Cellulose as an edible ingredient for 3D Printing

Sonia Holland
Presentation Overview

- Cellulose structure and chemistry
- Achieving desired properties
- Application to an additive manufacturing process – Binder Jetting

Designer Particles  Complex Structures

Figure 3–3-D reconstructions of (A) biscuit and (B) breadstick samples.
Cellulose Structure and Chemistry

- β-1-4 linked glucose units
- Strong hydrogen bonding
- Predominantly rigid and crystalline, few amorphous regions
- Not digested by human enzymes → Zero calorie ingredient
- Typical solvents unsuitable for food

Native form in food: ‘filler’ or ‘separating agent’ (beverages)
Modified MCC can be effective as fat replacer

Image from: http://bio1151.nicerweb.com/Locked/media/ch05/cellulose.html
Ball Milling Cellulose – Process

Left: Native Cellulose
Right: Sample ball milled for 500 min at 400 rpm
Size reduction and loss of high aspect ratio, fibrillar form (both scale bars 10 μm)

Ball Milling Cellulose - Effect

\[ [\eta] = K D_p^\alpha \]

Measured Value \[ [\eta] = K D_p^\alpha \] Values from Literature

<table>
<thead>
<tr>
<th>Sample</th>
<th>K (cm(^{-3})g(^{-1}))</th>
<th>(\alpha)</th>
<th>Viscosity Average Dp</th>
</tr>
</thead>
<tbody>
<tr>
<td>Native Cellulose</td>
<td>2.45*</td>
<td>0.7*</td>
<td>1339</td>
</tr>
<tr>
<td></td>
<td>1.87**</td>
<td>0.771**</td>
<td>980</td>
</tr>
<tr>
<td>Ball Milled for 500min at 400rpm</td>
<td>2.45*</td>
<td>0.7*</td>
<td>724</td>
</tr>
<tr>
<td></td>
<td>1.87**</td>
<td>0.771**</td>
<td>560</td>
</tr>
<tr>
<td>Ball Milled for 30min at 800rpm</td>
<td>2.45*</td>
<td>0.7*</td>
<td>411</td>
</tr>
<tr>
<td></td>
<td>1.87**</td>
<td>0.771**</td>
<td>335</td>
</tr>
</tbody>
</table>

Values for cellulose in Cupriethylenediamine (CED): *Kes and Christensen, 2013; **Lojewski et al. 2010
Ball Milling Cellulose - Effect

Sequential Ball Milling of Cellulose at 400rpm

<table>
<thead>
<tr>
<th>Ball Milling Time (min)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>27</td>
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<tr>
<td>10</td>
<td>21</td>
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<tr>
<td>20</td>
<td>20</td>
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<tr>
<td>40</td>
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<tr>
<td>60</td>
<td>14</td>
</tr>
<tr>
<td>80</td>
<td>13</td>
</tr>
<tr>
<td>120</td>
<td>11</td>
</tr>
<tr>
<td>300</td>
<td>&lt;5</td>
</tr>
<tr>
<td>500</td>
<td>&lt;5</td>
</tr>
</tbody>
</table>
Recrystallising Amorphous Cellulose

- Understanding amorphous → crystalline transition is key
- Experimenting with 1:1 mixtures of cellulose with Locust Bean Gum, Konjac Glucomannan and β-Glucan

Left: DVS trace of Ball Milled Cellulose-KGM equilibrated over $P_2O_5$ (2%RH), temperature 25°C throughout

Right: DSC trace of Ball Milled Cellulose-KGM equilibrated over NaCl (75%RH)
Binder Jetting

- Powder building material
- Liquid binding material
- Layer by layer approach – 3D model split into 2D cross sections of a defined thickness
- Binder deposition nozzle diameter 21μm (10pL) or down to 10 μm (1pL)
- Potential for 24-bit colour printing

Binder Jetting

• Brittle nature of parts
  → Infiltrate with strengthening material e.g. epoxy resin

• Inherent due to binder ‘coating and sticking’ particles
  → Recrystallising approach providing strength in lateral and vertical planes

• Making use of cellulose-polysaccharide synergies
Future Work

• Ascertain temperature-moisture profile boundaries for recrystallisation

• Development of binder ‘ink’

• Combine powder and binder in AM process → Working model to build a simple structure

• Testing different polymer combinations in powder and binder

Cellulose co-ball milled with Locust Bean Gum (left) and Konjac Glucomannan (right) then hydrated
Thank you for your attention, Any questions?

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Sequential Ball Milling of Cellulose at 800rpm

Intensity vs 2θ

0min
10min
20min
30min
40min
60min
300min

400 a.u.
Mark-Houwink-Sakurada Equations

\[ \eta_{rel} = \frac{\eta}{\eta_0} = \frac{t}{t_0} \]

\[ \eta_{sp} = \eta_{rel} - 1 \]

\[ [\eta] = \frac{(2(\eta_{sp} - \ln\eta_{rel}))^{1/2}}{c} \]

\[ [\eta] = KD_p^\alpha \]

Image Courtesy of:
http://media.noria.com/sites/archive_images/backup_200203_KinemVisc-Fig1.gif