastic properties, our methods are quantitative, sensitive to a wide range of material response, and they remove artifacts brought about by heterogeneities within the structure. In this study we modify wood with ethylene glycol and monitor the changes in properties of SCWL and CCML. Ethylene glycol was chosen because it is a small, hydrophilic molecule that has a large effect on bulk wood properties. Ethylene glycol will not react chemically with wood components, but it will disrupt hydrogen bonding within the components. We find that ethylene glycol plasticizes both SCWL and CCML, but the effects are larger in the SCWL. We attribute the difference to differences in composition and structural organization.

Nanoindentation analyses

Standard analysis



Assumes material indented can be represented by infinite half-space



Meyer's Hardness: $H = \dfrac{P_0}{A(h_c)}$ $A(h_c)$ = Area based on contact depth (h_c)

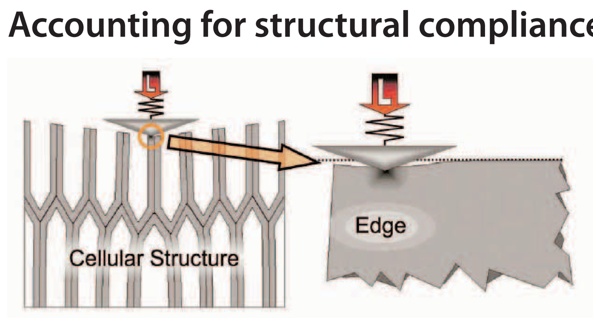
Effective Modulus: $E_{\text{eff}} = \dfrac{S}{A(h_c)^{1/2}}$

Calculate Young's Modulus (E_s) from: $\dfrac{1}{E_{\text{eff}}} = \dfrac{1}{\beta}\left[\dfrac{1-\nu_s^2}{E_s} + \dfrac{1-\nu_d^2}{E_d}\right]$

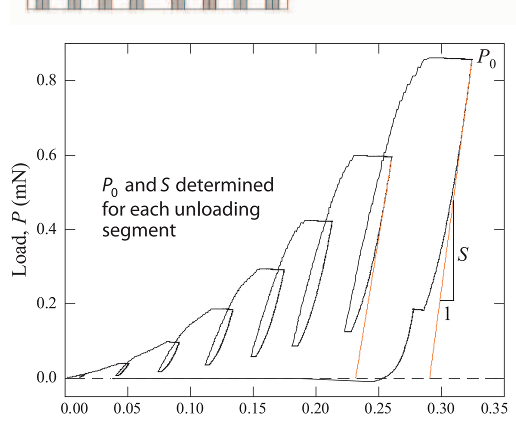
β = Correction factor (1.23)[1]

E_i and ν_i are Young's Modulus and Poisson's Ratio for specimen (s) and indenter (d) respectively

Accounting for structural compliance



Need to account for specimen-scale flexing and edge effects



The effects of specimen-scale flexing and edges can be removed by including a structure compliance (C_s) in the analysis.[1]

C_s behaves similar to the machine compliance (C_m), and the Stone, Yoder, and Sproul (SYS)[3] method to measure C_m can easily be extended to also measure C_s.

SYS plot[1,3]

$$C_t P_0^{1/2} = (C_m + C_s)P_0^{1/2} + \frac{H^{1/2}}{E_{\text{eff}}}$$

If H, E_{eff}, and C_s are independent of load, a plot of $C_t P_0^{1/2}$ vs. $P_0^{1/2}$ will yield a straight-line plot with slope ($C_m + C_s$). The data to construct an SYS plot can come from a single multiload indent.

After C_s is determined, the load-depth traces can be corrected and analyzed using the standard analysis. However, we also find it advantageous to measure areas directly from residual indent images. The corrected analysis uses measured areas.

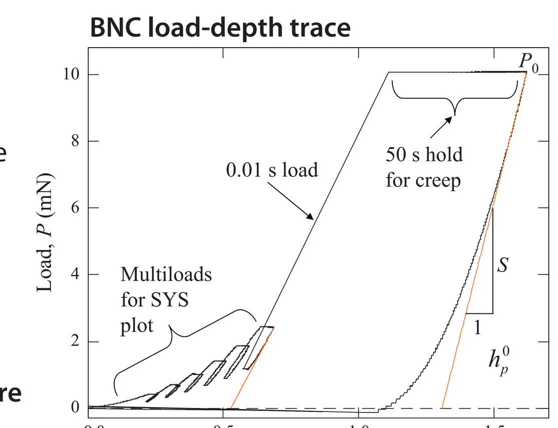
Broadband nanoindentation creep (BNC)

A BNC load-depth trace consist of two parts:

(1) Multiload segments from which a SYS plot is created to determine C_s and

(2) 50 s hold segment from which the creep properties (hardness vs. indentation strain rate) are determined.

