Nanocellulose: preparation and modification

CHEM-E2140
Cellulose-based fibres

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Outline

(1) Different types of nanocellulose: Terminological issues
(2) Preparation of nanocellulose:
   - nanofibrillar cellulose (NFC) (including bacterial cellulose)
   - cellulose nanocrystals (CNC)
(3) Modification of NFC
(4) Modification of CNC
(5) Summary: comparison between NFC and CNC
Outline

(1) Nanofibrillar cellulose
   - mechanically isolated microfibrils
   - chemically isolated microfibrils (TEMPO-oxidation)
   - bacterial cellulose

(2) Cellulose nanocrystals
   - rods of highly crystalline cellulose, isolated by acid hydrolysis
Types of nanocellulose: terminological issues

(1) Nanofibrillar cellulose
   Synonyms (used in literature) for mechanically isolated nanofibrillar cellulose:
   - microfibrillar cellulose
   - cellulose nanofibrils
   - cellulose microfibrils

(2) Cellulose nanocrystals
   Synonyms used in literature:
   - cellulose whiskers
   - cellulose nanowhiskers
   - cellulose microfibrils
   - \textit{microcrystalline cellulose}
   - nanocrystalline cellulose

Note: microcrystalline cellulose is in its more common use a completely different material (micron-sized cellulose crystals).
Why do we want nanocellulose?

Alternatives to plastics
- reduce the use of oil
- ultimate goal: renewable, biodegradable materials with good strength properties

Why nanocellulose?
- high strength
- low density
- renewable and abundant
- very high aspect ratio (length/width especially in the case of nanofibrils)
Why do we want nanocellulose?

Example
Nanocomposite made of poly(lactic acid) as a continuous matrix and nanofibrillar cellulose as the reinforcing phase

More esoteric potential applications
- viscosity enhancers
- security papers (liquid crystal phases)
Nanofibrillar cellulose: preparation
Ultrastructure of native cellulose

Individual fibre

Cellulose microfibril

Diameter: 2-20 nm
(In wood: 3-4 nm)

Crystalline array of molecules in a micelle

Cellulose microfibril

Individual cellulose molecules

Cellulose molecules

Polysaccharides (other than cellulose)
Ultrastructure: cellulose microfibrils

Aggregates: 12-20 nm (or more)

Individual microfibrils: ~3.5 nm

AFM image of a surface of bleached birch kraft pulp; sample untreated.

Imaged by M. Suchy 2008.

TEM image of longitudinal cross-section of chlorite delignified pine cell wall; freeze-dried and stained.

Nanofibrillar cellulose

Preparation of nanofibrillar cellulose aims at isolating the individual microfibrils (nanofibrils) from the cell wall structure.

Seminal challenges in isolation:
- tight, hierarchical structure of the plant cell wall
- inherent tendency of cellulose to aggregate
Preparation of nanofibrillar cellulose: mechanical disintegration

EARLY EXAMPLES OF INDIVIDUALIZATION OF MICROFIBRILS

METHOD: ULTRASONICATION

From aspen holocellulose

From valonia alga

S.K. Asunmaa

Gardner and Blackwell
Preparation of nanofibrillar cellulose: mechanical disintegration

First attempt to isolate microfibrils for materials science purposes.

Preparation of nanofibrillar cellulose: mechanical disintegration

Enzymatic pretreatment to bleached sulphite pulp.

Microfibrils and microfibril aggregates, ca. 5-10 nm in size.

Preparation of nanofibrillar cellulose: mechanical disintegration

Wood powder, delignified by chlorite, hemicellulose matrix leached out by alkaline treatment → 1 pass through Masuko grinder

Highly monodisperse 15 nm wide microfibril aggregates

Abe et al. Biomacromolecules 2007, 8, 3276.
Preparation of nanofibrillar cellulose: chemical isolation

**TEMPO-mediated oxidation**
- 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO) is an oxidation catalyst
- TEMPO-NaBr-NaClO –system selectively oxidized primary alcohols in polysaccharides, i.e., C6 position in cellulose

Pioneered for polysaccharides:

Pioneered for cellulose:
Preparation of nanofibrillar cellulose: chemical isolation

TEMPO-mediated oxidation of native fibres

Mechanical stirring

Centrifugation

RESULT: highly monodisperse microfibrils (3-4 nm width)

Preparation of nanofibrillar cellulose: chemical isolation

Why do we get individual microfibrils from TEMPO-oxidation?

