Nanocellulose Part I

Preparation and modification

Aalto University
School of Chemical
Engineering

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3rd October 2023

Assignment

Take a couple of minutes to answer “before the lecture” questions on the paper in front of you

Learning objectives

After this lecture, you should be able to:

- **Explain why nanocellulose is important**
- **Distinguish cellulose nanofibres (CNFs) and cellulose nanocrystals (CNCs)**
- **List the main preparation routes to CNFs and CNCs**
- **List the main challenges in CNF and CNC preparation**
- **Be aware of the main approaches and bottlenecks in chemical modification of CNFs and CNCs**

Outline

(1) Different types of nanocellulose: Terminological issues

(2) Preparation of nanocellulose:

- Cellulose nanofibres (CNF) (including bacterial cellulose)
- Cellulose nanocrystals (CNC)

(3) Modification of CNF

(4) Modification of CNC

(5) Summary: comparison between CNF and CNC

Types of nanocellulose

(1) Cellulose nanofibres

- Mechanically isolated microfibrils
- Chemically isolated microfibrils (TEMPO-oxidation)
- Bacterial cellulose

(2) Cellulose nanocrystals

- Rods of highly crystalline cellulose, isolated by acid hydrolysis

Nanocellulose: contradiction in terms

(1) Cellulose nanofibres

Synonyms used in literature:

- nanofibrillar cellulose (NFC)

- microfibrillar cellulose

- cellulose nanofibrils

- cellulose microfibrils

(2) Cellulose nanocrystals

Synonyms used in literature:

- cellulose whiskers

- cellulose nanowhiskers

- cellulose microfibrils

- nanocrystalline cellulose

- microcrystalline cellulose

Note: microcrystalline cellulose is in its more common use a completely different material (micron-sized cellulose crystals).

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Why nanocellulose?

Alternatives to non-renewable materials

- Reduce the use of, e.g., fossil-based components for materials
- Ultimate goal: renewable, biodegradable materials with unique properties

Why nanocellulose?

- High strength
- Low density
- Renewable and abundant
- Very high aspect ratio (length/width especially in the case of nanofibrils)
- Can be chemically modified for functional properties
- Specific response to water

Why nanocellulose?

Example
Nanocomposite made of poly(lactic acid) as a continuous matrix and nanofibrillar cellulose as the reinforcing phase
→ Fully bio-based and biodegradable alternative to plastics

Other potential applications
- Viscosity modifiers
- Hydrogels for tissue growth
- Hydrogels for wound healing
- Drug release matrices
- Sensor materials
- Paper-based electronics
- Templates for chiral materials
- Platforms for asymmetric catalysis
- Security papers (liquid crystal phases)

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Cellulose nanofibres (CNFs): preparation

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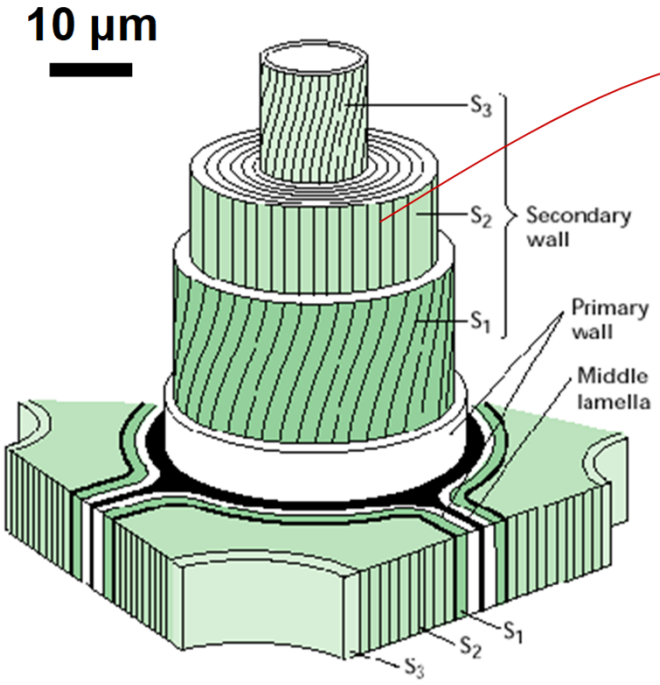
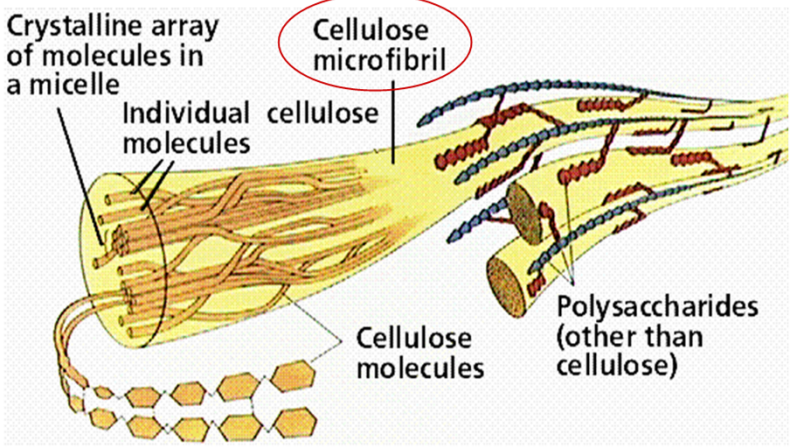
Recap: ultrastructure of plant fibres

Individual fibre

Cellulose microfibril

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





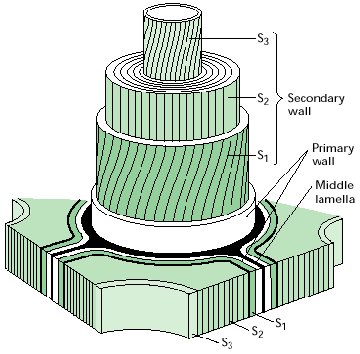
Cellulose microfibrils

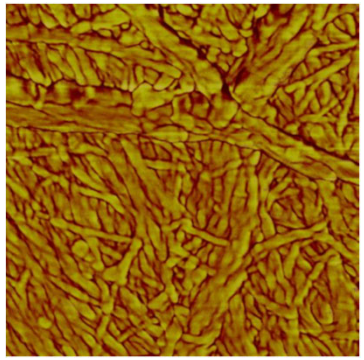
- **Preparation of nanofibrillar cellulose aims at isolating the individual microfibrils or microfibril bundles from the cell wall structure**
- **When a microfibril is isolated from the cell wall, it becomes a nanofibre**

Microfibril – biological definition
Nanofibre – definition in materials science

Seminal challenges in isolation:

- **Tight, hierarchical structure of the plant cell wall**
- **Inherent tendency of cellulose to aggregate**





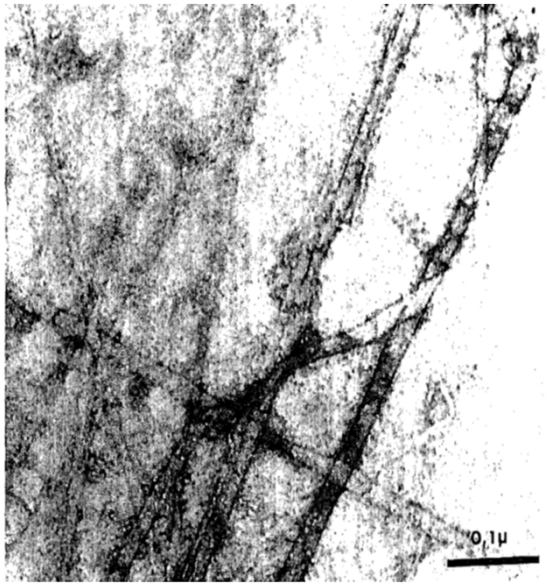
CNF: mechanical isolation

EARLY EXAMPLES OF INDIVIDUALIZATION OF MICROFIBRILS

METHOD: ULTRASONICATION

S.K. Asunmaa
Tappi **1967**, *49*, 319.

