Individualization of nano-sized plant cellulose fibrils achieved by direct surface carboxylation using TEMPO catalyst

Department of Biomaterial Sciences
The University of Tokyo
Akira ISOGAI
TEMPO / NaBr / NaClO oxidation of polysaccharides at pH 10

Advantages points:
- Aqueous media at pH 10
- Highly regioselective reaction at C6-OH
- Proceeds under mild conditions (at room temp, < 2 h)
- Formation of some aldehyde groups

- TEMPO-mediated oxidation proceeds similarly to enzymatic reactions but more rapidly.
TEMPO-mediated oxidation of various celluloses

Cellulose fibers (1 g)
Water (100 mL)
TEMPO (0.0125 g)
NaBr (0.125 g)

Cellulose fibers / water slurry at room temp. and pH 10

NaClO / water
0.4M NaOH addition to keep pH 10

Isolation & washing process

TEMPO-oxidized cellulose

Analyses
Research projects of TEMPO-oxidized celluloses in our lab

- TEMPO oxidation of various cellulosics, chitins & other polysaccharides
- Preparation & characterization of water-soluble TEMPO-oxidized cellulose (celluronic acid) prepared from regenerated cellulosics
- TEMPO oxidation of paper pulps to improve paper properties by introducing carboxyl & aldehyde groups
- Preparation & characterization of TEMPO-oxidized cellulose nanofibers, supported by JSPS
- NEDO Nanotech Challenge Project for high gas-barrier packaging materials
- JSPS Bio-Nanofibril Project for fundamental research
- Applying METI National Project with companies, university labs & government for new bio-nanofibers (undecided)
Hierarchical structure of highly crystalline cellulose in plants

- **Tree**
- **Fiber assembly**
  - **Single fiber**
  - **Bundle of microfibrils**
  - **Cellulose microfibril**
  - **Cellulose chain**

**Wood**

**Wood tissue**
- Width: 20 – 30 µm
- Length: 1 – 3 mm

**Fiber surface**
- Width: > 15 nm
- Length: > 5 µm

**Crystallinity**
- 70 – 90 %

**Cellulose microfibril**
- Width: 3 – 4 nm
- Length: > 5 µm

**Cellulose chain**
- Width: 0.4 nm
- Length: 500 nm
Cellulose single nano-fibers from abundant biomass resources

Abundant wood biomass

Cellulose single nano-fiber

- Width: 3 – 4 nm
- Length: > 5 µm
- Crystallinity: 70 – 90 %

Downsizing processing

Bottom-up processing
Optical microphotographs of the original and TEMPO-oxidized wood celluloses (never-dried)

Original wood cellulose

TEMPO-oxidized wood cellulose

Even though a significant amount of carboxylate groups is formed in TEMPO-oxidized cellulose, no swelling of fibers in water is observed.

Saito et al., Biomacromolecules, 2007
Metal ion content in TEMPO-oxidized cotton celluloses after ion-exchange treatment

TEMPO-oxidized cellulose-COONa → TEMPO-oxidized cellulose-COOM

Metal ion content (mmol/g)

Metal ion treated

- Pb, Ca & Ag can form carboxylate salt almost 1:1 by molar ratio.

Saito & Isogai, Carbohydrate Polymers, 2005
Biodegradation of TEMPO-oxidized cellulose

TEMPO-oxidized cellulose suspension in water

Disintegration

- Domestic blender at 12,000 rpm < 4 min
- Ultrasonic homogenizer < 2 min
- Magnetic stirrer at 1,500 rpm ~ 12 days

Transparent dispersion

TEM observation

50 nm
TEMPO-mediated oxidation of various native cellulosics

- Effective surface modification of cellulose microfibril -

Plants (tree):

- CH₂ OH

Hemicellulose region

20-30 µm

4-5 nm

0.5 nm

Wood fiber

Cellulose microfibrils

Anhydroglucose unit

TEMPO

Electrostatic repulsion

Cellulose nanofiber dispersion in water

Disintegration in water

TEMPO-oxidized cellulose fibers suspended in water

- COO⁻ Na⁺

- CH₂OH

: -CH₂OH

: Hemicellulose region

: TEMPO
Wood cellulose fibers are the most suitable resources for preparing TEMPO-oxidized cellulose nano-fibers.

