Fiber spinning of biopolymers containing nanowhiskers: Possibilities and challenges

Aji P. Mathew and Kristiina Oksman

Wood and Bionanocomposites, Division of Materials Science
Luleå University of Technology, Sweden

IAWS 2011, Stockholm Augst 31st - Sept 2nd
Outline

- Concept and aim
- Fiber spinning of biopolymer with nanowhiskers
  - Melt spinning
  - Electrospinning
- Characterisation
  - Structure
  - Mechanical properties
  - Thermal stability
- Conclusions and path forward
Concept and aim

- Produce continuous fibers using biobased materials, for use in composite processing, biomedical products, industrial textiles etc
- Use as an alternative for non-biobased fibers
- Use as an alternative for natural fibers
Concept and aim

• Today’s fibers are produced by
  Melt spinning, Electrospinning, Wet spinning

• All are industrial scale processes

Our goal

• Biopolymer fibers using cellulose / chitin nanowhiskers as functional additives
• Biobased nanocomposites with directional properties (aligned nanoparticles?)

Challenges are

• Temperature sensitivity of biobased materials
• Dispersion on nanoparticles in the biopolymer matrix
Raw materials

- Polylactic acid: ESUN™, Melt spinning grade, Shenzhen Brightchina Industrial Co. China.
- Cellulose Acetate: Sigma-Aldrich Chemistry, USA; density, 1.3 g/cm³
- Chitosan: Mw 100,000-2,000,000, Cognis Deutschland GmbH & Co.
- Cellulose whiskers: Isolated from MCC by HCl/ H₂SO₄ hydrolysis
- Chitin whiskers: Isolated from crab shell by HCl hydrolysis
Melt spinning process

Polymer melt is forced through spinnerets with large number of holes, Eg: PET, Nylon, PP etc.
Melt spinning of PLA/CNW fibers

**Fiber preparation**

- Master batch preparation(PLA/10CNW)
- Melt compounding
- Melt spinning

<table>
<thead>
<tr>
<th>Sample</th>
<th>Master batch (gms)</th>
<th>Bulk PLA (gms)</th>
<th>Final composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA</td>
<td>20 (20/0)</td>
<td>180</td>
<td>PLA 100</td>
</tr>
<tr>
<td>PLA-CNW1</td>
<td>20 (18/2)</td>
<td>180</td>
<td>PLA/CNW 99/1</td>
</tr>
<tr>
<td>PLA-CNW3</td>
<td>60 (54/6)</td>
<td>140</td>
<td>PLA/CNW 97/3</td>
</tr>
</tbody>
</table>
Meltspinning Process

PLA + Master batch

Vacuum vent

Water bath

Pelletiser

Fast godet

Heated godets

Uptake godets

Extruder and Spinneret

Winder

210 200 200 190

Pellets
Morphology

- Uniform fiber diameters
- Diameters in the similar range
- Surface roughness on nanocomposite fibers, increased with CNWs
Morphology: Nano Scale

- Aggregates in the range of 1 microns
Thermal stability

- Increased thermal stability with the addition of CNWs

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak deg. temp. [°C]</th>
<th>Temp. [°C]</th>
<th>Char at 600°C [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>@ 10% mass loss</td>
<td>@ 80% mass loss</td>
</tr>
<tr>
<td>PLA</td>
<td>370</td>
<td>328</td>
<td>371</td>
</tr>
<tr>
<td>PLA-CNWW1</td>
<td>380</td>
<td>348</td>
<td>396</td>
</tr>
<tr>
<td>PLA-CNWW3</td>
<td>393</td>
<td>348</td>
<td>399</td>
</tr>
</tbody>
</table>
Thermal shrinkage

- Lower thermal shrinkage for nanocomposite fibers
- CNWs probably restrict the polymer chain mobility
Electro spinning process

Polymer solution droplet is spun into a nanofiber by projecting onto a collector under the influence of electrostatic force $E_g \cdot CA$