From aspen holocellulose

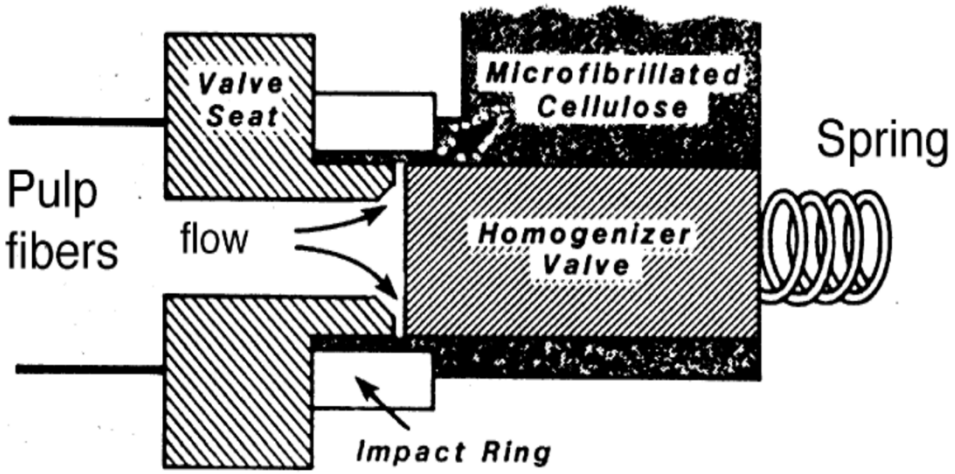


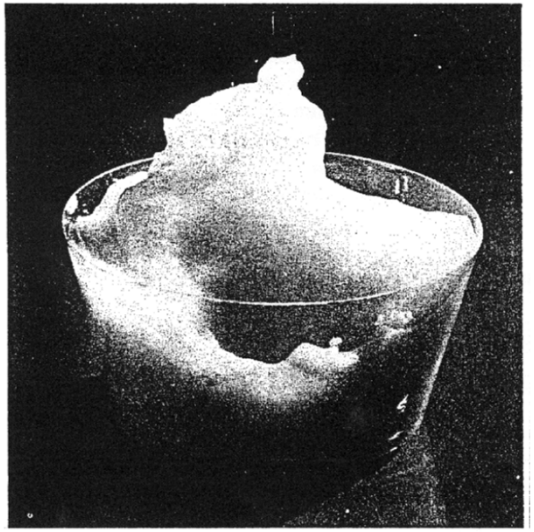
From valonia alga

Gardner and Blackwell
J. Polym. Sci. C
1971, *36*, 327.

CNF: mechanical isolation

First attempt to isolate microfibrils for materials science purposes.



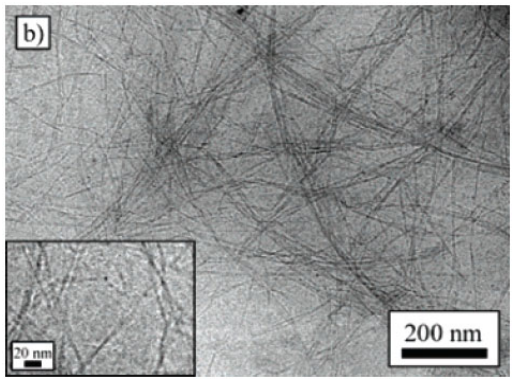


Turbak et al. *J. Appl. Polym. Sci. Appl. Polym. Symp.* **1983**, *37*, 815.

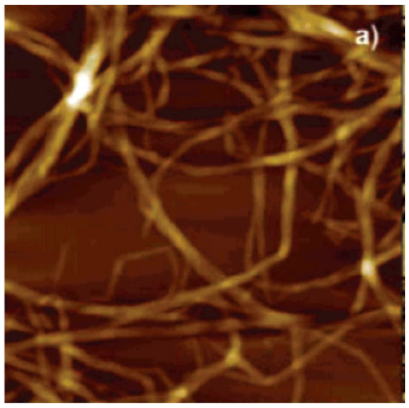
CNF: mechanical isolation

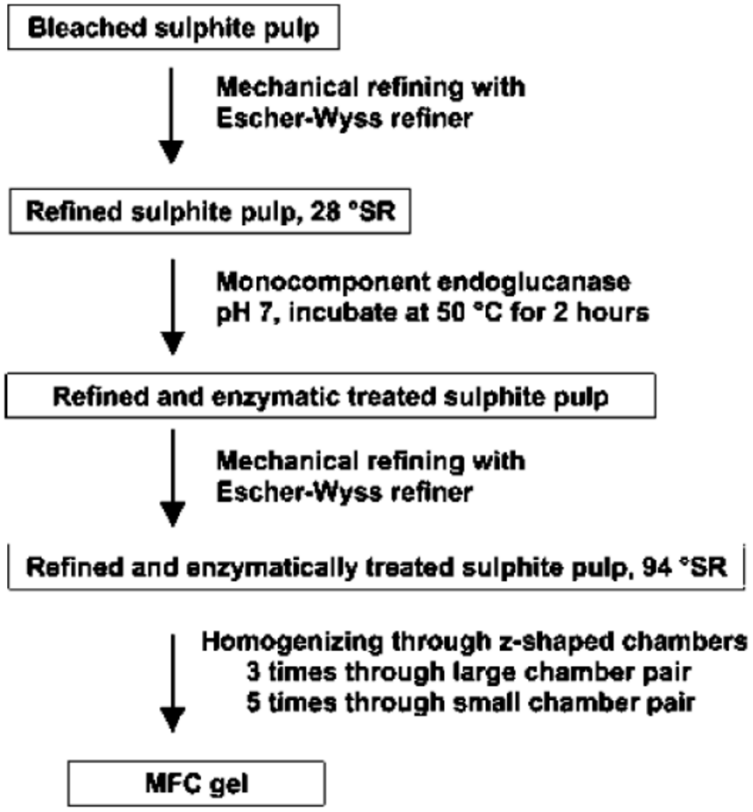
Enzymatic pretreatment to bleached sulphite pulp.

TEM



AFM





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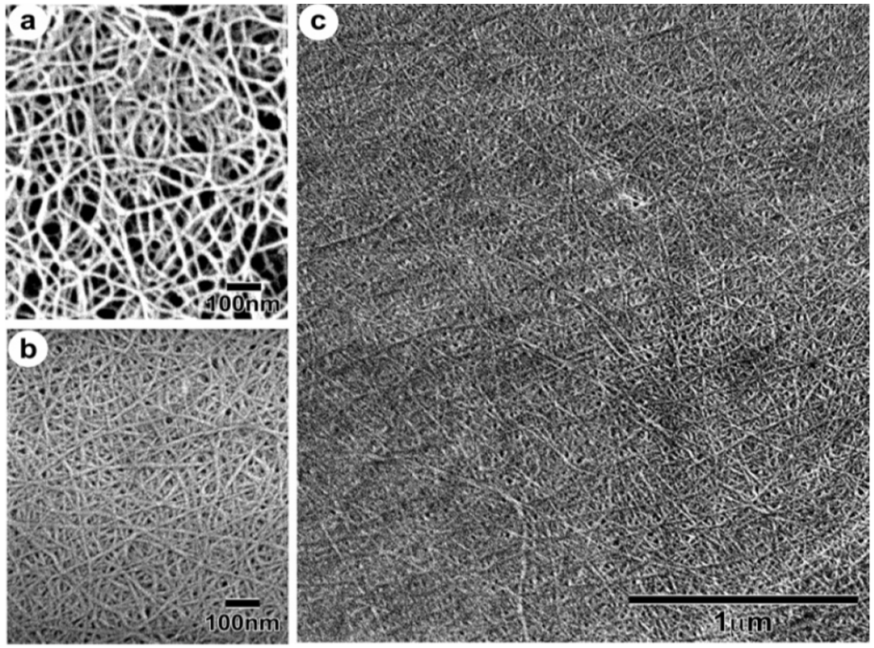
Microfibrils and microfibril aggregates, ca. 5-10 nm in size.

Pääkkö et al. *Biomacromolecules* **2007**, *8*, 1934.

CNF: mechanical isolation

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



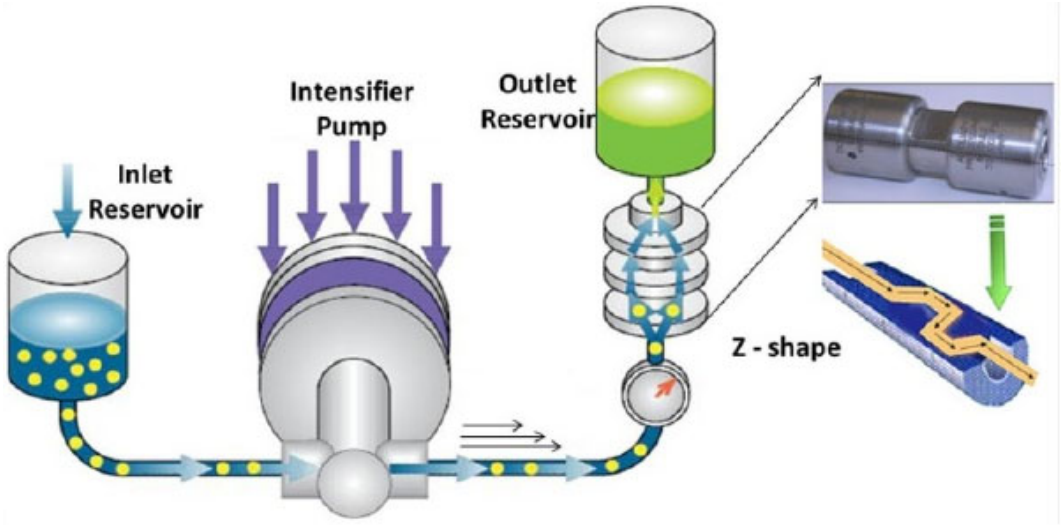
Highly monodisperse 15 nm wide microfibril aggregates

Abe et al. *Biomacromolecules* **2007**, *8*, 3276.

