Material processing based on wood nanofibrillated cellulose

Houssine Sehaqui
(currently post-doc at EMPA - Switzerland)
Introduction

- 100 million tons plastics from petroleum produced annually, 40% used as packaging → waste (not biodegradable)

Polymers from renewable resources of interest; abundant, low cost, biodegradable, need good properties and low environmental impact
Wood structure

3 components:
• Cellulose nanofibrils
• Hemicellulose
• Lignin
Nanofibrillated cellulose

1. Turbak et al JAPS (1983)

3wt% NFC suspension
Diameter of the fibrils is 25 – 100 nm

2wt% NFC suspension
Diameter of the fibrils is 10 – 30 nm

0.6wt% TEMPO- NFC suspension
Diameter of the fibrils is 4 – 5 nm
Nanofibrillated cellulose

- High modulus about 140 GPa.\(^1\)
- High aspect ratio and surface area
- Network formation ability through hydrogen bonds and secondary interactions

- This can be exploited in materials elaboration and reinforcement in composites

\(^1\)Iwamoto et al Biomacromolecules (2009)
Materials from NFC

1. Evaporation → NFC nanopaper
2. Supercritical drying → NFC aerogel
3. Freeze drying → NFC foam
1. NFC nanopaper by liquid evap.
NFC nanopaper

- NFC nanopaper: mat of cellulose nanofibrils.
- Prepared by vacuum filtration and drying

*Henriksson et al. Biomacrom. (2008)*
*Sehaqui et al. Biomacrom. (2010)*
Nanopaper Structure

Surface SEM

Cross section SEM
Nanopaper properties

- Density $\sim 1300\text{kg/m}^3$, Porosity $\sim 15\%$
- Transparent and flexible
- Smooth (low surface roughness)
- High barrier properties\(^1\) and low surface area
- Low thermal expansion\(^2\)

\(^1\text{Liu et al Biomacrom. (2011)}\)
\(^2\text{Yano et al Adv. Materials (2009)}\)
Mechanical properties in tension

\[ E_{\text{nanopaper}} = 13 \text{ Gpa} \]
\[ \sigma_{\text{nanopaper}} = 230 \text{ Mpa} \]
\[ \varepsilon_{\text{nanopaper}} = 5 \% \]
\[ \text{Toughness} = 7.5 \text{ MJ/m}^3 \]

\[ E_{\text{paper}} = 8 \text{ Gpa} \]
\[ \sigma_{\text{paper}} = 100 \text{ Mpa} \]
\[ \varepsilon_{\text{paper}} = 3 \% \]
\[ \text{Toughness} = 1.7 \text{ MJ/m}^3 \]

Sehaqui et al, Composites Science and Technology 2011
Improving mechanical properties

- Goal: partially aligning the fibrils in the wet gel by stretching

*Sehaqui et al*,
ACS Applied Materials and Interfaces 2012

Unstretched: DR=1

Stretched: DR=1.6

DR=L_f/L_0
Degree of orientation by XRD

\[ f = \frac{(3 < \cos^2 \phi > -1)}{2} \]

Graph showing the Hermans orientation parameter \( f \) as a function of drawn ratio. The graph compares ‘Edge’ and ‘Through’ orientation.
## Tensile Mechanical Properties

<table>
<thead>
<tr>
<th>Drawing ratio</th>
<th>1</th>
<th>1.2</th>
<th>1.4</th>
<th>1.6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modulus (GPa)</td>
<td>10.3 (0.8)</td>
<td>17.3 (4.0)</td>
<td>24.6 (0.4)</td>
<td><strong>33.3</strong></td>
</tr>
<tr>
<td>Strength (MPa)</td>
<td>185 (7.7)</td>
<td>345 (40)</td>
<td><strong>428 (15)</strong></td>
<td>397</td>
</tr>
<tr>
<td>Strain at break (%)</td>
<td>5.26 (0.56)</td>
<td>3.55 (1.21)</td>
<td>2.46 (0.23)</td>
<td>1.79</td>
</tr>
</tbody>
</table>

![Stress-Strain Curve](image)

- **DR=1**: Base material
- **DR=1.2**: Moderate drawing ratio
- **DR=1.4**: High drawing ratio
- **DR=1.6**: Extreme drawing ratio
2. NFC aerogel by supercritical drying