- Nanofibre-reinforced composites
- Membranes and smart cloths
- Biomedical usage
- Enzyme and catalyst supports
- Sensors, Electrode
- Electronic and optical devices
- Sacrificial templates
Basic electrospinning setup

- 1- Polymer solution
- 2- HV generator
- 3- Needle tip
- 4- Jet
- 5- Collector

- CA with cellulose nanowhiskers
- Chitosan with chitin nanowhiskers
- Chitosan with cellulose nanowhiskers
Spinning of CA/CNW nanofibers

- Cellulose acetate / CNW solution conc.: 10 wt%
- Solvent: Acetone/ Acetic acid 50:50
- Gap distance: 15- 20 cm
- Applied Voltage: 15 kV

Nanofibers were spun and collected on the collector
Randomly oriented nanocomposite fibers

- Different CNW contents 1, 3, 5 wt%
- Beadless, uniform nanofibers in all cases
- Decreased fiber diameter when nanocrystals are present
- 1100 nm → 300nm

Herrera, Mathew, Wang, Oksman Plastics, Rubber and Composites: Macromolecular Engineering, 40 (2011) 57-64.
### Mechanical Properties- Tensile tests

<table>
<thead>
<tr>
<th>Material</th>
<th>Initial elastic modulus (MPa)</th>
<th>Strain (%)</th>
<th>Stress (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CA perp</td>
<td>219.7 ± 50.6</td>
<td>2.88 ± 0.45</td>
<td>4.36 ± 0.61</td>
</tr>
<tr>
<td>Pure CA paral</td>
<td>174.5 ± 28.6</td>
<td>2.84 ± 0.61</td>
<td>3.48 ± 0.13</td>
</tr>
<tr>
<td>CA-CNW1.0, perp</td>
<td>468.5 ± 43.9</td>
<td>2.24 ± 0.03</td>
<td>8.43 ± 0.41</td>
</tr>
<tr>
<td>CA-CNW1.0, paral</td>
<td>450.2 ± 55.1</td>
<td>2.32 ± 0.32</td>
<td>5.79 ± 0.31</td>
</tr>
<tr>
<td>CA-CNW3.0 perp</td>
<td>310.5 ± 50.2</td>
<td>1.94 ± 0.59</td>
<td>4.09 ± 0.92</td>
</tr>
<tr>
<td>CA-CNW3.0 paral</td>
<td>303.6 ± 86.2</td>
<td>1.71 ± 0.34</td>
<td>3.11 ± 0.65</td>
</tr>
<tr>
<td>CA-CNW5.0, perp</td>
<td>125.3 ± 13.6</td>
<td>3.81 ± 0.33</td>
<td>3.64 ± 0.19</td>
</tr>
<tr>
<td>CA-CNW5.0, paral.</td>
<td>146.2 ± 33.9</td>
<td>2.34 ± 0.26</td>
<td>2.71 ± 0.42</td>
</tr>
</tbody>
</table>

- Improved strength and modulus for nanocomposite fibers at lower concentrations
Mechanical Properties-DMA

- Improved storage modulus, especially at low CNW content

<table>
<thead>
<tr>
<th>Material</th>
<th>Storage modulus E´ (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At 30° C</td>
</tr>
<tr>
<td>Pure CA</td>
<td>81.1 ± 19.3</td>
</tr>
<tr>
<td>CA-CNW(_{1.0})</td>
<td>825.2 ± 183.1</td>
</tr>
<tr>
<td>CA-CNW(_{3.0})</td>
<td>411.7 ± 47.0</td>
</tr>
<tr>
<td>CA-CNW(_{5.0})</td>
<td>109.6 ± 33.2</td>
</tr>
</tbody>
</table>
Aligned nanocomposite fibers

- Possible to spin aligned fibers
- Orientation was lost with longer spinning time
- Nanocomposite fibers had lower diameters

