Dissolution and regeneration of cellulose

Puu-23.6080 - Cellulose Chemistry
Michael Hummel
Content

- Classification of cellulose dissolution
- Short history of cellulose dissolution
- Types of cellulose dissolution
  - Intermediate Derivatization
  - Stable derivatives
  - Non-derivatizing – aqueous
  - Non-derivatizing – non-aqueous
Cellulose products
Non-covalent bonds in cellulose

O3-H-O5 intrachain
O2-H-O6 intrachain
O6-H-O3 interchain
intersheet H-bond
Cellulose dissolution - overview

Cellulose solvent

- derivatizing
  - intermediate (no isolation)
  - stable (isolation possible)
- non-derivatizing
  - aqueous
    - Inorganic complexes (Coen, Cuoxam)
    - Aqueous bases (NaOH (+urea(thiorurea))
  - non-aqueous
    - With solution mediator
    - Organic solvent with inorganic salts
    - direct
      - NMMO
      - IL
      - DES

- xanthate
- nitrate
- formate
- carbamate
- acetate
History of cellulose solvents
1846: Cellulose nitrate

Swan developed the process to spin cellulose nitrate and de-nitrate the cellulose using ammonium bisulfate; yet he did not pursue this process further.

= guncotton, highly flammable
1889: Chardonnet silk

Developed spinning of cellulose nitrate to a commercial level. Nowadays called the Father of “Father of Rayon” and the founder of the MMCF industry.
1892: The viscose process

1892: Charles Frederick Cross, Edward John Bevan, Clayton Beadle file a patent describing today’s viscose process

1905: Courtauld Fibres installs first commercial viscose plant in Coventry, UK
Schweizer's reagent is an alkaline solution of copper sulfate in ammonia, $\text{[Cu(NH}_3\text{)}_4\text{]}(\text{OH})_2\cdot3\text{H}_2\text{O}$, named after Matthias Eduard Schweizer (1818-1860).
1934: direct dissolution

Charles Graenacher: father of direct solvents:
organic solvents that are capable of dissolving cellulose without derivatization or additional solubilization-mediator
Types of cellulose dissolution (and regeneration)
Intermediate Derivatization
Cellulose nitrate

- Alternately in DMF/N₂O₄
- Cellulose nitrate soluble in ether/ethanol/acetone
- Solution spun through nozzles into regeneration bath containing (NH₄)(HSO₄)
- Flammable ("mother-in-law silk")
Cellulose nitrate - Celluloid

Celluloid = thermoplastic containing cellulose nitrate and camphor

1856 first created by Alexander Parkes; called it Parkesine
1870 John Wesley Hyatt patents it as „Celluloïd“ to be sold through the Celluloid Manufacturing Company
Cellulose xanthate soluble in caustic solution
Solution spun through nozzles into regeneration bath containing H$_2$SO$_4$ / Na$_2$SO$_4$ and additives
Through variation in the coagulation process and pulp quality a wide spectrum of viscose fibers can be manufactured.

<table>
<thead>
<tr>
<th></th>
<th>Viscose</th>
<th>Tyre cord</th>
<th>Modal</th>
<th>Polynosic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titre [dtex]</td>
<td>1.4</td>
<td>1.9</td>
<td>1.3</td>
<td>1.8</td>
</tr>
<tr>
<td>Tenacity cond. [cN/tex]</td>
<td>23.9</td>
<td>52.3</td>
<td>33.1</td>
<td>38.2</td>
</tr>
<tr>
<td>Elongation cond. [%]</td>
<td>20.1</td>
<td>15.1</td>
<td>13.5</td>
<td>9.7</td>
</tr>
<tr>
<td>Tenacity wet [cN/tex]</td>
<td>12.5</td>
<td>38.4</td>
<td>18.4</td>
<td>26.0</td>
</tr>
<tr>
<td>Elongation wet [%]</td>
<td>22.0</td>
<td>22.9</td>
<td>14.1</td>
<td>11.0</td>
</tr>
</tbody>
</table>

Röder et al. Lenzinger Berichte, 2009, 87, 98-105
Viscose – Cellophane

Good barrier properties regarding air and grease
Coating needed to decrease water permeability

www.historybyzim.com
Viscose – Cellophane

Viscose dope
Extraction & Recovery
Viscose extrusion
Film regeneration
Washing and optional coloring
Softening
Base film
Drying