CNF: mechanical isolation

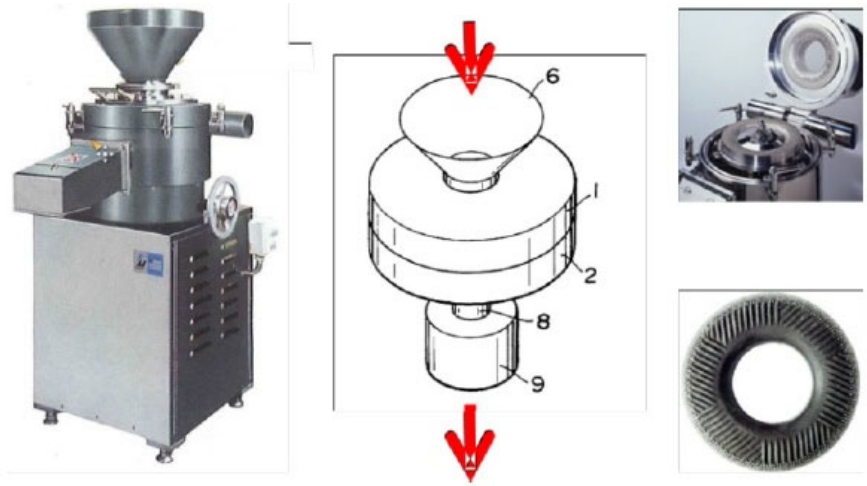
INSTRUMENTS USED

Fluidizer



Fibres are pumped at high pressure through a z-shaped chamber

Masuko grinder



Two rotating plates very close to each other

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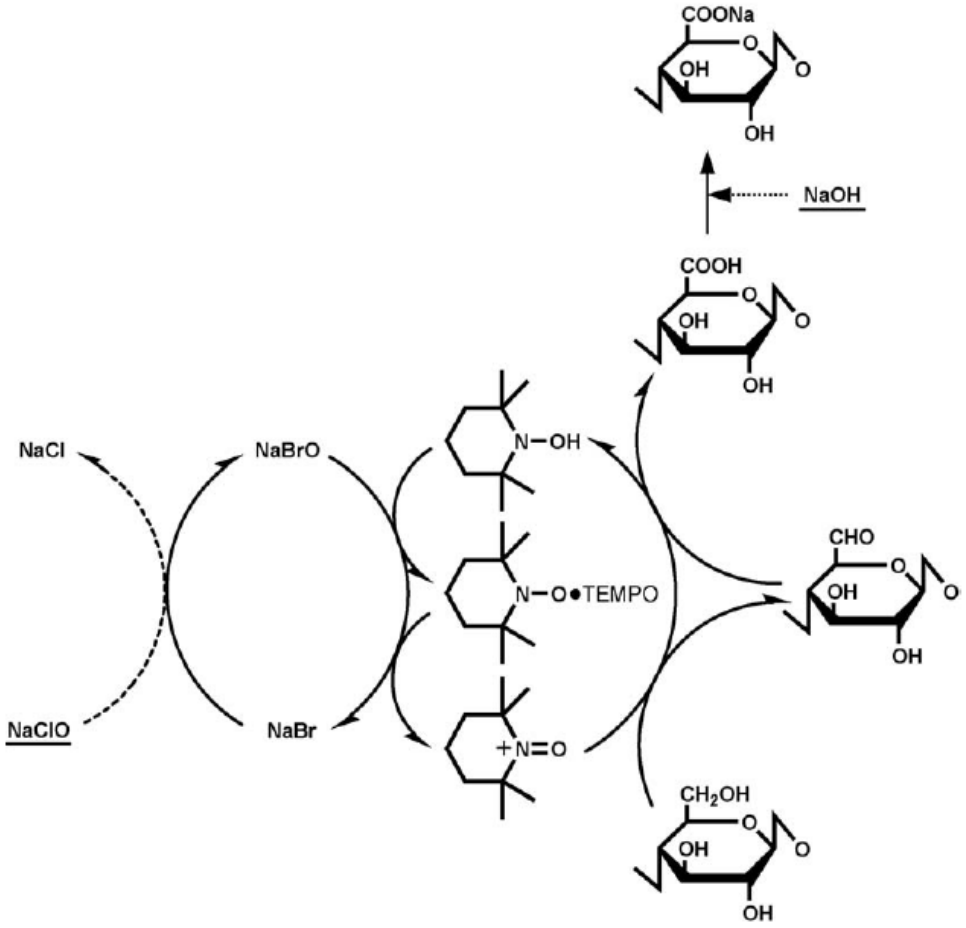
CNF: chemical isolation

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:
de Nooy et al. *Carbohydr. Res.* **1995**, *269*, 89.

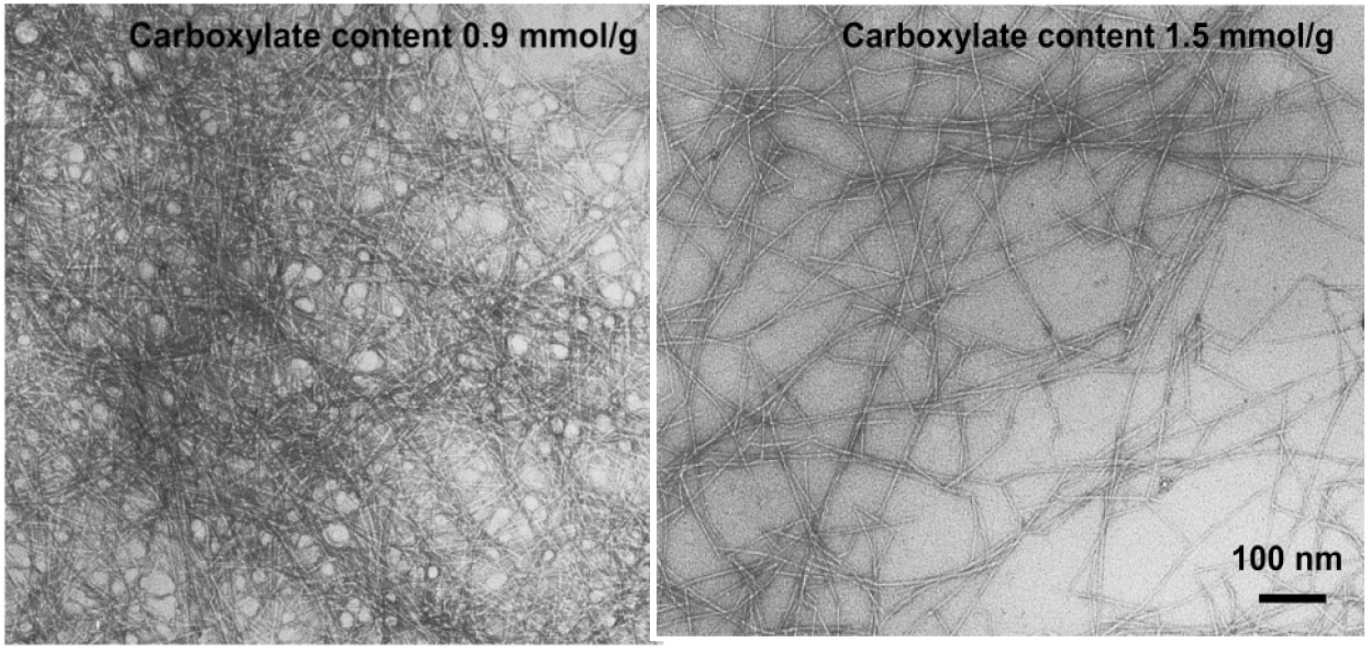
Pioneered for cellulose:
Isogai and Kato *Cellulose* **1998**, *5*, 153.



CNF: chemical isolation

TEMPO-mediated oxidation of native fibres → **Mechanical stirring** → **Centrifugation**

↓ **supernatant**



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

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Saito et al. *Biomacromolecules* **2006**, *7*, 1687.
Saito et al. *Biomacromolecules* **2007**, *8*, 2485.

CNF: chemical isolation

Why do we get individual microfibrils from TEMPO-oxidation?