Mechanical Properties

- Fiber bundles were tested
- No improvement with the addition of nanowhiskers

<table>
<thead>
<tr>
<th>Material</th>
<th>Initial elastic modulus (MPa)</th>
<th>Strain (%)</th>
<th>Stress (Mpa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure CA</td>
<td>532 ± 272</td>
<td>2.7 ± 0.7</td>
<td>19.6 ± 3.5</td>
</tr>
<tr>
<td>CA-CNW0.3</td>
<td>361 ± 117</td>
<td>2.7 ± 0.5</td>
<td>10.6 ± 5.2</td>
</tr>
<tr>
<td>CA-CNW0.6</td>
<td>300 ± 187</td>
<td>3.3 ± 0.6</td>
<td>8.3 ± 3.3</td>
</tr>
<tr>
<td>CA-CNW0.9</td>
<td>264 ± 55</td>
<td>2.8 ± 0.3</td>
<td>7.8 ± 3.1</td>
</tr>
<tr>
<td>CA-CNW1.2</td>
<td>256 ± 109</td>
<td>2.6 ± 0.6</td>
<td>7.7 ± 2.2</td>
</tr>
<tr>
<td>CA-CNW1.8</td>
<td>252 ± 135</td>
<td>2.5 ± 0.6</td>
<td>5.5 ± 1.7</td>
</tr>
</tbody>
</table>
Morphology

- Fiber cross-sections were not uniform
- Ribbon-like, flattened fibers, doublets
- Porosity in the fibers
- Agglomeration of CNWs
# Chitosan based nanofibers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Concentration (wt %)</th>
<th>CH</th>
<th>ChW</th>
<th>CNW</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>100</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>CH-ChW_{1.25}</td>
<td>98.75</td>
<td>1.25</td>
<td>1.25</td>
<td>1.25</td>
</tr>
<tr>
<td>CH-ChW_{2.5}</td>
<td>97.5</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
</tr>
<tr>
<td>CH-ChW_{5}</td>
<td>95</td>
<td>5</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>CH-CNW_{1.25}</td>
<td>98.75</td>
<td></td>
<td>1.25</td>
<td></td>
</tr>
<tr>
<td>CH-CNW_{2.5}</td>
<td>97.5</td>
<td></td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>CH-CNW_{5}</td>
<td>95</td>
<td></td>
<td>5</td>
<td></td>
</tr>
</tbody>
</table>

- Solution concentration: 2 wt%
- Solvent: TFA/DCM, 50/50
- Gap distance: 20 cm
- Applied Voltage: 15 kV
Chitosan based nanofibers

- Uniform, smooth nanofibers without beads
- Diameters decreased with whiskers addition and its concentration

<table>
<thead>
<tr>
<th>Sample</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH</td>
<td>213</td>
</tr>
<tr>
<td>CH-ChW₁₂₅</td>
<td>171</td>
</tr>
<tr>
<td>CH-ChW₂₅</td>
<td>163</td>
</tr>
<tr>
<td>CH-ChW₅</td>
<td>143</td>
</tr>
<tr>
<td>CH-CNW₁₂₅</td>
<td>174</td>
</tr>
<tr>
<td>CH-CNW₂₅</td>
<td>165</td>
</tr>
<tr>
<td>CH-CNW₅</td>
<td>160</td>
</tr>
</tbody>
</table>
Conclusions

- Melt spinning and electrospinning of biopolymers with nanowhiskers were successful.
- Electrospun random mats showed improved mechanical properties at 1% CNW content, but not the aligned fibers.
- Addition of CNWs decreased the diameter of electrospun fibers.
- CNW dispersion in biopolymer matrix needs improvement:
  - New processing routes
  - Use of compatibilisers
- Studies on dye-ability, biocompatibility etc.
Acknowledgements

• NanoFiber (VINNOVA) for financial support

• Swedish research links (SIDA) for collaboration support with SA (no. 348-2008-6009)

• Dr. Rajesh D. Ananjiwala, Dr. Maya Jacob John, Valencia Jacobs, CSIR, South Africa for support with fiber processing and characterisation

• Natalia Herrera and Luyi Wang for electrospinning data

• Liva Rozite for tensile test data
Thank you for your attention..