BNC load-depth trace



BNC load-depth traces are calculated as follows:
Plastic depth calculated using[4–7]

$$h_p(t) \cong h_p^0 + \frac{h_t(t) - h_p^0 - P(t)C_p^0 + P(t)C_p^0(1-\zeta_p)\dfrac{P(t)-P_0}{2P_0}}{1 - \dfrac{P(t)C_p^0}{h_p^0}\zeta_p}$$

where superscript or subscript "0" indicates parameter from final unloading segment, h_t is total depth, $h_p^0 = h_t^0 - C_p^0$, and ζ_p is a power law exponent to correct proportionality factor between A and h_p.[4,6,7]

Calculate $A(t)$ at each point during creep using

$$A(t) = A_{\text{meas}} \exp\left[2\zeta_p \ln\left(\frac{h_p(t)}{h_p^0}\right)\right]$$

Calculate $H(t)$ at each point during creep using $H(t) = \dfrac{P(t)}{A(t)}$

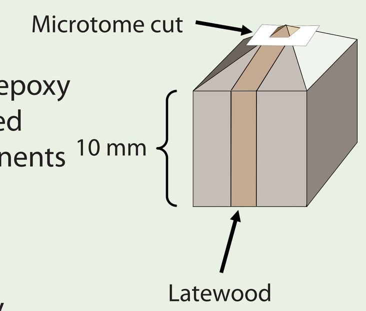
Calculate indentation strain rate ($\dot{\varepsilon}_H(t)$) at each point using $\dot{\varepsilon}_H(t) \equiv \dfrac{d\ln\sqrt{A(t)}}{dt}$

Plot $\ln(H)$ vs. $\ln(\dot{\varepsilon}_H)$ for each point during creep

Experimental procedure

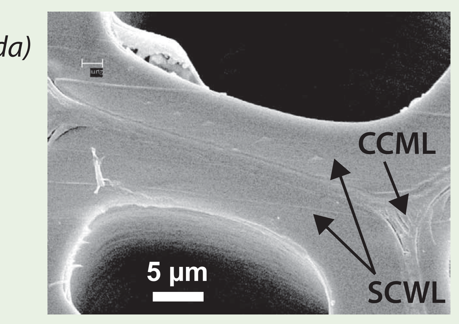
1. Sample preparation

- Currently in literature, wood specimens are embedded in epoxy and then surfaces are prepared
  - Diffusion of epoxy components may diffuse into cell wall, altering its properties
- We developed techniques to prepare surfaces without any embedment



2. Materials indented with Hysitron (Minneapolis, MN, USA) Triboindenter®

- Compound corner middle lamella (CCML) and S2 cell wall lamina (SCWL) of latewood loblolly pine (*Pinus taeda*)
  - Unmodified and modified with ethylene glycol
  - BNC multiload indents
- From previous work, we find ζ_p = 1.16 and 0.97 for SCWL ad CCML, respectively



3. Measuring areas from AFM images

Quesant (Agoura Hills, CA, USA) AFM

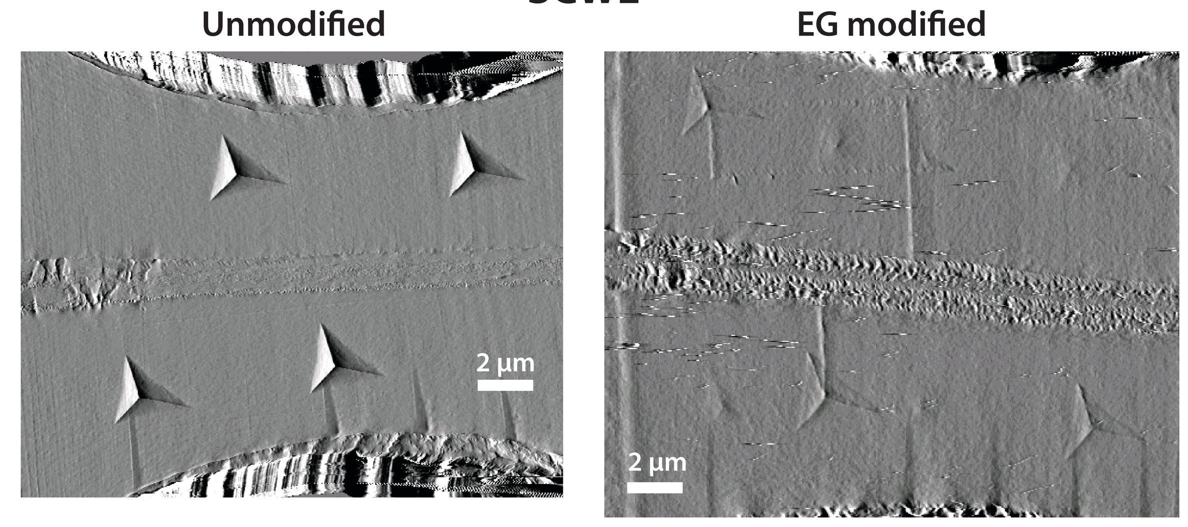
- Calibrated with an Advanced Surface Microscopy Inc. (www.asmicro.com) calibration standard
  - Pitch = 292 ± 0.5 nm
- 4 µm scans of each indent
- Areas measured using ImageJ (http://rsb.info.nih.gov/ij/) image analysis software
  - Based on contact edges