Only the surface of the microfibrils is oxidized → electrostatic repulsion.

Image from:
Preparation of nanofibrillar cellulose: chemical isolation

Effect of starting material

- Wood pulp
- Cotton
- Tunicate
- Bacterial cellulose

Preparation of nanofibrillar cellulose: chemical isolation

- TEMPO-mediated oxidation of cellulose reduces DP, especially with regenerated cellulose grades
- however, recent research points out that at neutral conditions in a TEMPO/NaClO/NaClO₂ system, the DP reduction is minimized

Original DP: **680**

DP after TEMPO/NaClO/NaClO₂ (oxidation for 3 days, pH 5.8): **490**

DP after TEMPO/NaBr/NaClO (2 hours, pH 10): **40**

Preparation of nanofibrillar cellulose: chemical isolation

Neutral conditions (TEMPO/NaClO/NaClO$_2$) system result in straighter microfibrils (less defects).
Nanofibrillar cellulose: bacterial cellulose

- a species of bacteria (*acetobacteria xylinum*) is able to produce pure cellulose microfibrils from sugars
- individual microfibrils are formed on spot
- macroscopically, bacterial cellulose forms a gel like many other types of nanofibrillar cellulose

- the microfibrils from bacterial cellulose are larger than in plant cellulose: cross section > 70-140 nm × 7 nm

Cellulose nanocrystals: preparation
Crystallographic data presents evidence that cellulose within microfibrils is not totally crystalline.

Proposition:
cellulose runs through alternating crystalline and “amorphous” regions.
Crystallite length (i.e. length of crystalline domains) by SANS agrees with the level-off degree of polymerization (LODP).

* Small angle neutron scattering

Cellulose nanocrystals

Preparation of cellulose nanocrystals is based on the fringed fibrillar structure of the native cellulose microfibril.

Proposition: controlled acid hydrolysis leads to disruption of amorphous domains leaving crystalline cellulose intact.
Cellulose nanocrystals - dimensions

Nanocrystal dimensions depend on the starting material (botanical source).

- Microcrystalline cellulose
- Tunicate
- Sisal
- Straw

Cotton
Ramie
Bacterial cellulose
Sugarbeet

Cellulose nanocrystals - dimensions

Nanocrystals prepared from kraft pulp

(a) Never dried
maximum length: 630 nm

(b) Dried in 110°C
maximum length: 380 nm

(c) Dried in RH50%

(d) Never dried, beaten

Average length is roughly similar in all samples (~60 nm) → corresponds to LODP of kraft pulp

- higher number of longer nanocrystals in never dried samples

- higher amount of shorter nanocrystals in dried samples

ACID HYDROLYSIS IS MORE EFFECTIVE ON DRIED FIBRES.

Kontturi and Vuorinen
Cellulose 2009, 16, 65.
When prepared with sulfuric acid, organic sulphate groups are introduced on the surface of the nanorods. This results in electrostatic repulsion, allowing for a stable suspension in water.
Cellulose nanocrystals – liquid crystals

Cellulose nanocrystals spontaneously forms a liquid crystal phase in solution.

Photograph of rodlike nanocrystals in aqueous suspension. The liquid crystal phase has been formed.

Cholesteric axis

Cellulose crystallites

Chiral nematic phase formed by cellulose crystallites

tight packing by the chiral interaction of screwlike rods

Nanofibrillar cellulose: modifications
Strategies for NFC modification

- NFC modification is *always* surface modification.
- Functional groups are attached on the surface of NFC and the interior semi-crystalline microfibril remains intact.
- NFC modification can be performed either before NFC preparation (pre-treatment) or after the NFC has been isolated.
Carboxymethylation of NFC

- Carboxymethylation is performed on dissolving pulp prior to NFC preparation (mechanical isolation of NFC)
- Additional carboxymethyl units on NFC surface result in highly charged NFC

Cationization of NFC

- The reaction is performed on dissolving pulp prior to NFC preparation
  → Highly charged NFC

Aulin et al. *Biomacromolecules* 2010, 11, 872.
Olszewska et al. *Cellulose* 2011, 18, 1213.
Acetylation of NFC

NFC is acetylated in dimethyl formamide (DMF) with a pyridine catalyst.