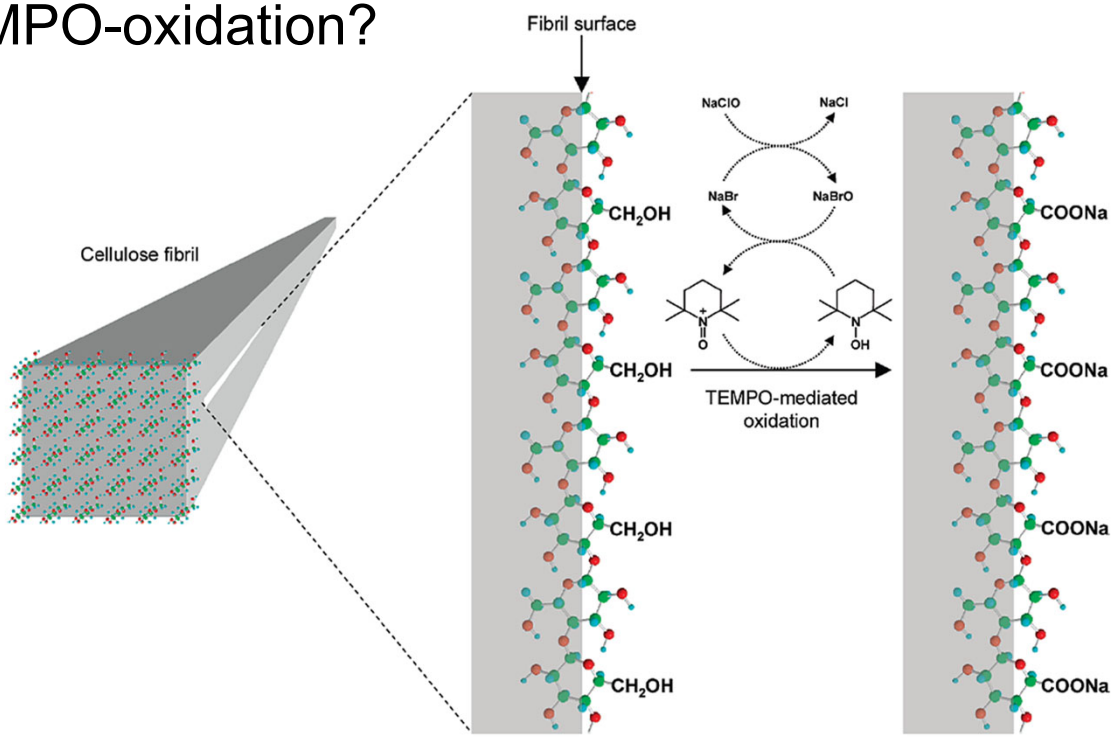


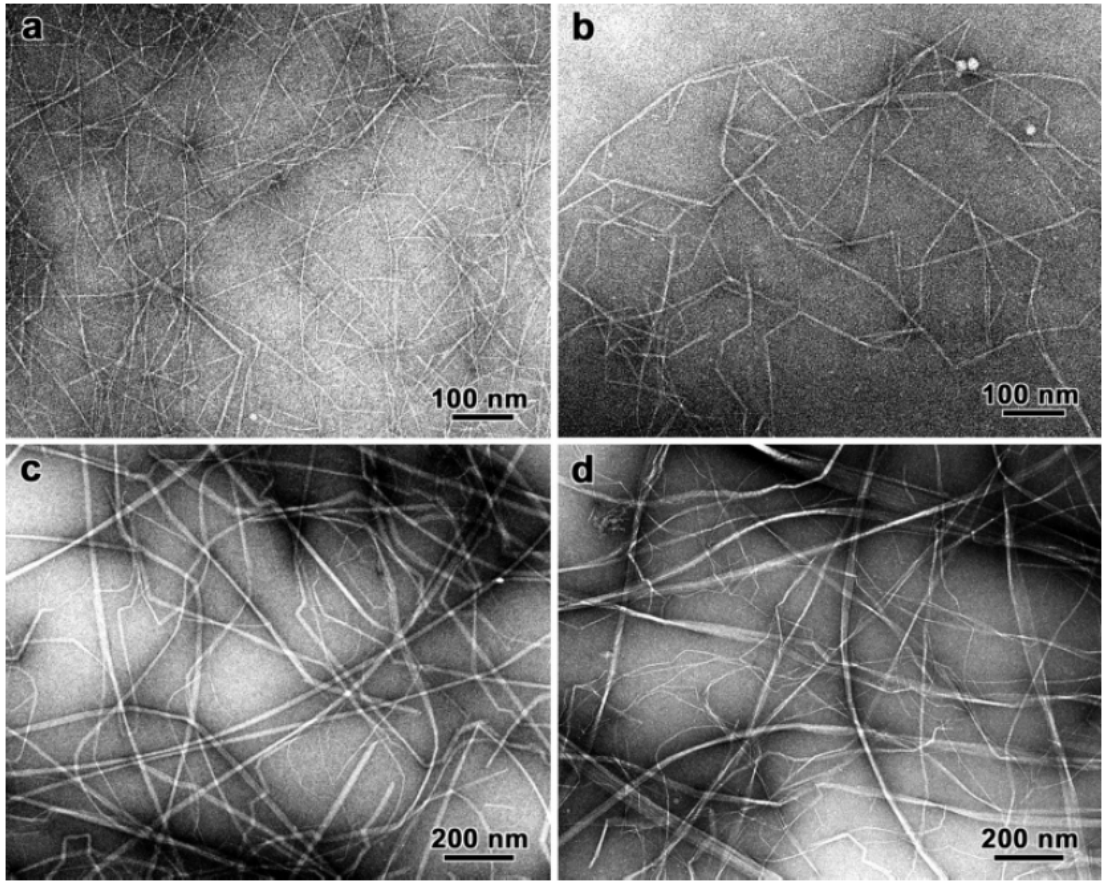
Image from:
Okita et al.
Biomacromolecules
2010, *11*, 1696.

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

CNF: chemical isolation

Effect of starting material

wood pulp



cotton

tunicate

bacterial cellulose

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Saito et al. *Biomacromolecules* **2006**, *7*, 1687.

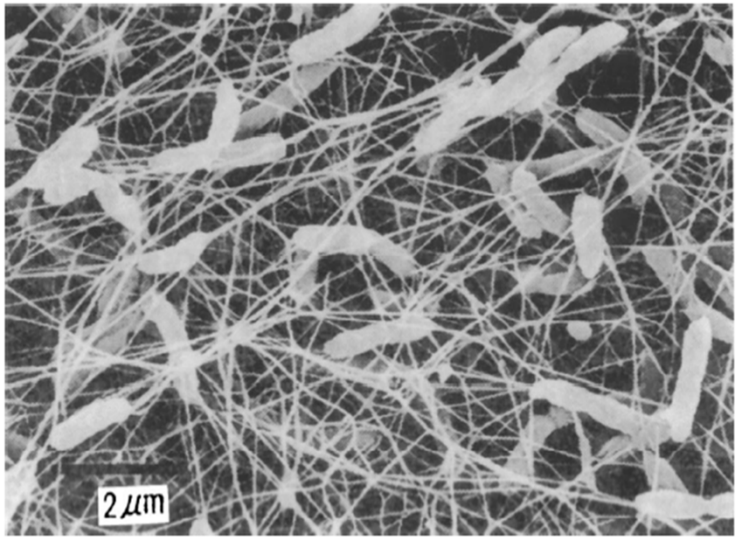
Summary on CNF isolation

- Mechanical isolation leads always to bundles of microfibrils being isolated as cellulose nanofibres
- TEMPO-oxidation is the only method that can reliably isolate individual cellulose microfibrils into cellulose nanofibres
- The width of a TEMPO-CNF is dictated by the width of a microfibril

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 cellulose nanofibres

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



Iguchi et al. *J. Mater. Sci.* **2000**, *35*, 261.