Results

Young's Modulus (E_s) and hardness (H)

SCWL

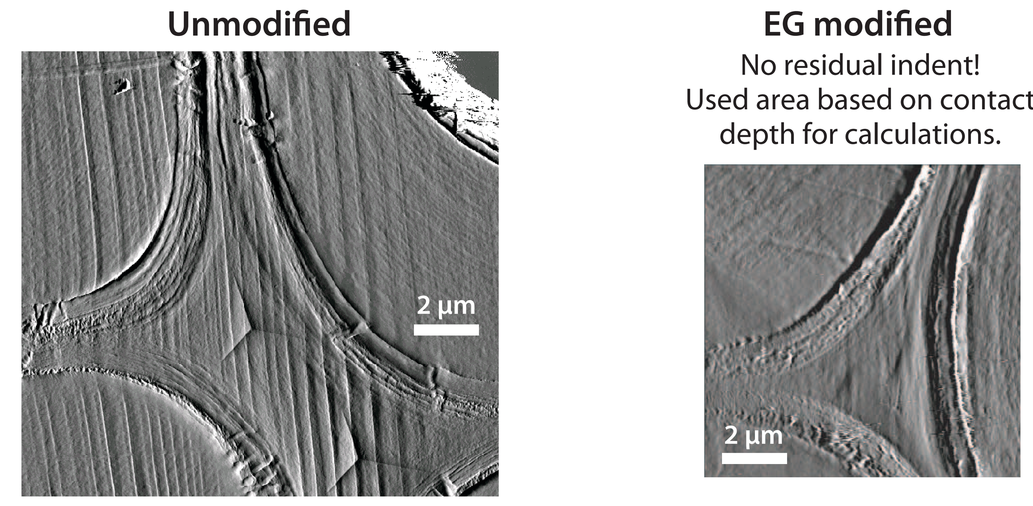
Unmodified | EG modified



CCML

Unmodified | EG modified

No residual indent!
Used area based on contact depth for calculations.



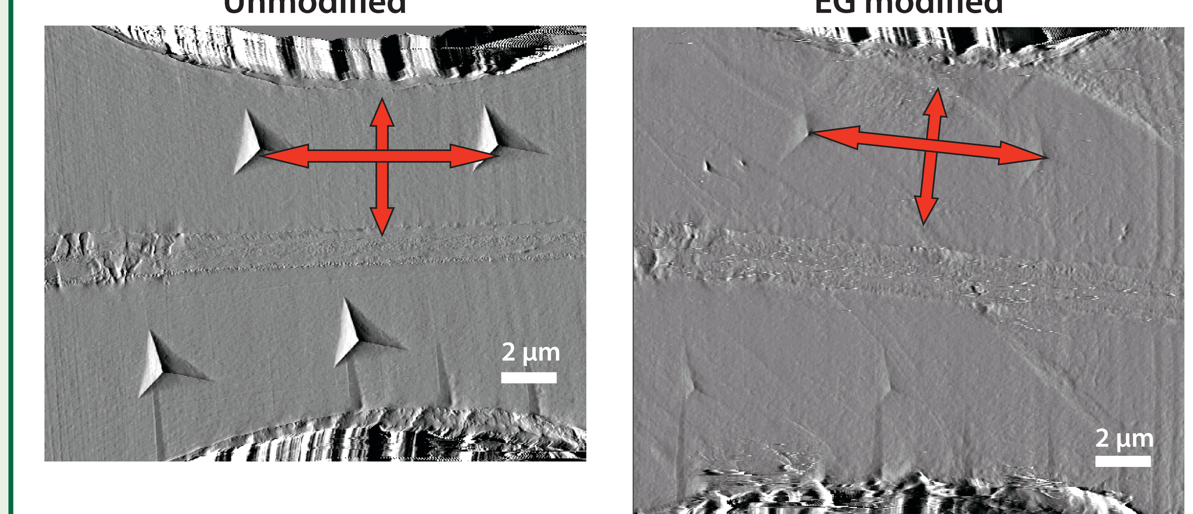
	CCML		SCWL	
	Untreated	EG treated	Untreated	EG treated
E_s (GPa)	6 ± 2	2.2 ± 0.3	20 ± 2	6.9 ± 0.5
H (MPa)	290 ± 20	110 ± 20	380 ± 20	80 ± 10
n	18	18	21	18