Table II
Mechanical Anisotropy of Test Specimens

<table>
<thead>
<tr>
<th>Specimen</th>
<th>$\delta = 0^\circ$</th>
<th>$\delta = 10^\circ$</th>
<th>$\delta = 20^\circ$</th>
<th>$\delta = 30^\circ$</th>
<th>$\delta = 45^\circ$</th>
<th>$\delta = 60^\circ$</th>
<th>$\delta = 90^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-1-D_{ex}</td>
<td>7.7</td>
<td>7.6</td>
<td>7.3</td>
<td>6.8</td>
<td>6.0</td>
<td>5.6</td>
<td>5.4</td>
</tr>
<tr>
<td>C-1-D_{el}</td>
<td>6.2</td>
<td>6.2</td>
<td>6.1</td>
<td>5.6</td>
<td>5.3</td>
<td>4.7</td>
<td>4.7</td>
</tr>
<tr>
<td>C-1-D_{st}</td>
<td>5.4</td>
<td>5.3</td>
<td>5.2</td>
<td>4.5</td>
<td>4.4</td>
<td>4.0</td>
<td>3.7</td>
</tr>
<tr>
<td>C-1-W</td>
<td>0.21</td>
<td>0.20</td>
<td>0.18</td>
<td>0.14</td>
<td>0.11</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>C-2-D_{ex}</td>
<td>7.7</td>
<td>7.2</td>
<td>7.0</td>
<td>6.8</td>
<td>6.3</td>
<td>5.9</td>
<td>5.5</td>
</tr>
<tr>
<td>C-2-D_{el}</td>
<td>6.8</td>
<td>6.4</td>
<td>6.4</td>
<td>5.6</td>
<td>5.2</td>
<td>4.7</td>
<td>4.5</td>
</tr>
<tr>
<td>C-2-D_{st}</td>
<td>5.6</td>
<td>5.4</td>
<td>5.0</td>
<td>4.6</td>
<td>4.3</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>C-2-W</td>
<td>0.20</td>
<td>0.20</td>
<td>0.17</td>
<td>0.15</td>
<td>0.11</td>
<td>0.09</td>
<td>0.08</td>
</tr>
<tr>
<td>C-3-D_{ex}</td>
<td>6.7</td>
<td>6.6</td>
<td>6.5</td>
<td>6.1</td>
<td>5.5</td>
<td>5.5</td>
<td>5.4</td>
</tr>
<tr>
<td>C-3-D_{el}</td>
<td>6.0</td>
<td>5.7</td>
<td>5.6</td>
<td>5.4</td>
<td>4.7</td>
<td>4.5</td>
<td>4.6</td>
</tr>
<tr>
<td>C-3-D_{st}</td>
<td>5.0</td>
<td>4.9</td>
<td>4.7</td>
<td>4.5</td>
<td>4.1</td>
<td>4.0</td>
<td>3.8</td>
</tr>
<tr>
<td>C-3-W</td>
<td>0.16</td>
<td>0.16</td>
<td>0.14</td>
<td>0.12</td>
<td>0.10</td>
<td>0.09</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* Measured by the Viscoelastic spectrometer at 20°C. The modulus is the real part of the tensile complex dynamic modulus at 11.0 cps.

* The angle $0^\circ$ corresponds to the $x_1$ axis (the machine direction); and $90^\circ$ corresponds to the $x_2$ axis (the transverse direction) within the film plane; $\delta$ is the angle between the direction of tensile deformation and the machine direction.


Regeneration in acidic spin bath.

Conditioned fiber strength comparable to viscose; extremely low wet strength
Stable derivatives
Acetate

full acetylation

primary acetate
DS 3)

partial de-acetylation

secondary acetate
(DS 2.0 – 2.5)

thermoplastic

soluble in acetone

Acetate

Melt processed:
- Frames for glasses
- First Lego bricks (today acrylonitrile butadiene styrene)
- TAC films for LCD

Solution spun:
- Fiber tows for cigarette filters
- Fortisan fibers: spun as secondary acetate and subsequently saponified; high orientation of cellulose molecules enables high mechanical properties
Non-derivatizing – aqueous
Metal complexes

- Cuoxam: tetraammine diaqua copper hydroxide,
  $[\text{Cu(NH}_3\text{)}_4(\text{H}_2\text{O})_2](\text{OH})_2$
- Cuen: Copper(II) ethylenediamine hydroxide
- Nioxam ([Ni(NH}_3\text{)}_6][\text{OH}]_2$
- Zincoxen ([Zn(NH}_2\text{CH}_2\text{NH}_2\text{)}_3][\text{OH}]_2$
- Cadoxen ([Cd(NH}_2\text{CH}_2\text{NH}_2\text{)}_3][\text{OH}]_2$
- Nitren ([Ni(NH}_2\text{CH}_2\text{CH}_2\text{)}_3\text{N}][\text{OH}]_2$
- Pden ([Pd(NH}_2\text{CH}_2\text{NH}_2\text{)}_3][\text{OH}]_2$
- Ferric sodium tartrate complex $\text{Na}_6[\text{Fe(III)}(\text{C}_4\text{H}_3\text{O}_6\text{)}_3]$

Dissolution through complex formation; spun into acidic spin bath which causes de-complexation and regeneration of cellulose

Commercial cupro fiber (Cuoxam, tradename Bemberg™ fiber) produced on a scale of ca. 25000 t/a as specialty fiber
1850: Mercerisation (John Mercer)

1930s: Davidson: Dissolution of certain cellulose in aqueous NaOH solution within a certain concentration range of NaOH and at low temperature (typically <0 °C)
NaOH solutions

Deconstruction of intramolecular O₃-H…O₅’ and O₂-H…O₆’ H-bonds

NaOH solutions

Best dissolution performance of pure NaOH solution at 7-8 wt% NaOH, corresponding to 4 NaOH units per AGU