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Cellulose nanocrystals (CNCs): preparation state-of-the-art

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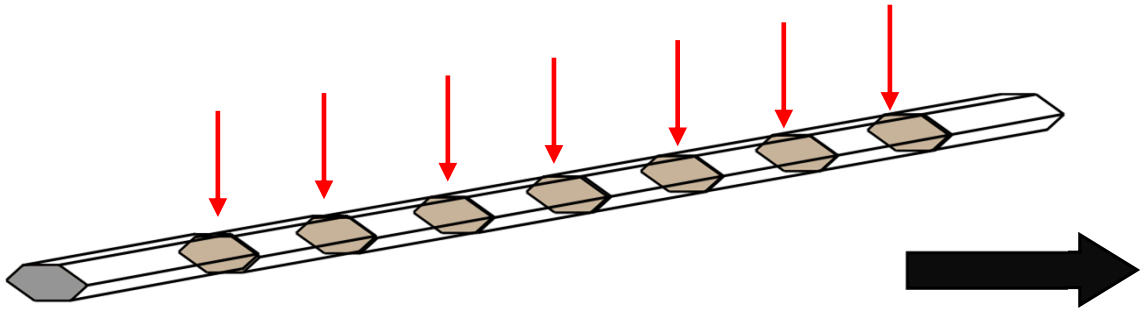
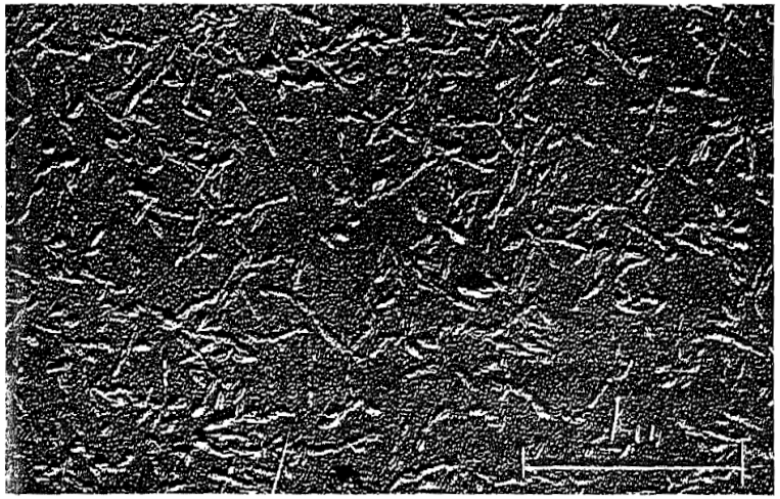
Principle of preparation

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



Controlled acid hydrolysis leads to disruption of disordered domains leaving crystalline cellulose intact.



Result: cellulose nanocrystals

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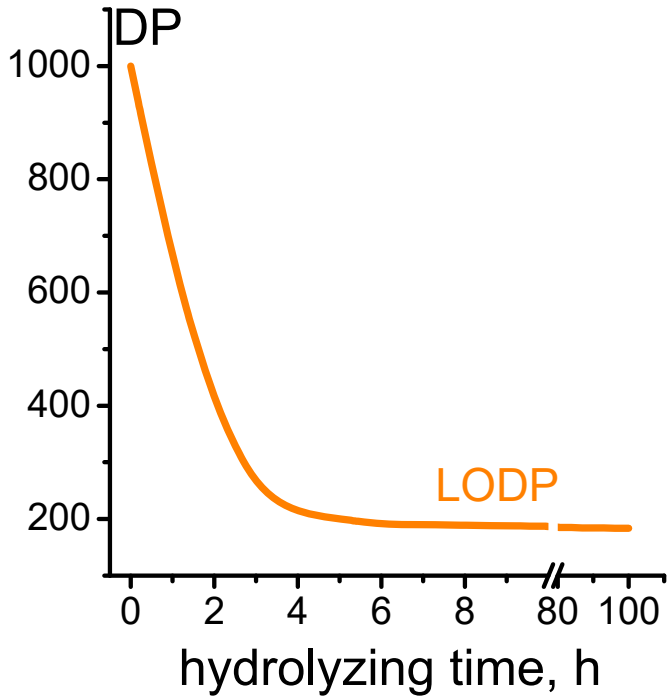
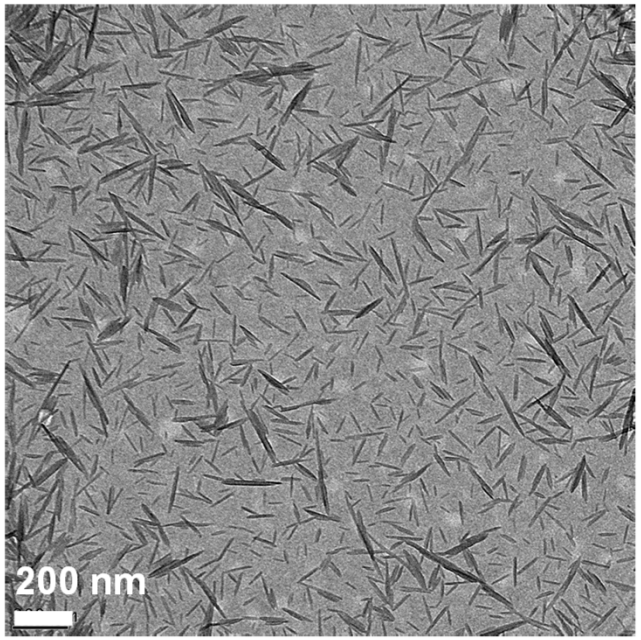
Rånby *Discuss. Faraday Soc.* **1951**, *11*, 158.

Principle of preparation



- Note: this is the same phenomenon as levelling-off degree of polymerisation
- When milder acid concentrations are used, DP first drops fast, after which it almost halts, hitting the LODP
- Common explanation for LODP: “amorphous” regions are hydrolysed and crystallites are left intact

CNC preparation: state-of-the-art



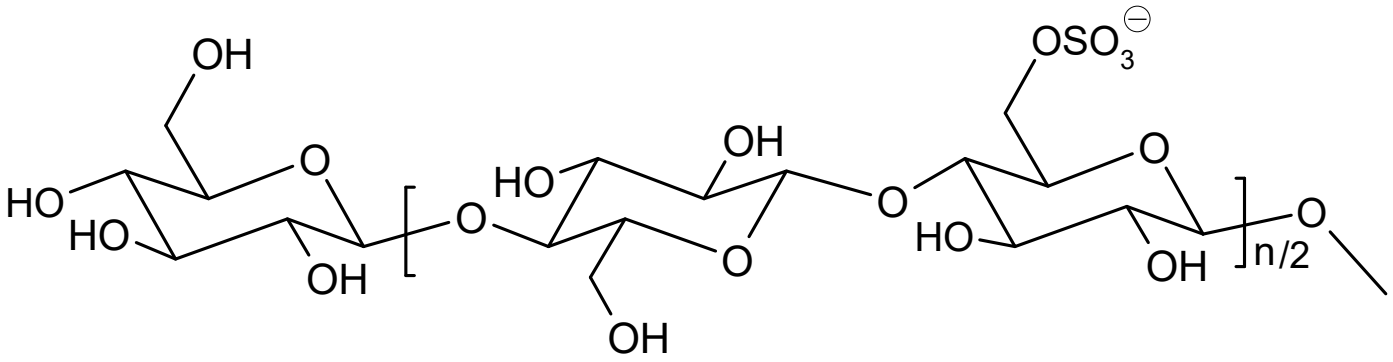
- Source: Whatman 1 (from cotton linters)
- Temperature: 45ºC
- Acid concentration: 64% (w/w) H_2SO_4 (aq)
- Time: 45 min

Purification steps:

- Centrifugation
- Dialysis (~7 days)
- Filtering

- Yields are generally low: 20-50%
- Water consumption is huge

CNC preparation: surface charge



When prepared with sulfuric acid, organic sulphate groups are introduced on the surface of the nanorods.