Wood cellulose microfibrils

TEMPO-mediated oxidation

Disintegration in water

ζ-potential : –80mV

Wood cellulose fibers

Hemicellulose & disordered region

Glucose unit

Glucuronate unit – COO⁻
Structural model of TEMPO-oxidized cellulose nanofiber

TEMPO-oxidized cellulose nanofiber

4 nm

- CH$_2$OH

Glucose unit

- COO$^-$

Glucuronate unit

1.7 Carboxylate groups / nm$^2$
TEMPO / NaBr / NaClO oxidation of polysaccharides at pH 10

Advantages points:
- Aqueous media at pH 10
- Highly regioselective reaction at C6-OH
- Proceeds under mild conditions (at room temp, < 2 h)
- Formation of some aldehyde groups

TEMPO-mediated oxidation proceeds similarly to enzymatic reactions but more rapidly.
TEMPO-mediated oxidation of cellulose using NaClO₂ at pH 3-7

Advantages:
- Aqueous media at pH 3-7
- Highly regioselective reaction at C6-OH
- No aldehydes are present in the oxidized products
- Proceeds under mild conditions (at 20-80°C, 2-24 h)
- β-Elimination and depolymerization is avoidable.

Others:
- TEMPO-Peroxidase-H₂O₂
- TEMPO-Laccase-O₂

Saito et al., Biomacromolecules, 2009
**Carboxylate content and DP of TEMPO-oxidized celluloses**

<table>
<thead>
<tr>
<th>pH</th>
<th>Oxidation time (h)</th>
<th>Carboxylate content (mmol/g)</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.8</td>
<td>2</td>
<td>0.65</td>
<td>1,100</td>
</tr>
<tr>
<td>6.8</td>
<td>18</td>
<td>0.71</td>
<td>1,000</td>
</tr>
<tr>
<td>6.8</td>
<td>54</td>
<td>0.78</td>
<td>910</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
<td>0.44</td>
<td>220</td>
</tr>
<tr>
<td>10</td>
<td>0.3</td>
<td>0.93</td>
<td>200</td>
</tr>
</tbody>
</table>

Original wood cellulose

Oxidized celluloses prepared by TEMPO / NaClO / NaClO₂

Oxidized celluloses prepared by TEMPO / NaBr / NaClO

DP values were determined by cuen viscosity method

TEMPO-oxidized celluloses prepared at pH 6.8 by TEMPO / NaClO / NaClO₂ had higher DPs, although longer oxidation times were required.

*Saito et al., Biomacromolecules, 2009*
TOCN covers new nano-fiber region at nm-level diameters in the map, which has not been prepared from other polymers or by other processes.
Differences in morphology and consumed energy between micro-fibrillate cellulose and TEMPO-oxidized cellulose nano-fibers

Micro-fibrillated cellulose

![Image of micro-fibrillated cellulose](image)

Disintegration energy > 200 kwh / kg
More than 10 times cycles by high-pressure homogenizer

TEMPO-oxidized cellulose nanofibers

![Image of TEMPO-oxidized cellulose nanofibers](image)

Disintegration energy < 2 kwh / kg
The TOCN films obtained are transparent and bendable.

Fukuzumi et al., Biomacromolecules, 2008
The extremely low CTE of TOCN films is available for electronic and flexible display devices. The CTE of glass is ca. 8 ppm / K.

Fukuzumi et al., Biomacromolecules, 2008
Changes in water contact angle on TOCN films by 0.05% AKD treatment

The surface hydrophilicity of TOCN films is controllable by simple soaking treatment in AKD dispersion and drying.

Fukuzumi et al., Biomacromolecules, 2008
Development of environment compliant high-capability packaging components using cellulose single nano-fiber

Organizations: Kao Corporation, Nippon Paper Industries, The University of Tokyo
Project Leader: Akira Isogai (The University of Tokyo)

Outline: TEMPO-oxidized cellulose single nanofibers (TOCN) are new bio-based nano-materials with various potential applications. During the development research of applying TOCN to environmentally-compatible and high-performance packaging components, we work toward the creation of sustainable society.

Development of environment compliant high-performance packaging components using TEMPO-oxidized cellulose single nano-fibers (NEDO project)

Background

General waste in Japan
5.2 Mt / y

- Containers/ packaging: 3.67 Mt, 70.6%
- Household: 1.05 Mt, 20.2%
- Electricity / machinery: 0.18 Mt, 3.4%
- Others: 0.3 Mt, 5.8%

Industrial waste in Japan
4.9 Mt / y

- Containers packaging: 1.14 Mt, 23.5%
- Production Processing waste: 0.92 Mt, 18.9%
- Electricity Machinery: 1.2 Mt, 24.7%

- Others: 0.21 Mt, 3.3%
- Household commodity: 0.19 Mt, 3.9%
- Agriculture Forestry Fisheries: 0.19 Mt, 3.9%
- Transportation: 0.33 Mt, 6.8%

Incineration disposal: 53% (5.4 Mt/y)

CO₂ emission: 6.7 M t / year

New environmentally compatible packaging materials are needed.

Goal

Development of environmentally friendly packaging materials with high-barrier properties, from TEMPO-oxidized cellulose nanofibers and bioplastics