X-Ray diffraction study of wood cellulose behaviour during drying

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Principle: evaluation of the change in 004 lattice spacing

Bragg’s law: \[ d_{004} = \frac{\lambda}{2 \sin \theta_{004}} \]
Measurement of Cellulose Strains using X-Ray Diffraction

Principle: evaluation of the change in 004 lattice spacing

Crystal strain: \[ \varepsilon = \frac{d_004' - d_{004}}{d_{004}} \]

Bragg’s law:

\[ d_{004} = \frac{\lambda}{2\sin\theta_{004}} \]

\[ d_{004}' = \frac{\lambda}{2\sin\theta_{004}'} \]
Measurement of Cellulose Strains using X-Ray Diffraction

004 diffraction peak

Mean Lattice Spacing $d_{004}$ \( (\text{End-Ini}) / \text{Ini} = \text{Crystal strain} \)
Measurement of Cellulose Strains using X-Ray Diffraction

Separating the signal associated to different Microfibril Angles

X-ray impacting sample at $\theta$

$=>$ Diffraction azimuth $\phi=\mu$ microfibril angle
Measurement of Cellulose Strains using X-Ray Diffraction

004 diffraction peak

For each sector
Position (R) ↔ Lattice

Azimuth (ϕ) ↔ MFA

Mean Lattice Spacing for each sector

3 Sectors: 0-5°, 5-10°, 10-15°

(Dry-Wet) / Wet = Crystal strains for each sector

Workshop “Wood structure/function relationships”
Hamburg, 5-8 October 2010
Aims and Methodology

Studying the crystal strains $\varepsilon(\mu)$ associated to different MFA during wood dimensional changes

$\Rightarrow$ (Hygro-thermal recovery of green wood)

$\Rightarrow$ Drying shrinkage

Methodology

- Measurement of macroscopic strains $\varepsilon_T$ and $\varepsilon_L$
- Measurement of crystal strains by MFA $\varepsilon(\mu)$
- “Null” model: $\varepsilon(\mu) = \cos^2(\mu)\varepsilon_L + \sin^2(\mu) \varepsilon_T$

Assumptions: no shear, no microfibril slippage

- More complex mechanisms: $\varepsilon_{\text{sample}} \neq \varepsilon_{\text{wall}}$ ... strain localisation

$\Rightarrow$ Information about mechanisms involved
Material and Methods

Plant material
• Poplar
• Tension wood // Opposite wood
• 18 + 18 samples

Drying shrinkage
• Specimens 60 x 12 x 1.5 mm
• Green => Air-dry
• L and T shrinkage
Results: macroscopic drying shrinkage

Graph showing L Drying Shrinkage and T Drying Shrinkage with data points for Tension Wood and Opposite Wood.

⇒ Very high values (-1%) of L shrinkage for Tension Wood

Usual for species with G-layer tension wood as poplar
Results: diffraction patterns

Opposite wood

Tension wood

Azimuthal patterns $\Leftrightarrow$ MFA dispersion

G-Layer $\Leftrightarrow$ large signal at small MFA
Results: crystal strains by MFA

$\varepsilon_\mu = \varepsilon_{T\text{wall}} \sin^2(\mu)$

Consistent with $\varepsilon_{T\text{wall}} = 4\%$

$\varepsilon_{T\text{sample}} = 7\%$

Opposite wood

$\varepsilon_{15^\circ} < \varepsilon_{10^\circ} < \varepsilon_{5^\circ} < 0$
Results: crystal strains by MFA

L Drying Shrinkage

0-5°  5-10°  10-15°

-1.4% -1.2% -1.0% -0.8% -0.6% -0.4% -0.2% 0.0% 0.2% 0.4%

Microfibril shrinkage

Very low crystal strains!

Case of straight microfibrils (~0°):

\( \varepsilon_\mu \ll \varepsilon_L \)
Hypothesis: microfibril buckling

In drying G-layer: crystal strain $\ll$ macroscopic strains

**Microfibril “buckling”**  
*Clair et al. 2006  Biophysical Journal*

= bending (waving) instead of compression

facilitated by compliant matrix

would explain large L shrinkage

\[ \varepsilon_\mu = \varepsilon_L = 0 \]
\[ \varepsilon_\mu = \varepsilon_L < 0 \]
\[ |\varepsilon_\mu| < |\varepsilon_L| \]
Assuming buckling strain $\varepsilon_{\mu}^{\text{max}} = -0.2\%$
Results: crystal strains by MFA