Eagle et al. Biomacromolecules 2007, 8, 2282-2287
NaOH solutions

- Major limitation of NaOH as solvent: solubility of cellulose strongly dependent on DP
- Upper limit for relevant cellulose concentration;
- Limited mechanical properties of regenerated products

Budtova, Navard Cellulose 2016, 23, 5-55
NaOH solutions

- second limitation of NaOH as solvent: tendency of solutions to gel irreversibly
- Gelling over time
- Pronounced gelling upon temperature increase

Roy et al. Biomacromolecules 2003, 4, 259-264
NaOH solutions – additives

Various additives tested:
• amongst longest known: ZnO
• also urea and thiourea

No confirmed effect on solubility maximum; but stabilization of solution state and hampering of gelation

Liu et al. Cellulose 2011, 18, 663-673
Non-derivatizing – non-aqueous
Electrolyte solutions

**LiCl/DMAc:**

Significant importance in analysis; mobile phase in SEC to determine MMD of cellulose

Minor role for processing

**DMSO/TBAF·3H₂O:**

Minor role as TBAF is prone to side reactions

Catalyzes some homogeneous reactions

Östlund et al. *Biomacromolecules* 2009, 10, 2401–2407
Initial development started at the very end of the 1960s by American Enka/Akzona Inc. It took until 1992 when Courtauld started its first full-scale production plant in Mobile (USA), followed by Lenzing AG in Heiligenkreuz (Austria) in 1997. Today, Lenzing owner of all spinning sites (Grimsby, UK)
Superphosphoric acid

phosphoric acid: ca. 54–62% P$_2$O$_5$ (75–85% H$_3$PO$_4$)
superphosphoric acid: 70% P$_2$O$_5$ (almost 100% H$_3$PO$_4$)

Cellulose dissolved in SPA forms anisotropic solutions (liquid crystalline-like) i.e. cellulose have structured; structure lost upon heating.

Clearing temperature depending on DP and concentration

Pre-orientation can be used to prepare highly orientated cellulose products such as fibers = Fiber B (Bocell): 90 cN/tex

Boerstoel et al. Polymer 2001, 42, 7371-7379
Deep Eutectic Solvents

- The difference in the freezing point at the eutectic composition of a binary mixture of A + B compared to that of a theoretical ideal mixture, $\Delta T_f$, is related to the magnitude of the interaction between A and B.
- The larger the interaction; the larger will be $\Delta T_f$. 

Smith et al. Chem. Rev. 2014, 114, 11060-11082
Deep Eutectic Solvents

Type I: Quaternary ammonium salt + metal chloride
Type II: Quaternary ammonium salt + metal chloride hydrate
Type III: Quaternary ammonium salt + hydrogen bond donor
Type IV: Metal chloride hydrate + hydrogen bond donor

Smith et al. Chem. Rev. 2014, 114, 11060-11082
Deep Eutectic Solvents

Extensively researched for
- Metal processing applications (plating, coating)
- Synthesis medium

Slowly entering field of Biomass solubilization and transformation

choline chloride / urea

Smith et al. Chem. Rev. 2014, 114, 11060-11082
Deep Eutectic Solvents

Limited cellulose dissolution ability

- Swelling / de-crystalizing
- Example for delignification

<table>
<thead>
<tr>
<th>Reagent</th>
<th>ChCl/Reag</th>
<th>Temperature of delignification (°C)</th>
<th>Lignin in wheat straw (g)</th>
<th>Yield after delignification (%)</th>
<th>Lignin in delignified wheat straw</th>
<th>Decrease of lignin content (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea</td>
<td>1:2</td>
<td>80</td>
<td>0.437</td>
<td>94.93</td>
<td>0.431</td>
<td>1.3</td>
</tr>
<tr>
<td>Malonic acid</td>
<td>1:1</td>
<td>60</td>
<td>0.433</td>
<td>90.57</td>
<td>0.417</td>
<td>3.8</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>1:9</td>
<td>60</td>
<td>0.433</td>
<td>85.28</td>
<td>0.369</td>
<td>14.6</td>
</tr>
<tr>
<td>Malic acid*</td>
<td>1:1</td>
<td>80</td>
<td>0.436</td>
<td>80.74</td>
<td>0.341</td>
<td>21.6</td>
</tr>
<tr>
<td>Lactic acid</td>
<td>1:10</td>
<td>60</td>
<td>0.433</td>
<td>83.49</td>
<td>0.307</td>
<td>29.1</td>
</tr>
<tr>
<td>Oxalic acid x 2 H₂O</td>
<td>1:1</td>
<td>60</td>
<td>0.435</td>
<td>59.07</td>
<td>0.183</td>
<td>57.9</td>
</tr>
</tbody>
</table>

Jablonský et al. Bioresources 2015, 10, 8039-8047
Ionic Liquids

See subsequent lecture
Summary questions

- Why cellulose dissolution?
- Which are the 2 main categories of cellulose dissolution?
- Which cellulose derivatives are (or have been) of importance?
- 3 non-derivatizing cellulose solvents?
- Advantages and limitations of aqueous NaOH solution as cellulose solvent?
- What is the most important non-derivatizing – non-aqueous cellulose solvent? Why?