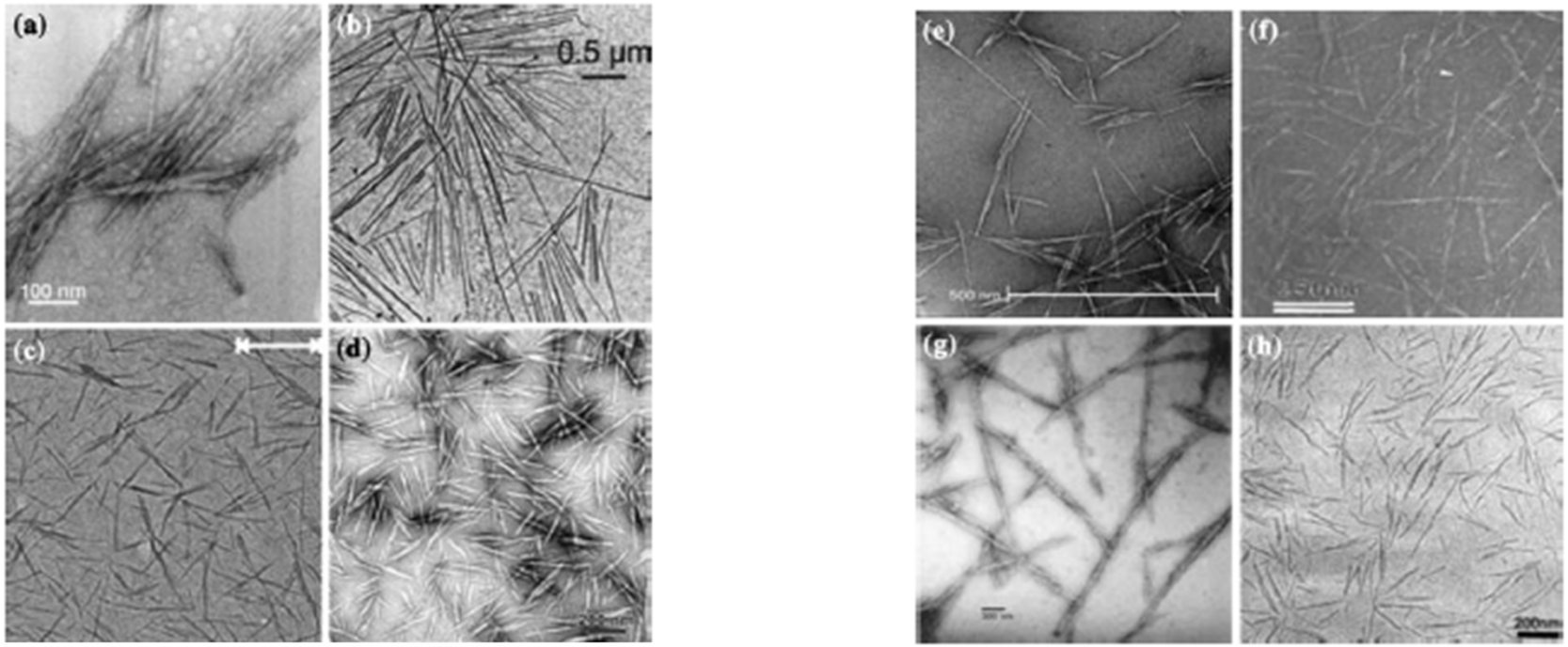
electrostatic repulsion

STABLE SUSPENSION IN WATER

CNC preparation: dimensions

- Nanocrystal width *and* length depend on the starting material (botanical source)

Microcrystalline cellulose | Tunicate | Sisal | Straw



Cotton | Ramie | Bacterial cellulose | Sugarbeet

Eichhorn et al. *J. Mater. Sci.* **2010**, *45*, 1.

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CNC preparation: HCl gas route

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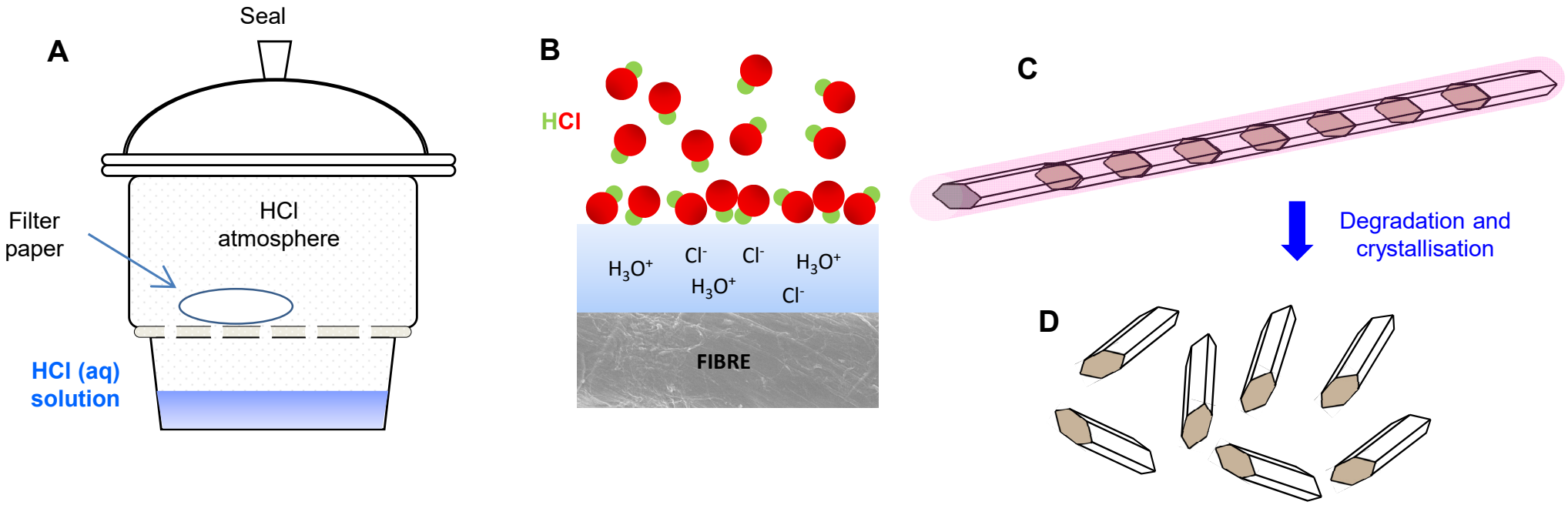
Concept with HCl gas



- Hydrogren chloride (HCl) vapor adsorbs on fibre surface
- Fibre surface is always covered by water in ambient conditions

→ HCl dissociates in water, i.e., it becomes an acid

→ Acid and water degrade cellulose until the LODP

→ Nanocrystals can be isolated from the hydrolysed fibres

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Procedure with HCl gas

Hydrolysis with HCl vapour:
35% HCl, 4 h, room temperature

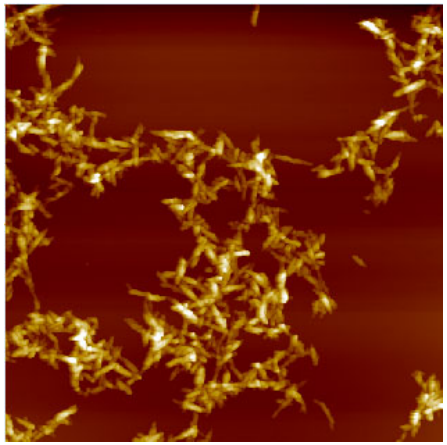
↓

Grinding the hydrolysed substrate in a Wiley mill

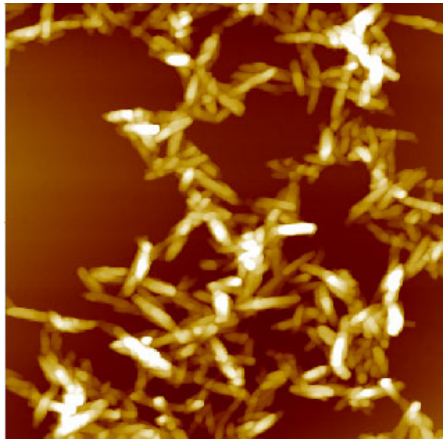
↓

Dispersing the powder in formic acid (heavy sonication)

Note: hydrolysis with HCl(g) is easy, dispersion of CNCs is difficult



5×5 μm^2



2×2 μm^2

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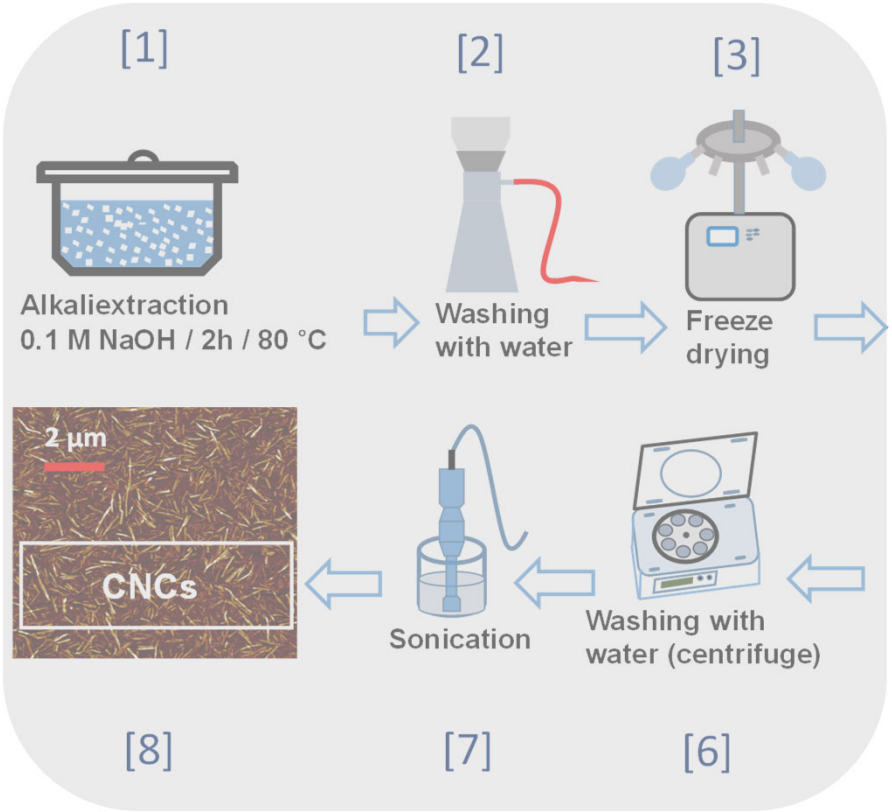
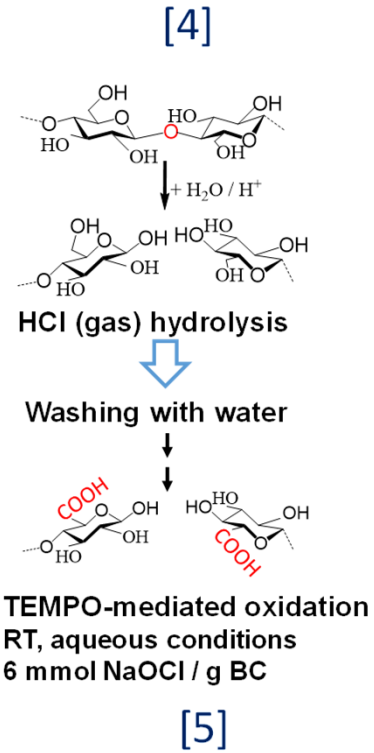
Angew. Chem. Int. Ed. **2016**, *55*, 14455.

