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BioMediTech Institute of Biosciences and Medical Technology

Potential of MFC and nanocellulose for AIP

Sampo Tuukkanen

Ph.D., Assistant Professor

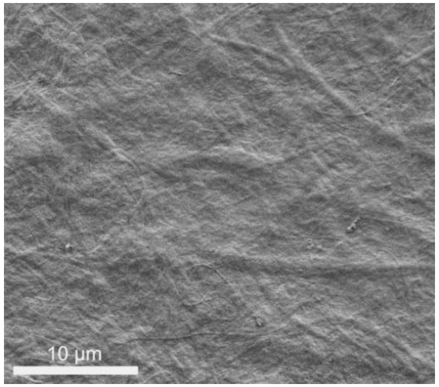
BioMediTech Institute and Faculty of Biomedical Sciences and Engineering (BMT),

Tampere University of Technology (TUT)

Outline

- Introduction to wood-based and bacterial nanocellulose
- Advantages and applications
- Fibrillation method developed at TUT
- Oxygen barrier properties
- Piezoelectricity of nanocellulose
- Conclusions

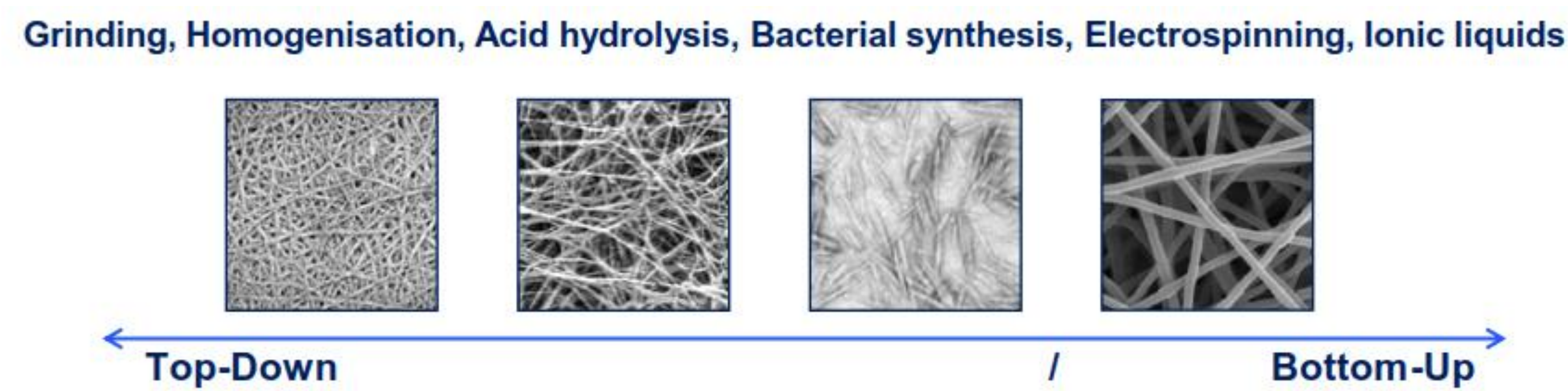
INTRODUCTION TO NANOCELLULOSE



Raw materials and manufacturing

- Cellulose is the most abundant polymer on earth!
- Examples of raw material sources for nanocellulose:

- Examples of manufacturing processes:

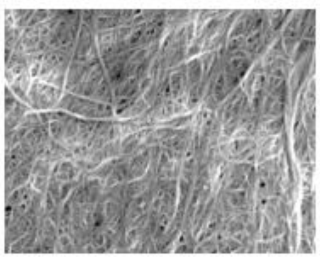


[Figures from: Heli Kangas & Ulla Forsström, VTT, ”Nanocellulose – A promising material for future packages”, Helsingin Messukeskus 4.9.2013]

Nanocellulose types?

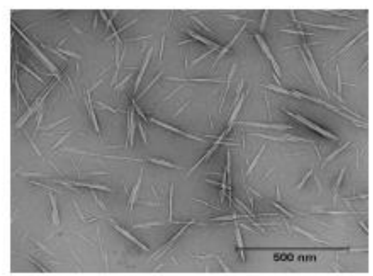
- Nanocellulose dimensions and structures vary depending on source, manufacturing, treatments etc.
  - Can be divided to three main types:

Micro/Nanofibrillated cellulose (M/NFC) (or CNF)



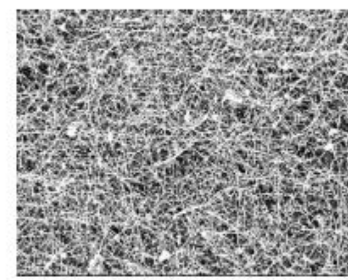
Width: 5-6 nm
(cellulose fibrils)
Width: 10-20 nm
(fibril aggregates)
Length > 1μm

Nanocrystalline cellulose (NCC) (or CNC)



Width: 2-20 nm
Length: 100-600 nm

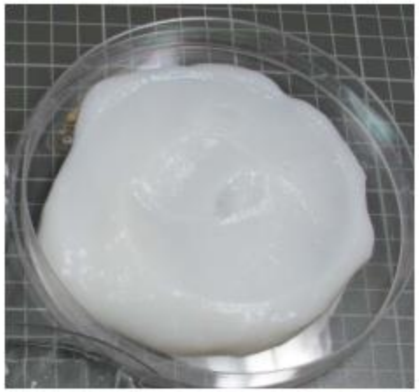
Bacterial cellulose (BC)