Acetyl content can be easily tuned with reaction time.
Acetylation of NFC

- Acetylation dramatically improves the dispersibility of NFC in chloroform

Modification with octadecyl isocyanate

Overall degree of substitution (DS) of 0.07 is reached with NFC

Modification with palmitoyl chloride

- Reaction is performed with gaseous palmitoyl chloride in a vacuum oven on freeze dried NFC suspension

Berlioz et al. *Biomacromolecules* 2009, 10, 2144.
Modification with palmitoyl chloride

Table 1. Reaction Conditions and Degree of Substitution (DS) of Esterified Tunicin Whiskers and Bacterial Cellulose

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>160 °C/4 h</th>
<th>170 °C/4 h</th>
<th>170 °C/6 h</th>
<th>170 °C/13 h</th>
<th>180 °C/4 h</th>
<th>190 °C/2 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tunicin whiskers DS</td>
<td>0.15</td>
<td>0.25</td>
<td>0.61</td>
<td>1.17</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>Bacterial cellulose DS</td>
<td>1.47</td>
<td>2.7</td>
<td></td>
<td>1.8</td>
<td>2.01</td>
<td></td>
</tr>
</tbody>
</table>

Untreated bacterial cellulose nanofibrils

Bacterial cellulose nanofibrils modified with palmitoyl chloride

Berlioz et al. *Biomacromolecules* 2009, 10, 2144.
Modification with palmitoyl chloride

The reaction proceeds from the microfibril surface:

Figure 9. Scheme of the progress of the gas-phase esterification of cellulose whiskers or microfibrils with palmitoyl chloride with (a) DS = 0, (b) DS = 0.25, (c) DS = 0.75, and (d) DS = 1.5.
Click reaction with NFC (I)

- Azide ($\text{N}_3$) and alkyne react quantitatively with each other in so-called “click” reactions

Azide modification of NFC surface:

Pahimanolis et al. Cellulose 2011, 18, 1201.
Click reaction with NFC (II)

Click reaction on an azide modified NFC surface:

Cellulose nanocrystals: modification
General issues on CNC modifications

- Like NFC, CNC modification aims at surface functionalization, leaving the crystalline core intact
- Because of the sulphate groups on the CNC surface, they disperse extremely well in water
- However, water is a tricky medium for organic synthesis: most reactions will not work
- Nearly all CNC modification methods are designed to occur after the CNC preparation (no pre-treatments because of harsh preparation conditions)
- Grafting of polymer chains on CNC surface is particularly popular at present
Cellulose nanocrystals – dispersions

Problem with cellulose nanocrystals:
- they disperse almost only in water (if charged with sulphate groups)
- they do not disperse in nearly anything if they are not charged
→ the use in hydrophobic composite matrix is difficult (aggregation)

Notable exceptions with dispersing solvents:
- m-cresol (A)
- formic acid (B)

Otherwise, there are intensive research efforts to chemically modify the surface of nanocrystals to improve their dispersion in various media.

van den Berg et al. Biomacromolecules 2007, 8, 1353.
CNC modification with its preparation

Acetylation simultaneously with CNC preparation (HCl + acetic acid)

Acid Dissociation and Cellulose Hydrolysis:

\[ \text{HCl} \rightarrow \text{H}^+ + \text{Cl}^- \]

Fischer Esterification of Hydroxyls:

\[ \text{H}^+ \rightarrow \text{CH}_3\text{C}=\text{O}-\text{Cell} + \text{H}_2\text{O} \]

CNC modification with palmitoyl chloride

\[
\text{CNC} + \text{Palmitoyl chloride} \xrightarrow{160-190^\circ C} \text{Modified CNC}
\]

- The method for NFC works also for freeze dried CNC

Berlioz et al. *Biomacromolecules* 2009, 10, 2144.
Click chemistry with CNCs (I)

- CNCs are TEMPO-oxidized to bear a carboxyl group (COOH)
- Amine (NH$_2$), bearing an azide moiety, is linked to the carboxyl group

Filpponen and Argyropoulos *Biomacromolecules* 2010, 11, 1060.
Click chemistry with CNCs (II)

• Similar functionalization on CNCs is then carried out with an alkyne group.
Finally, the azide and alkyne bearing CNCs are click reacted and thus cross-linked.
Polymer grafting on CNCs

Polymer grafting onto nanocrystal surface is particularly trendy.