Merging HCl gas and TEMPO-oxidation





- Hydrolysis by HCl gas to remove disordered cellulose first
- TEMPO-oxidation to introduce charge second

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Pääkkönen et al. *ACS Sustainable Chem. Eng.* **2019**, *7*, 14384.

Summary on CNC preparation

- Surface charge is required to disperse CNCs in water
- Sulfuric acid hydrolysis removes disordered cellulose and introduces charge simultaneously
- HCl gas hydrolysis needs to be combined with an additional step (e.g. TEMPO-oxidation) for charge introduction
- Yields in HCl gas hydrolysis are superior to those from sulfuric acid hydrolysis

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CNC modification

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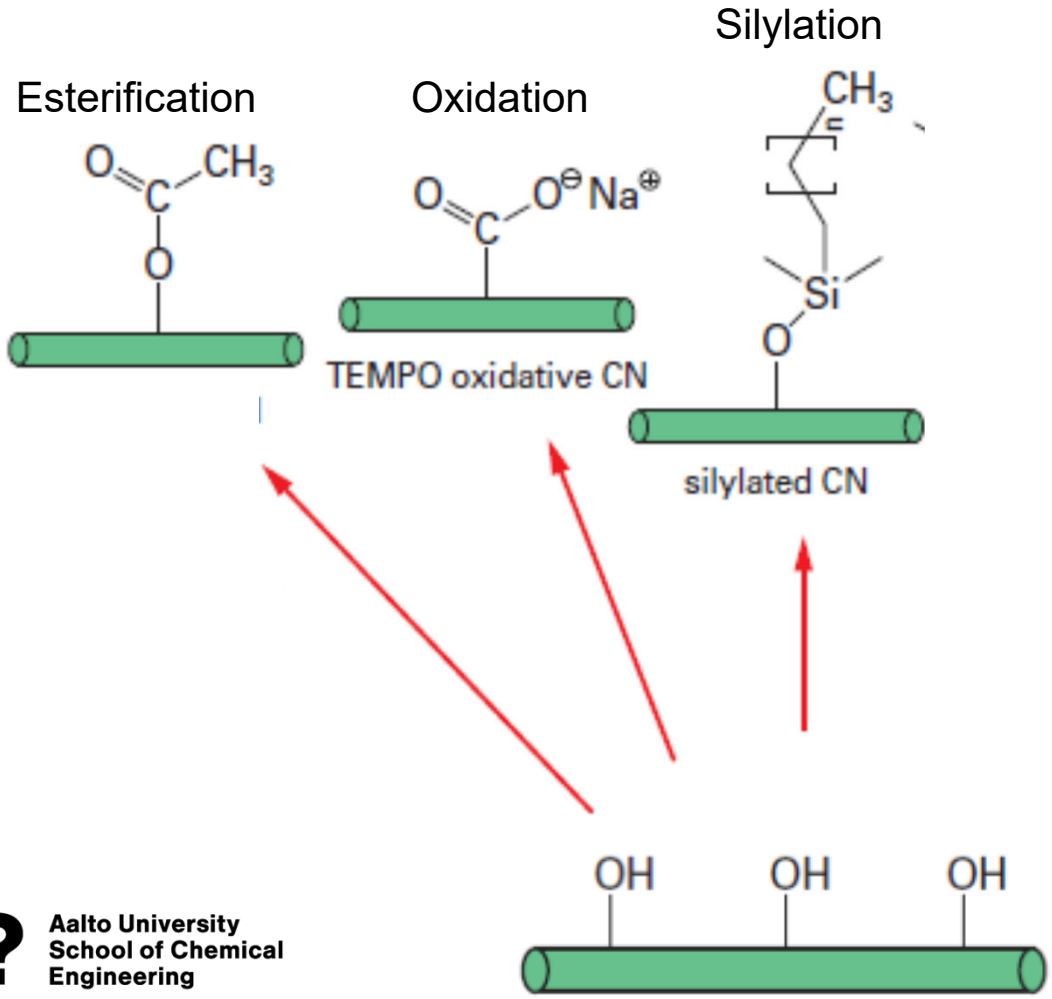
General issues

- CNC modification aims at surface functionalization, leaving the crystalline core intact
- Because of the charged groups on the CNC surface, they disperse very 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 one of the most popular approaches at present

CNC modification routes

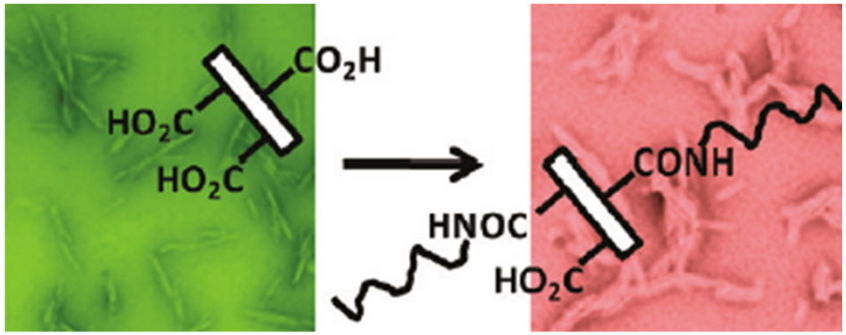


Note:
Etherification is not generally considered for already isolated CNCs

Polymer grafting on CNCs

TEMPO-oxidation on CNC surface

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

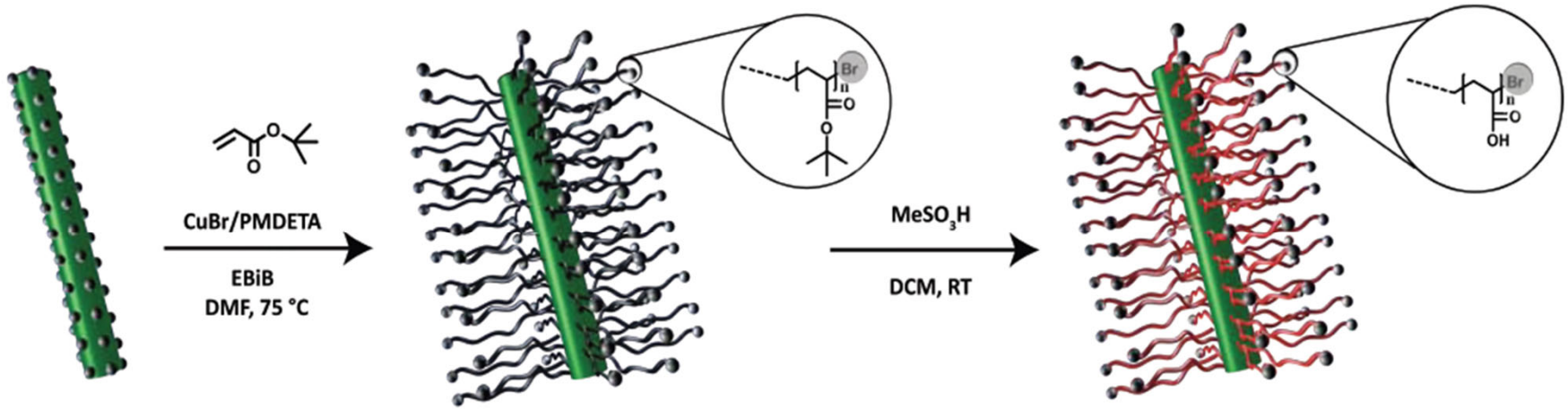


NOTE: Polymer grafting on CNCs is usually performed to improve their compatibility in polymer composites

Harrison et al. *Biomacromolecules* **2011**, *12*, 1214.

Polymer grafting on CNCs

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



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Majoinen et al. *Biomacromolecules* **2011**, *12*, 2997.