After EG modification, Young's modulus and hardness decreased for both CCML and SCWL, suggesting a plasticizing effect.

Swelling and shape memory effect

SCWL

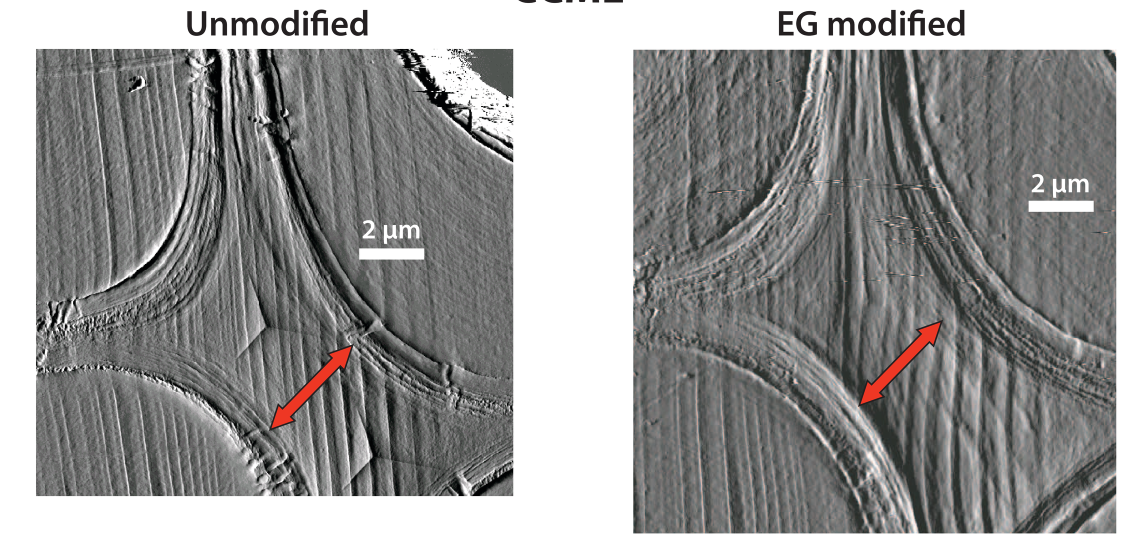
Unmodified | EG modified



After modification, indents partially recovered (a shape memory effect) and cell wall thickness increased.

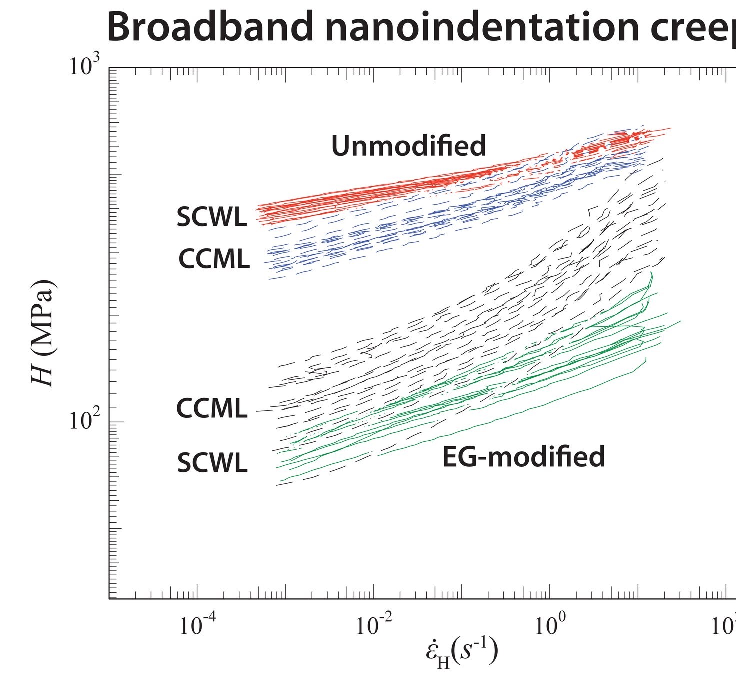
CCML

Unmodified | EG modified



After modification, indents completely recovered (a shape memory effect) and the CCML increased in dimensions.