L Drying Shrinkage

-1.4% -1.2% -1.0% -0.8% -0.6% -0.4% -0.2% 0.0% 0.2% 0.4%

Microfibril shrinkage

0-5° 5-10° 10-15°

ε_{5°} < ε_{10°} < ε_{15°}

Not consistent with

\[ \varepsilon_T < \varepsilon_L < 0 \ldots \]

\[ \varepsilon(\mu) = \cos^2(\mu)\varepsilon_L + \sin^2(\mu)\varepsilon_T \]

Wall level

\[ \varepsilon_{L\text{wall}} \neq \varepsilon_{L\text{sample}} \]
\[ \varepsilon_{T\text{wall}} \neq \varepsilon_{T\text{sample}} \]

ε_{T\text{wall}} > 0 ???

Tension wood

ε_{5°} < ε_{10°} < ε_{15°}
Hypothesis: heterogeneity of $\varepsilon_T$ across the cell-wall

Observations of drying strains in cell-wall layers

**Fang et al. 2007** *Wood Sci. Tech.*

<table>
<thead>
<tr>
<th></th>
<th>Wood sample</th>
<th>Outer walls</th>
<th>Inner walls</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>WET</strong></td>
<td>$\varepsilon_T^{\text{sample}} &lt; 0$</td>
<td>$\varepsilon_T^{\text{out}} &lt; 0 \sim \varepsilon_T^{\text{sample}}$</td>
<td>Normal / Tension wood</td>
</tr>
<tr>
<td><strong>DRY</strong></td>
<td></td>
<td>$\varepsilon_R^{\text{out}} &lt; 0$</td>
<td>$\varepsilon_T^{\text{in}} &lt; 0$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>$\varepsilon_R^{\text{in}} &lt; 0$</td>
</tr>
</tbody>
</table>

At lumen border:

- **Normal wood**
  - “Inward Shrinkage”
  - “Outward Shrinkage”

- **Tension wood**
  - “Inward Shrinkage”
  - “Outward Shrinkage”
Modelling: consistence between assumptions and observations?

L Drying Shrinkage

-1.4% -1.2% -1.0% -0.8% -0.6% -0.4% -0.2% 0.0% 0.2% 0.4%

Microfibril shrinkage

0-5° 5-10° 10-15°

Tension wood

\[ \varepsilon_{5^{\circ}} < \varepsilon_{10^{\circ}} < \varepsilon_{15^{\circ}} \]

Opposite wood

\[ \varepsilon_{15^{\circ}} < \varepsilon_{10^{\circ}} < \varepsilon_{5^{\circ}} < 0 \]
Modelling: drying strains gradients in a multi-layer cell

Multiscale Model:

Wood = set of cells
   (unit volume = cell)
   + fiber-end effect

Cell = multi-layer cylinder
   no torsion
   no slippage between layers

Wall layers = microfibrils + matrix
   orientation (MFA+variation)
   no microfibril slippage

Matrix: shrinks when dries
   different in G and S layers

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Modelling: drying strains gradients in a multi-layer cell

MODEL

Wall layers structure:
MFA, thickness

Properties of constituents:
Stiffness, anisotropy

Loading:
Drying stress

Boundary conditions

Macroscopic shrinkage

Strain and stress fields

Direct calculation: upscaling
Modelling: drying strains gradients in a multi-layer cell

Properties of constituents: Stiffness, anisotropy

Loading: Drying stress

Boundary conditions

Macroscopic shrinkage

Wall layers structure: MFA, thickness

Strain and stress fields

Inverse calculation: downscaling

Crystal strains
Simulations: crystal strains for different MFA and cell types

L Drying Shrinkage

-1.4% -1.2% -1.0% -0.8% -0.6% -0.4% -0.2% 0.0% 0.2% 0.4%

Microfibril shrinkage

Thick G-layer
Tension wood

No G-layer
Opposite wood
Simulations: crystal strains for different MFA and cell types

Correct trends and orders of magnitude

but it is only a “proof of principle”...
Conclusion: multi-scale observations and modelling

X-ray diffraction and micromechanics
• combining MFA analysis and Lattice analysis
• testing assumptions about mechanisms at lower levels

Evidence of heterogeneous state of stress within the cell-wall
• drying => eigenstresses
• initial state => maturation eigenstresses
• hygro-thermal treatments => thermal eigenstresses
• Consequences on non-linear behaviours!
• Application: mechanical preconditioning?

Thank you for your attention... questions?