Cellulose Nanocrystal/Polymer Composites Processing Strategies and Impacts on Polymer Crystallization

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April 10, 2012
Shofner Research Group
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- Research mission: understand & manipulate material microstructure to produce multiscale, functional structures
- Research area: polymers and nanocomposites
- Core Competencies
  - Processing
  - Thermomechanical testing
  - Thermal analysis
- External Collaborators
  - Clark Atlanta University
  - Loughborough University
- Current Funding
  - IPST at Georgia Tech
  - USDA Forest Products Laboratory
  - NSF
  - DARPA
  - Solvay Specialty Polymers
Shofner Group Facilities

- Modular polymer processing system
  - Batch mixing
  - Single screw extrusion (general purpose and mixing screws)
  - Twin screw extrusion (conical counter-rotating)

- Dynamic mechanical analysis
  - 40 N maximum load
  - Bending, shear, tension, and compression

- High speed differential scanning calorimetry
  - Maximum heating rate: 40,000 K/s
  - Maximum cooling rate: 4000 K/s

- Fume hoods and equipment for solution processing

- Other characterization equipment available in MSE User Facility
  - Thermogravimetric analysis
  - Modulated differential scanning calorimetry
  - Rheology
  - Dynamic mechanical analysis
Polymer nanocomposites are emerging materials with a long history

**Origins**
- Filled elastomers

**Renewed Interest**

**Today**
- Number of published papers increases every year
- Projected global market of ~$9 billion in 2025

Freedonia Research Group (2008)
- Podsiadlo et al., Science (2007)
Cellulose: A Renewable Biomaterial

Cellulose Nanoparticle Morphology

<table>
<thead>
<tr>
<th>Particle Type</th>
<th>Length (µm)</th>
<th>Width (nm)</th>
<th>Height (nm)</th>
<th>Cross-Section</th>
</tr>
</thead>
<tbody>
<tr>
<td>WF and PF</td>
<td>&gt; 2000</td>
<td>20–50 (µm)</td>
<td>20–50 (µm)</td>
<td>—</td>
</tr>
<tr>
<td>MCC</td>
<td>10–50</td>
<td>10–50 (µm)</td>
<td>10–50 (µm)</td>
<td>—</td>
</tr>
<tr>
<td>MFC</td>
<td>0.5–10’s</td>
<td>10–100</td>
<td>10–100</td>
<td>—</td>
</tr>
<tr>
<td>NFC</td>
<td>0.5–2</td>
<td>4–20</td>
<td>4–20</td>
<td>—</td>
</tr>
<tr>
<td>CNC</td>
<td>0.05–0.5</td>
<td>3–5</td>
<td>3–5</td>
<td>Square</td>
</tr>
<tr>
<td>t-CNC</td>
<td>0.1–4</td>
<td>~20</td>
<td>~8</td>
<td>Parallelogram</td>
</tr>
<tr>
<td>AC (Valonia)</td>
<td>&gt; 1</td>
<td>~20</td>
<td>~20</td>
<td>Square</td>
</tr>
<tr>
<td>(Micrasterias)</td>
<td>&gt; 1</td>
<td>20–30</td>
<td>5</td>
<td>Rectangular</td>
</tr>
<tr>
<td>BC (Acetobacter)</td>
<td>&gt; 1</td>
<td>30–50</td>
<td>6–10</td>
<td>Rectangular</td>
</tr>
<tr>
<td>(Acetobacter)</td>
<td>&gt; 1</td>
<td>6–10</td>
<td>6–10</td>
<td>Square</td>
</tr>
<tr>
<td>Cellulose II</td>
<td>Filament</td>
<td>—</td>
<td>—</td>
<td>Cylindrical</td>
</tr>
</tbody>
</table>

a. Wood Fiber (WF)
b. Microcrystalline Cellulose (MCC)
c. Microfibrillated Cellulose (MFC)
d. Nanofibrillated Cellulose (NFC)
e. Cellulose Nanocrystals (CNC)
f. Tunicate Cellulose Nanocrystals (t-CNC)
g. Algae Cellulose (AC)
h. Bacterial Cellulose (BC)

Moon et al., Chem Soc Rev, 2011
Wood Fiber (WF), Plant Fiber (PF), Microcrystalline Cellulose (MCC), Microfibrillated Cellulose (MFC), Nanofibrillated Cellulose (NFC), Cellulose Nanocrystals (CNC), Tunicate Cellulose Nanocrystals (t-CNC), Bacterial Cellulose (BC)

Moon et al., Chem Soc Rev, 2011
Current Shofner Group Research Topics

- Processing of Tensegrity-Inspired Nanocomposites

- Rheology of Carbon Fiber Precursor Solutions

- Negative Poisson’s Ratio Materials: Reverse Engineering the Structure of Paper (IPST Ph.D. Fellowship with Professor Anselm Griffin in MSE)

- Water-based processing strategies for cellulose/polymer nanocomposites (IPST Ph.D. Fellowship)

- Crystallization of CNC/polyhydroxybutyrate (PHB) nanocomposites (IPST Ph.D. Fellowship)

- Fundamental Aspects of Thermal Stability and Adhesion in Cellulose-Based Aerospace Composites (with Professor Carson Meredith in ChBE)
Water-based Processing Strategies for Cellulose/Polymer Nanocomposites

