Nanoindentation as a Tool for Understanding Nano-Mechanical Properties of Cell Wall and Biocomposites

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Introduction

- Most wood products (70%) go to residential markets

**Consumer is 2/3rds of U.S. Economy**

GDP = Consumer Spending + Business Investment + Residential Investment + Govt. Spending + Net Exports

- 69.2% Personal Consumption
- 18.0% Housing
- 12.2% Business Investment
- 4.4% Residential Investment
- 16.8% Government Spending

2001 GDP = $10.208 Trillion*

Housing is about 20% of GDP When we include housing services, electricity and gas plus investment

*net exports (Exports - Imports) = - 3.2%

Sources: Al Schuler, USDA Forest Service
Introduction

• Wood-plastic composite is a very promising material to achieve durability without using toxic chemicals.

Deck and fence

Pool and docks

Door panel (Audi A2)

Source from Nexwood website
Introduction

• Issues addressed: what is mechanical properties at the wood cell wall level and interphase region between reinforcing fibers and matrix?

• Approach: characterizing cell wall and interphase using nanoindentation and AFM
Nanoindentation Instrument and Indentation Procedure

Schematic of the NANO II Indenter

- Loading Coil (±75nN)
- Support Spring
- Normal Displacement Gage (±0.04 nm)
- Lateral Displacement Gage
- Indenter Tip
- Specimen
- X-Y-Z Table (±0.2 µm)

Indent marks
Nanoindentation Instrument and Indentation Procedure

**Hardness (H):**

\[ H = \frac{P_{\text{max}}}{A} = \frac{P}{24.5h_c^2} \]

**Elastic modulus (E_s):**

(Oliver and Pharr)

\[ E_s = \left(1 - \nu_s^2\right) \left(\frac{1}{E_r} - \frac{1 - \nu_i^2}{E_i}\right)^{-1} \]

\[ E_r = \frac{dP}{dh} \frac{1}{2} \frac{\sqrt{\pi}}{\sqrt{A}} \]

\[ E_i \] is the modulus of the indenter (1141 GPa).

\[ V_s \] and \[ V_i \] (0.07) are the Poisson’s ratios of the specimen and indenter, respectively.

\[ E_r \] is reduced elastic modulus, which accounts for the fact that elastic deformation occurs in both the sample and the indenter.
Continuous stiffness measurement: One of the significant improvements in nanoindentation test.

With single experiment, cycles of indentation, each of which consists of incremental loading and partial unloading, are performed until a final desired depth is attained.

Each loading-and-partial unloading cycle provides a series of values of hardness and elastic modulus.
Wood Cell Wall: Loblolly Pine

Depth-dependent longitudinal stiffness
Wood Cell Wall: Loblolly Pine

Longitudinal stiffness: Variability along the tree cross section

Error bars indicate data range of three measurements
Wood Cell Wall: Loblolly Pine

Longitudinal hardness: Variability along the tree cross section

Error bars indicate data range of three measurements
Wood Cell Wall: Loblolly Pine

Longitudinal stiffness of wood as a function of microfibril angles

Note: The density values plotted were used to adjust the cell-wall stiffness ($E_o$ or $E_{model}$) to wood stiffness.
# Hardness and Elastic Modulus of Lyocell Fibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (GPa)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lyo15 (L)</td>
<td>14.6</td>
<td>67.5</td>
</tr>
<tr>
<td>Lyo8 (L)</td>
<td>7.5</td>
<td>65.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mean value from 150 to 300 nm depth (GPa)</th>
<th>Unloading value at final indentation depth (GPa)</th>
<th>Intrinsic value (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$H_{\text{mean}}$</td>
<td>$E_{\text{mean}}$</td>
<td>$H_{u}$</td>
</tr>
<tr>
<td>Lyo15 (L)</td>
<td>0.44 (0.06)</td>
<td>13.19 (0.10)</td>
<td>0.45 (0.05)</td>
</tr>
<tr>
<td>Lyo15 (T)</td>
<td>0.32 (0.02)</td>
<td>6.77 (0.28)</td>
<td>0.33 (0.02)</td>
</tr>
<tr>
<td>Lyo8 (L)</td>
<td>0.33 (0.05)</td>
<td>11.51 (1.27)</td>
<td>0.33 (0.06)</td>
</tr>
<tr>
<td>Lyo8 (T)</td>
<td>0.30 (0.01)</td>
<td>6.01 (0.14)</td>
<td>0.30 (0.01)</td>
</tr>
<tr>
<td>Wood cell wall</td>
<td>0.52 (0.06)</td>
<td>18.36 (2.48)</td>
<td>0.49 (0.05)</td>
</tr>
</tbody>
</table>

Three dimensional AFM image of lyocell fiber (Lyo15 (T)), cut in transversal direction, after nanoindentation.
Time-dependent Mechanical Properties (Creep behavior)

Change in displacement when subjected to a constant load of 500 micro-Newton
Time-dependent Mechanical Properties (Creep behavior)

Effect of holding time on hardness under the load of 500 μN

Effect of holding time on elastic modulus under the load of 500 μN
Interphase Properties

- A better understanding of interphase, which will be very useful for the optimum design of final composite products.
Interphase Properties

Spacing (260 nm) Property transition zone from fiber to matrix, showing four indents (30 nm depth)

(A) Maleic anhydride and silane modified interphase in regenerated cellulose fiber-reinforced PP composite
Summary

• Nanoindentation was a useful tool to investigate wood cell wall and biocomposites and provided some new information.

• The longitudinal mechanical properties of the cell wall varied along the tree cross section.

• There are some challenges needed to be addressed when measuring nano scale mechanical properties.
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