Cellulose Under Pressure For New Biopolymer Materials

By: Josh Devorkin
Mentors: Dr. Susana Teixeira and Dr. Yimin Mao
Outline

• **Background: Cellulose and Nanomaterials**
  • Cellulose is a natural polymer
  • Tempo-oxidation to extract nanofibers
  • Building block for new materials

**Goal:**
Towards greener processing: can High hydrostatic pressure promote a more efficient oxidation reaction?
Assessing multi-characterization techniques to adequately probe the surface interactions and topography

• **Results:** SANS, AFM, POM

• Future work
Cellulose as a building block for novel materials

The abundance of cellulose gives rise for current and future novel applications.

Complex Hierarchy structure rich in hydrogen bonding from the crystallization during biosynthesis.

Adapted from T. Heinze et al.
Commercial Applications of Cellulose Nanocomposites for lightweight durable materials

Coatings for Medical devices
- Drug delivery
- Antibacterial resistance
- Good biocompatibility and wear

High aspect ratio films to collect small dust particles

New lightweight, durable material for 3-D printing

Paper industry
TEMPO-mediated oxidation for processing of cellulose

- Tempo treatment attacks the C6 primary hydroxyls on the surface of the individual cellulose microfibers
- Oxidation into carboxyl groups creates an electrostatic repulsion in water leading to the disintegration of the cellulose nanofibers/crystals

Major drawback is the price and toxicity arising from the use of TEMPO

**Motivation:** New methods to extract cellulose nanofibers using green chemistry to reduce the use of chemicals

Adapted from Okita et al.
High hydrostatic pressure as a probing tool

- Emerging as a useful tool for probing changes in the structure and functional properties of polymers
- Pressure does not introduce other agents into the system, helps aid with green chemistry
- Samples/Applications
  - Solutions of soft matter polymers
  - Proteins, lipids, polysaccharides
  - Pressure assisted self aggregation
  - Cellulose processing

Hypothesis: High pressure to aid in the oxidation of cellulose through the TEMPO-reaction to dissociate cellulose nanofibers

What neutrons can do

• Structure, conformation of biomaterials
  Function and behavior

Reciprocal space

\[ q = \frac{4\pi}{\lambda} \sin \theta \]

\( \lambda: \) neutron wavelength
\( \theta: \) scattering angle

0.001 Å\(^{-1}\) < q < 0.45 Å\(^{-1}\)
Pressure: up to 3.5 kbar.
Temperature: -15°C to +65°C
q-range: 0.001-0.6 Å⁻¹.

Sample volume: 2.5-5 ml

Teixeira et al. (2018) J. Neutron Res. 20(1)
Multiscale characterization of cellulose

Investigation of the optical properties of materials such as birefringent patterns

Scanning probe to measure surface topography

Scattering techniques used to investigate the structure of materials

AFM

SANS

Optical Microscopy
Recipe for extraction of nanofibers

1) Pristine bacteria Cellulose

2) Homogenizer

3) TEMPO treatment

4) Viscous gel solution at 1.5 wt%

After TEMPO treatment

POM images taken at UMD facilities

5 um
Simulated scattering curves using Sasview

Data fitted with a parallelepiped model with a uniform scattering length density

Assumption:
1. Rod-like particles due to the crystallographic packing
2. L is very long in the micron scale which SANS cannot probe with our configurations
3. b>a due to crystallographic packing of cellulose chains

\[ I(q) = \frac{\text{Scale}}{V} (\Delta \rho \cdot V)^2 \langle P(q) \rangle + \text{Background} \]

- \( I(q) \): Measured intensity
- \( P(q) \): Form factor to derive \( a/b \)

Guinier region shown for low \( q \) at 50nm.
Samples were collected on aliquots taken from the reaction mixture after quenching with ethanol, centrifuging and washing.
Ex-situ Fitting of Reaction (100% TEMPO) vs Time

I(q) = \frac{\text{Scale}}{V} (\Delta \rho \cdot V)^2 < P(q) > + \text{Background}

Cellulose SLD:
(1.65 \pm 0.2) \times 10^{-6} \text{ Å}^{-2}

Parallelepiped model
SASVIEW fits: http://www.sasview.org/

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>a (nm)</th>
<th>b (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1h</td>
<td>4.6 ± 0.3</td>
<td>38 ± 1.4</td>
</tr>
<tr>
<td>3h</td>
<td>4.1 ± 0.3</td>
<td>37 ± 1.3</td>
</tr>
<tr>
<td>3h30</td>
<td>3.9 ± 0.1</td>
<td>32 ± 0.5</td>
</tr>
<tr>
<td>4h</td>
<td>3.9 ± 0.1</td>
<td>19 ± 0.3</td>
</tr>
</tbody>
</table>
In-situ High pressure at 3kbar

Due to the complexity of the mixture (ex-situ data came from samples that were filtered and washed) the fits are more difficult. In the first 40 mins the presence of the long fibers still dominates the signal (upturn at low-q)
In-situ Reaction (50% TEMPO) Under High Pressure