TEMPO-oxidation on whisker surface

Attachment of poly(styrene) or poly(tert-butyl acrylate) on whisker surface (*grafting-to*)

Harrison et al. *Biomacromolecules* 2011, 12, 1214.
Polymer grafting on CNCs

Polymer grafting onto nanocrystal surface is particularly trendy.

Activation of nanocrystal surface with an initiator → atom transfer radical polymerization (ATRP) of poly(tert-butyl acrylate) (grafting-from) → acid hydrolysis to polyacrylic acid

Majoinen et al. Biomacromolecules 2011, 12, 2997.
Cellulose nanocrystals / poly(NiPAAm)

Scheme 1. Synthesis Route for the Grafting of Poly(NiPAAm) from the Surface of Cellulose Nanocrystals

Step 1:

Poly (N-isopropyl acrylamide) (poly(NiPAAm)) is grafted on a cellulose nanocrystal surface.

Step 2:

Cellulose nanocrystals / poly(NiPAAm)

Poly(NiPAAm) is a thermo-responsive polymer

→ Thermal nanocomposites incorporating cellulose nanocrystals

Generic modification method for all (nano)cellulosic materials:
Double click
Double click: method description

- Utilizes the adsorption of water soluble polysaccharides (like carboxymethyl cellulose (CMC) on cellulose surfaces

1. CMC is functionalized with azide or alkyne which enable click reaction
2. Modified CMC is adsorbed on cellulose surface
3. Click reaction on the modified CMC on the cellulose surface is performed
Double click: method description

Step 1: Adsorption of alkyne or azide modified carboxymethyl cellulose (CMC) on cellulose in aq. phase

Step 2: Aqueous click reaction of functional moieties R activated by azide or alkyne groups to adsorbed modified CMC

Double click: advantages

- Works with practically any cellulose surface: macroscopic fibres, paper, cellophane films, nanofibrillar cellulose, cellulose nanocrystals etc.
- Works in aqueous solutions at room temperature
- Enables the addition of practically any functionality on the cellulose surface
Summary:
Nanofibrillar vs. nanocrystalline (NFC vs. CNC)
## Different types of nanocellulose – a comparison

<table>
<thead>
<tr>
<th>Mechanically produced nanofibrillar cellulose</th>
<th>Chemically produced nanofibrillar cellulose (TEMPO-oxidized)</th>
</tr>
</thead>
<tbody>
<tr>
<td>- cheap (after suitable pretreatments)</td>
<td>- sodium hypochlorite is expensive</td>
</tr>
<tr>
<td>- polydisperse width, mostly higher than in native microfibrils</td>
<td>- monodisperse width that corresponds to the native microfibril</td>
</tr>
<tr>
<td>- unstable in dispersion</td>
<td>- stable dispersion because of the charged COOH-groups on the surface</td>
</tr>
<tr>
<td>- chemically pure cellulose (if left unmodified)</td>
<td>- not cellulose but uronic acid groups on the nanofibril surface</td>
</tr>
<tr>
<td>- predominantly European or Japanese research</td>
<td>- predominantly North American research</td>
</tr>
</tbody>
</table>
Different types of nanocellulose – a comparison

<table>
<thead>
<tr>
<th>Cellulose nanofibrils</th>
<th>Cellulose nanocrystals</th>
</tr>
</thead>
<tbody>
<tr>
<td>- very high aspect ratio (l/d can be ~1000)</td>
<td>- not very high aspect ratio</td>
</tr>
<tr>
<td>- behaviour not always well defined</td>
<td>- single crystals, very well defined and characterized</td>
</tr>
<tr>
<td>- research is at a fairly early stage (activity since ca. 2007 onwards)</td>
<td>- research is already matured (high activity since 1992)</td>
</tr>
<tr>
<td>- promising in large-scale industrial applications, especially composites because of the high aspect ratio</td>
<td>- promising in more esoteric applications which can utilize, e.g., liquid crystal properties</td>
</tr>
</tbody>
</table>
Recommended review articles

On all kinds of nanocellulose:

On nanofibrillar cellulose:
Siró and Plackett *Cellulose* 2010, 17, 459.

On cellulose nanocrystals:

On bacterial cellulose:

On nanocellulose modification:
Eyley and Thielemans *Nanoscale* 2014, 6, 7764.