Broadband nanoindentation creep (BNC)



- **Hardness of both the SCWL and CCML is decreased over all strain rates.**
- **EG has a larger effect on SCWL.**

Discussion

The diffusion of ethylene glycol into the SCWL and CCML is suggested by the

- Change in H, E_s and BNC data
- Swelling of the CCML and SCWL

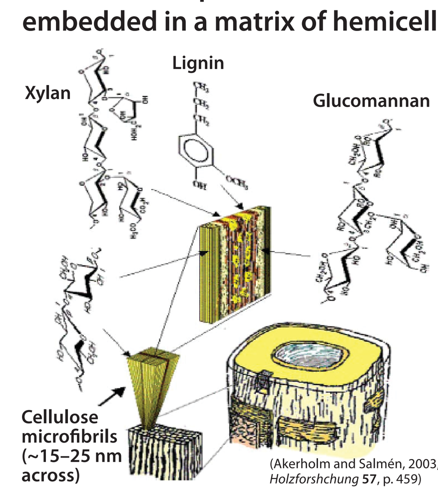
Once it has diffused into SCWL and CCML, ethylene glycol is expected to

- Plasticize both lignin and hemicellulose regions
- Have a higher affinity for the hemicellulose/pectin regions than the lignin regions because of solubility parameter considerations
- Not chemically react to form covalent bonds with cell wall components
- Not enter the crystalline regions of cellulose

The larger effect of ethylene glycol on the SCWL than the CCML may be caused by

- **Composition differences**
  - Higher percentage of hemicellulose in SCWL than in CCML
- **Structure differences**
  - In SCWL, hemicellulose forms a continuous network and serves as a transisition between cellulose microfibrils and lignin regions
  - In CCML, both hemicellulose and lignin form continuous networks
  - If ethylene glycol has a larger effect on hemicellulose, SCWL might be affected more because hemicellulose is a continuous phase and plays a larger role in determining the properties of the SCWL than in CCML, where the lignin regions also form a continuous network

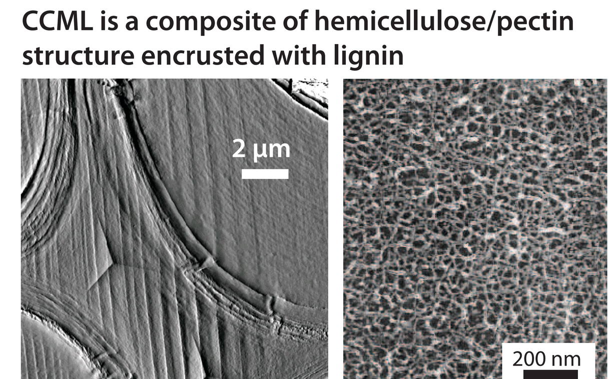
SCWL is a composite of cellulose microfibrils embedded in a matrix of hemicellulose and lignin



(Akerholm and Salmén, 2003, *Holzforshchung* **57**, p. 459)

Approximate composition
35% highly oriented semi-crystalline cellulose
20% amorphous cellulose
30% hemicellulose
15% lignin
Free volume also present

CCML is a composite of hemicellulose/pectin structure encrusted with lignin



Approximate composition
80% lignin
20% hemicellulose/ pectin
Free volume also present

TEM image of middle lamella after sodium chlorite treatment removing lignin, leaving the open cellular hemicellulose/pectin structure (Hafrén et al., 2000, *Holzforshchung* **54**, p. 234).

SCWL and CCML have different ultrastructure and composition

Summary

- BNC technique established to assess effects of modifications on the SCWL and CCML
  - Account for specimen-scale flexing and edge effects
- Ethylene glycol plasticizes SCWL and CCML
  - Effect greater on SCWL

Future work

Perform similar experiments with other types of wood modifications to help us understand the roles of composition and structure on the properties of SCWL and CCML

References

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