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CNF modification

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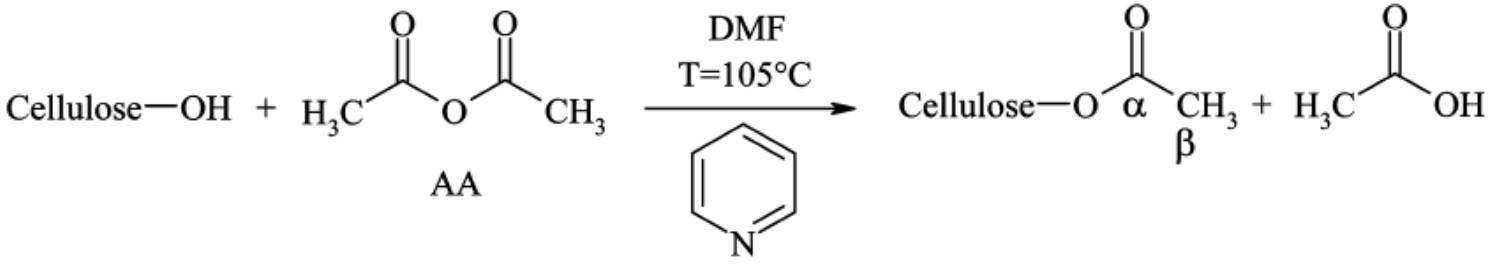
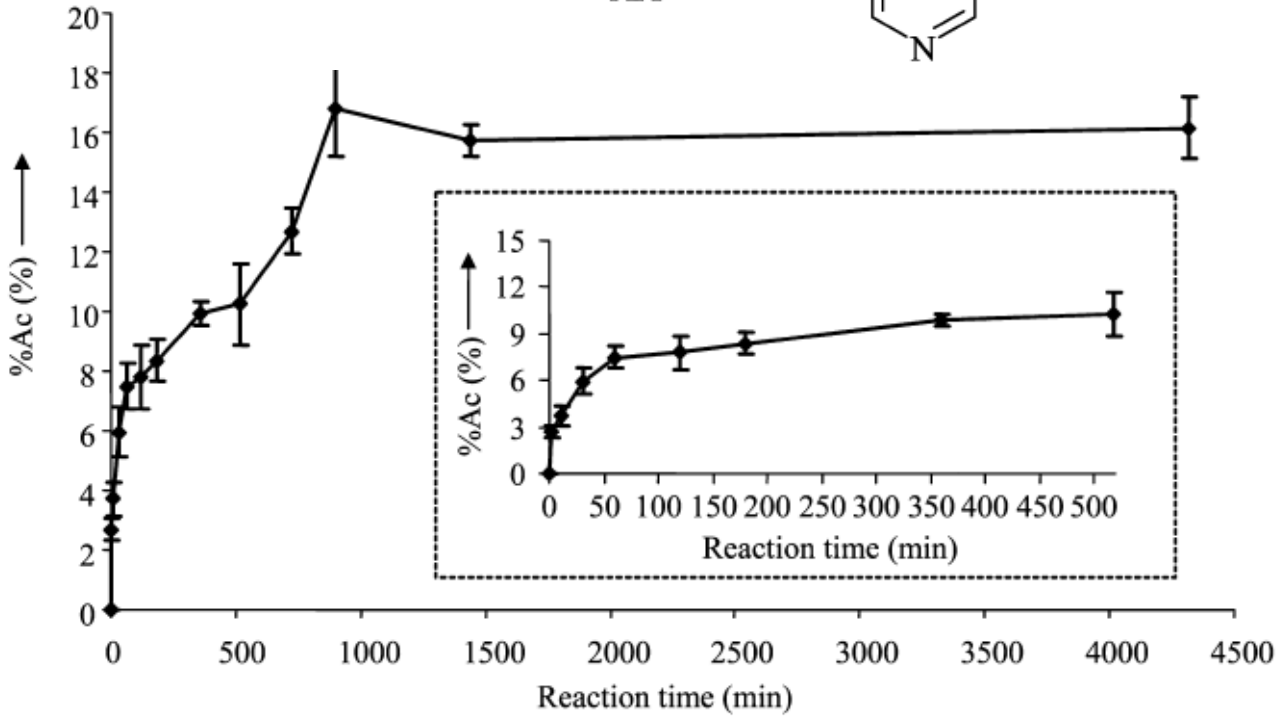
General issues

- **Like CNCs, CNF modification is *always* surface modification**
- **CNF modification can be performed either before CNF preparation (pre-treatment), during (like TEMPO-oxidation) or after the CNF has been isolated**
- **Often aims at better water dispersion (by increasing charge) or decreasing hydrophilic / hygroscopic nature (by introducing hydrophobic functional groups)**
- **NOTE: CNFs form gels, complicating the practical modification; their modification is not as researched as that of CNCs**

Example: acetylation of CNFs





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

Acetyl content can be easily tuned with reaction time.

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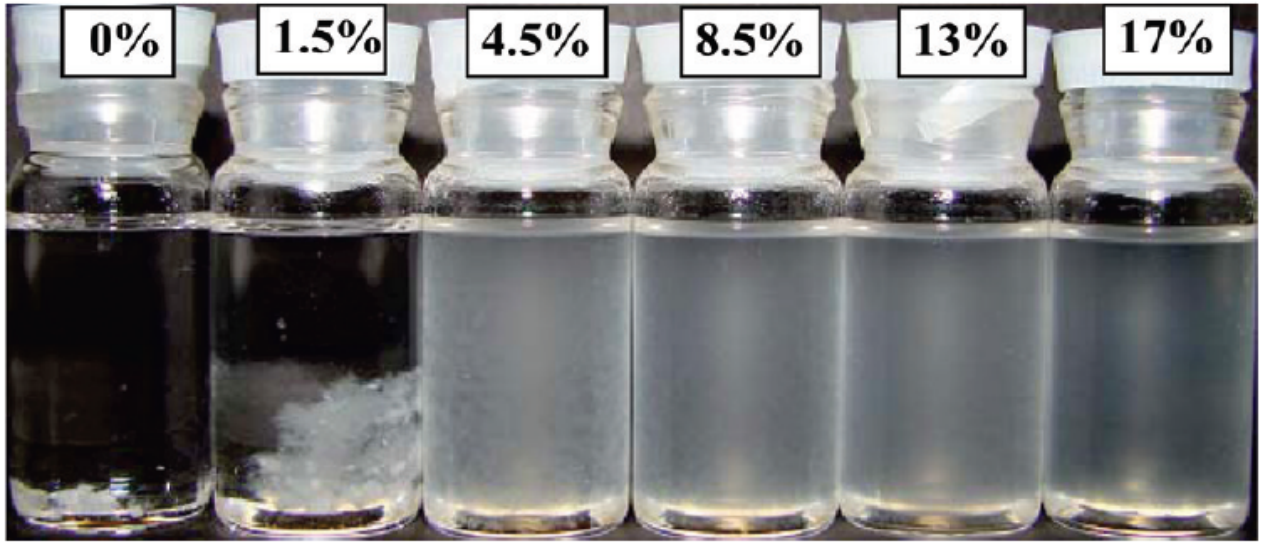
Tingaut et al. *Biomacromolecules* **2010**, *11*, 454.

Example: acetylation of CNFs

Acetyl content



- Acetylation dramatically improves the dispersibility of NFC in chloroform

Tingaut et al. *Biomacromolecules* **2010**, *11*, 454.

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Summarizing comparison:

- CNFs vs. TEMPO-oxidized CNFs
- CNFs vs. CNCs

CNFs vs. TEMPO-CNFs

Mechanically produced CNFs

- Cheap(ish) (after suitable pretreatments)
- Polydisperse width, mostly higher than in native microfibrils
- Not very stable in dispersion

- Always present with hemicellulose (anything between 3-25%) and traces of lignin

TEMPO-oxidized CNFs

- Sodium hypochlorite is expensive

- Monodisperse width that corresponds to the native microfibril
- Stable dispersion because of the charged COOH-groups on the surface
- Not pure cellulose but uronic acid groups on the nanofibril surface
- Includes also hemicellulose which is difficult to quantify because these CNFs resist acid hydrolysis

CNFs vs. CNCs

Cellulose nanofibres

- Gels at low concentrations (0.5-1.5 w%)
- Very high aspect ratio (l/d can be ~1000)
- Flexible, spaghetti-like shape
- Intensive research from 2007 onwards
- Promising in especially composites applications (reinforcing phase) and as hydrogels

Cellulose nanocrystals

- Fluid dispersion at low concentrations
- Not very high aspect ratio
- Rod-like: always straight shape
- Intensive research from 1992 onwards (although a surge after 2005 occurred)
- Promising as filler material, viscosity controller etc.
- Many high end applications have been proposed (incl. liquid crystal utilization)

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Assignment

Take a couple of minutes to answer “after the lecture” questions on the paper in front of you