### Reaction Table

<table>
<thead>
<tr>
<th>Reaction time</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>P (kbar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40min</td>
<td>5.0 ± 0.06</td>
<td>180 ± 33</td>
<td>0.001</td>
</tr>
<tr>
<td>1h20</td>
<td>4.5 ± 0.02</td>
<td>151 ± 12</td>
<td>3</td>
</tr>
<tr>
<td>2h</td>
<td>4.4 ± 0.03</td>
<td>152 ± 10</td>
<td>3</td>
</tr>
<tr>
<td>2h40</td>
<td>4.4 ± 0.01</td>
<td>151 ± 10</td>
<td>3</td>
</tr>
<tr>
<td>3h20</td>
<td>4.3 ± 0.03</td>
<td>137 ± 8</td>
<td>3</td>
</tr>
<tr>
<td>4h</td>
<td>4.2 ± 0.03</td>
<td>128 ± 7</td>
<td>3</td>
</tr>
<tr>
<td>5-6h</td>
<td>4.3 ± 0.02</td>
<td>128 ± 8</td>
<td>0.001</td>
</tr>
</tbody>
</table>

- **Pressurized**
- **De-pressurized**
Atomic Force Microscopy

- Complementary technique to SANS data
- Confirms the dissociation of bundles of fibers to individual nanofibers

Wood pulp courtesy of D. Henderson research group at UMD
Conclusions and Future work

- High pressure was able to alter the Tempo-oxidation reaction
- Dissociate nanofibers under high pressure using half the amount of reagents
- Produced long fibers able to form viscous gel solutions at low weight percentages
- Cross link individual nanofibers to create a hydrogel
- Alter surface properties, to create a biocompatible, antimicrobial wound dressing
Acknowledgements

NGB30 SANS instrument

Sample environment team at the NCNR

Surf organizers: Joe Dura, Julie Borchers

Mentors: Dr. Susana Teixeira and Dr. Yimin Mao

This work benefited from the use of the SasView application, originally developed under NSF award DMR-0520547.
Testing Ex-situ sampling effects on HP-cell TEMPO oxidation

**3 kbar, 50% TEMPO**

- **NG7 SANS**

**50% TEMPO**

- Filter, wash
- Resuspend
- Centrifuge

**Supernatant (SN)**

- **Pellet (Long Fibers)**

**Mix**

**Pellet**

**Quench**
Polarized Optical Microscopy

Control _ No tempo

Tempo

High pressure_ 3kbar

POM images taken at UMD facilities
Effects of Tempo reaction

- Sharp interface of NF
- Structural factor and indication of network
- Long fibers

Graph:
- $\sim q^{-1}$ Long fibers
- $\sim q^{-2}$ Structural factor and indication of network
- Sharp interface of NF

Legend:
- 1.5 wt% Cellulose, 100% TEMPO
- 1.5 wt% Cellulose, 50% TEMPO
- 3 wt% Cellulose, 100% TEMPO
- 3 wt% Cellulose, 50% TEMPO
<table>
<thead>
<tr>
<th>Reaction time</th>
<th>a (nm)</th>
<th>b (nm)</th>
<th>c (nm)</th>
<th>Chi2/#points</th>
<th># points</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h</td>
<td>3.3 ± 0.3</td>
<td>84 ± 4.8</td>
<td>12200 ± 684</td>
<td>1.66</td>
<td>174</td>
</tr>
<tr>
<td>1h</td>
<td>4.6 ± 0.3</td>
<td>38 ± 1.4</td>
<td>7632 ± 709</td>
<td>0.86</td>
<td>178</td>
</tr>
<tr>
<td>3h</td>
<td>4.1 ± 0.3</td>
<td>37 ± 1.3</td>
<td>3075 ± 686</td>
<td>1.21</td>
<td>161</td>
</tr>
<tr>
<td>3h30</td>
<td>3.9 ± 0.1</td>
<td>32 ± 0.5</td>
<td>1858 ± 460</td>
<td>1.95</td>
<td>168</td>
</tr>
<tr>
<td>4h</td>
<td>3.9 ± 0.1</td>
<td>19 ± 0.3</td>
<td>1536 ± 157</td>
<td>1.22</td>
<td>167</td>
</tr>
</tbody>
</table>
Ex-Situ investigation for time dependence of TEMPO reaction

Fibers cross-section size inversely related to the reaction time

Dissociation of NF’s after 4 hour of TEMPO-oxidation

Cross-section dimensions derived from SANS methods (one STD in parentheses)

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</tr>
</thead>
<tbody>
<tr>
<td>4hr</td>
<td>3.3271 (0.2201)</td>
<td>19.227 (0.2112)</td>
</tr>
<tr>
<td>3.5hr</td>
<td>3.4949 (0.1566)</td>
<td>30.877 (2.96)</td>
</tr>
<tr>
<td>3hr</td>
<td>4.7012 (1.198)</td>
<td>33.220 (7.8)</td>
</tr>
</tbody>
</table>

Figure 2: Scattering profiles of the time dependency of TEMPO-oxidation. 4 hour and 3.5 hour curves were offset to better illustrate the fitting.