Sehaqui et al Biomacrom. (2011)
High surface area nanopaper

- Previous NFC nanopaper has a low surface area (0.008m²/g).
- Goal: preserve the surface area of the nanopaper and study effects on mechanical properties

1/ Vacuum filtration
2/ Careful drying techniques
# High surface area nanopaper

<table>
<thead>
<tr>
<th></th>
<th>Direct drying</th>
<th>SC-CO$_2$ NFC</th>
<th>SC-CO$_2$ TEMPO-NFC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Density/ kg.m$^{-3}$</strong></td>
<td>1200</td>
<td>205</td>
<td>640</td>
</tr>
<tr>
<td><strong>Porosity/ %</strong></td>
<td>20</td>
<td>86</td>
<td>56</td>
</tr>
<tr>
<td><strong>Surface area / m$^2$ g$^{-1}$</strong></td>
<td>0.008</td>
<td>304</td>
<td>482</td>
</tr>
<tr>
<td><strong>Fibril diameter/ nm</strong></td>
<td>-</td>
<td>9.0</td>
<td>5.7</td>
</tr>
<tr>
<td><strong>Average pore diameter/ nm</strong></td>
<td>-</td>
<td>35.8</td>
<td>12.4</td>
</tr>
</tbody>
</table>
High surface area nanopaper

TEMPO-NFC nanopaper

NFC nanopaper

SSA=482 m$^2$/g

SSA=304 m$^2$/g
• Mechanical properties $\approx$ thermoplastics but much lower density
• Higher SSA correlates with higher ductility and lower stiffness
3. NFC foams by freeze drying

NFC foams

• Goal: Prepare high-porosity NFC foams of different densities and study the density effect on the mechanical properties.

NFC foam
Density = 7 -100 kg/m³
Porosity = 93-99.5%
Foam structure

- NFC foam: ice templated cellular structure with "nanopaper" cell wall
- Specific surface area 14-42 m²/g
NFC foams

- NFC foams have a wide range of mechanical properties. Ductile with yield behavior. High energy absorption.
Conclusion 1

- Different structure can be achieved by different drying of NFC suspension

Possible application:
- Packaging; display
- Filtration, storage, insulation
- Packaging; insulation, biomedical
NFC in composites
NFC composites

• NFC as load bearing component in 2 phase system
• 3 different methods have been used
  – Vacuum filtration and high T drying
  – Vacuum filtration and supercritical drying
  – Insitu polymerisation
1. NFC composites by filtration and high T. drying

Papermaking approach to NFC/HEC dispersion.

NFC: Nanofibrillated Cellulose
HEC: Hydroxyethyl Cellulose
NFC/HEC surface structure

- Note porosity in ref nanopaper (left)
- NFC embedded in HEC matrix (right)

Sehaqui et al. Soft Matter (2011)
NFC/HEC cross-section

NFC/HEC = 88 / 0

NFC/HEC = 54 / 28

NFC/HEC = 45 / 41
NFC/HEC structure

- Nanofibrillated Cellulose
- Soft HEC Matrix
NFC/HEC mechanical properties

- Strain-to-failure of 20% and strength of 180MPa
- Toughest cellulose composite reported
2. NFC composites by vacuum filtration and supercritical drying
2. NFC composites by vacuum filtration and supercritical drying

Porous membranes of HEC-coated nanofibrils as possible alternative to membranes by electrospinning

1/ Sehaqui et al. Soft Matter (2011)
3. NFC composites by in situ polymerisation

We start from high surface area nanopaper and graft polycaprolactone onto it.
NFC PCL Structure

Ungrafted nanopaper

Grafting and removal of free PCL

Grafted nanopaper

Up to 80% PCL in the composites

Boujemaoui et al.,
ACS Applied Materials and Interfaces 2012
NFC PCL properties

**DMA**

- High mechanical properties of the composites even at high temperatures due to NFC network

**Water uptake**

- Reduction of moisture uptake of NFC by 60% after PCL grafting
General conclusions
Conclusion

NFC widens properties of wood based products
Conclusion

• Density: 7-1300 kg/m³
• Porosity range: 15% - 99.5%
• Surface area: 0.01-480m²/g
• Property modification: HEC / PCL coatings
• → NFC is a versatile constituent offering numerous possibilities for material engineering
Acknowledgment

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• Thesis book of the present work available online at:
Thank you for your attention