• Motivation: Low energy processing methods using gelation

• Methodology
  – Rheological characterization of gels to guide processing
  – Characterization of microstructure and properties achieved

• Experimental
  – Materials: CNCs provided by USDA Forest Products Laboratory and polyvinyl alcohol polymers
  – Processing: solution processing and conventional shear processing
  – Formation: coagulation or drying

\[
\begin{align*}
T &: \text{Torque} \\
 s &: \text{motor speed} \\
 t &: \text{time}
\end{align*}
\]
Example Rheological Characterization
Polyvinyl Alcohol/Water Solutions
Crystallization of CNC/PHB nanocomposites

- **Motivation:** Naturally-derived nanocomposite materials

- **Methodology**
  - Understanding the impact of CNCs on PHB crystallization
  - Manipulating crystal structure to improve mechanical properties

- **Experimental**
  - Materials: CNCs provided by USDA Forest Products Laboratory and biologically-derived PHB homopolymer
  - Processing: sonication in solvent mixtures
  - Formation: solution casting (SC) or anti-solvent collection followed by compression molding (AS-CM)

Nuti *et al.*, *Canadian Journal of Microbiology*, 1972
## Research Methods: Conventional and High Rate Differential Scanning Calorimetry (DSC)

<table>
<thead>
<tr>
<th>Conventional DSC</th>
<th>Flash DSC</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="tainstruments.com" alt="Conventional DSC Image" /></td>
<td><img src="mt.com" alt="Flash DSC Image" /></td>
</tr>
<tr>
<td><strong>Sample Size:</strong> ~mg</td>
<td><strong>Sample Size:</strong> 10 ng – 1 µg</td>
</tr>
<tr>
<td><strong>Sample Carrier:</strong> aluminum pan</td>
<td><strong>Sample Carrier:</strong> ceramic microchip</td>
</tr>
<tr>
<td><strong>Heating Rate:</strong> up to 200 K/min</td>
<td><strong>Heating Rate:</strong> 30 – 2,400,000 K/min</td>
</tr>
<tr>
<td><strong>Cooling Rate:</strong> up to 100 K/min</td>
<td><strong>Cooling Rate:</strong> 6 – 240,000 K/min</td>
</tr>
<tr>
<td><strong>Temperature Range:</strong> -180 – 725 °C</td>
<td><strong>Temperature Range:</strong> -95 – 450 °C</td>
</tr>
</tbody>
</table>
Impacts of nanocomposite formation processes on PHB crystallization

<table>
<thead>
<tr>
<th></th>
<th>(T_m(°C)) peak, second cycle</th>
<th>(T_c(°C)) peak, second cycle</th>
<th>% Crystallinity second melting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat PHB (AS-CM)</td>
<td>165.8 ± 1.1</td>
<td>103.1 ± 0.3</td>
<td>66 ± 2</td>
</tr>
<tr>
<td>0.1% CNC/PHB (SC)</td>
<td>165.0 ± 1.9</td>
<td>102.8 ± 0.4</td>
<td>65 ± 4</td>
</tr>
<tr>
<td>0.1% CNC/PHB (AS-CM)</td>
<td>165.7 ± 0.2</td>
<td>105.6 ± 0.3</td>
<td>68 ± 2</td>
</tr>
<tr>
<td>0.5% CNC/PHB (SC)</td>
<td>163.9 ± 1.0</td>
<td>96.9 ± 1.2</td>
<td>70 ± 5</td>
</tr>
<tr>
<td>0.5% CNC/PHB (AS-CM)</td>
<td>165.9 ± 0.5</td>
<td>106.6 ± 0.5</td>
<td>69 ± 1</td>
</tr>
<tr>
<td>1.0% CNC/PHB (SC)</td>
<td>164.6 ± 0.7</td>
<td>102.4 ± 0.8</td>
<td>68 ± 4</td>
</tr>
<tr>
<td>1.0% CNC/PHB (AS-CM)</td>
<td>165.6 ± 0.1</td>
<td>107.2 ± 0.4</td>
<td>66 ± 1</td>
</tr>
</tbody>
</table>

Crystallization temperature
- unchanged or decreased with SC formation
- increased with AS-CM formation (promotes nucleation)

Characterization concerning the CNC dispersion attained with each formation process is ongoing to correlate with these initial results.
Flash DSC data: PHB and CNC/PHB composites

Samples cooled at 100 K/s and then heated at the rates shown

<table>
<thead>
<tr>
<th>Heating Rate (K/s)</th>
<th>Neat PHB (°C)</th>
<th>CNC/PHB (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_g$</td>
<td>$T_m$</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>126</td>
</tr>
<tr>
<td>200</td>
<td>4</td>
<td>126</td>
</tr>
<tr>
<td>400</td>
<td>8</td>
<td>126</td>
</tr>
<tr>
<td>600</td>
<td>14</td>
<td>127</td>
</tr>
<tr>
<td>800</td>
<td>15</td>
<td>130</td>
</tr>
<tr>
<td>1000</td>
<td>17</td>
<td>130</td>
</tr>
</tbody>
</table>
Summary

• CNCs are promising nanoparticles for use in polymer nanocomposites
  – High specific mechanical properties
  – Renewable sources

• Project 1: Hydrophilic nature provides opportunities for developing new processing strategies

• Project 2: Structure and morphology provide a template for polymer crystal structure modification and property modulation