Width: 20-100 nm
Length > 1μm

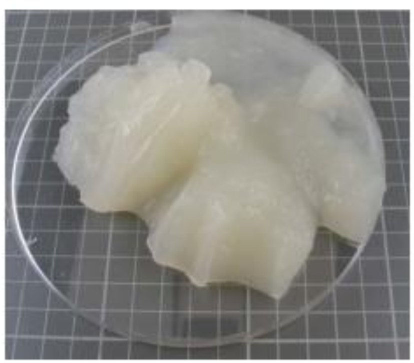
[Figures from: Heli Kangas & Ulla Forsström, VTT, ”Nanocellulose – A promising material for future packages”, Helsingin Messukeskus 4.9.2013]

MFC/CNF produced with different methods

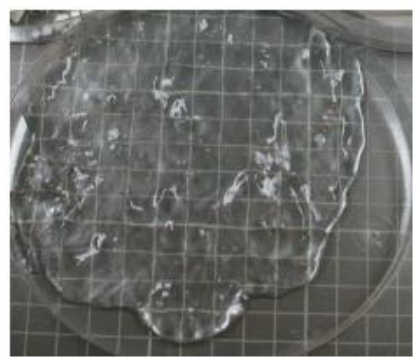


Grinding

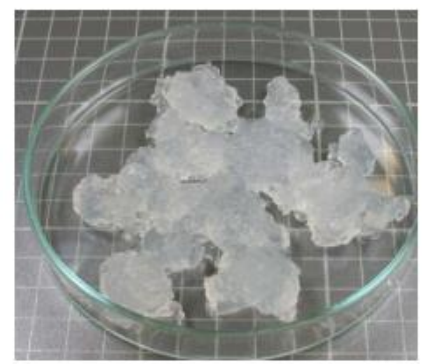
Homogenisation



Carboxymethylation



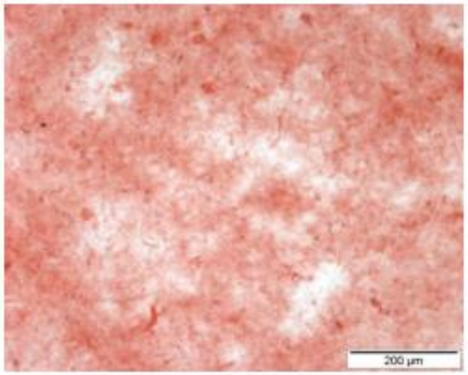
TEMPO -oxidation



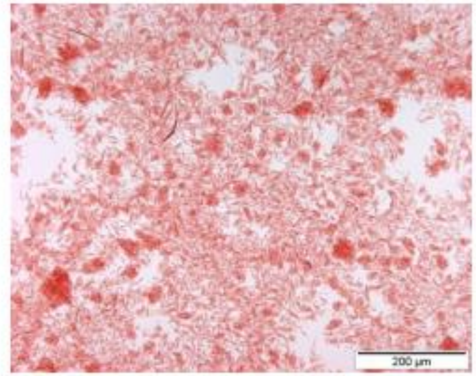
Cationisation

[Figure from: Tiina Pöhler et al, 2010 TAPPI International Conference on Nanotechnology for the Forest Product Industry]

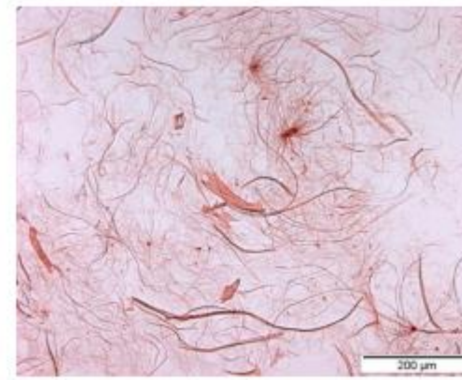
Different MFC and CNF under microscope



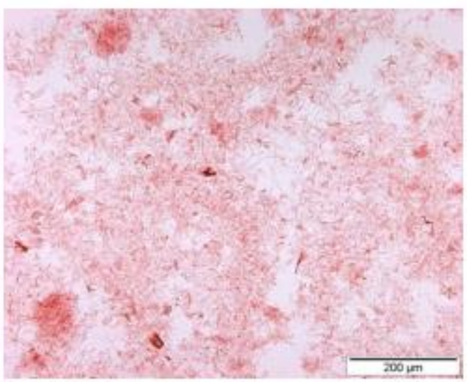
Grinding



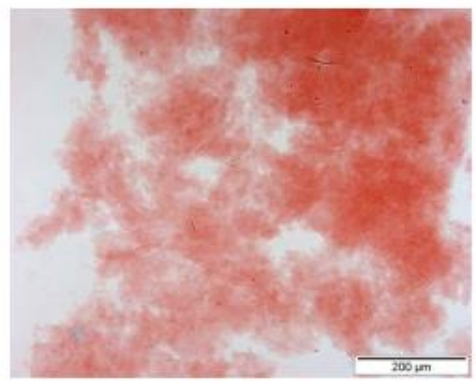
Homogenisation



Commercial MFC



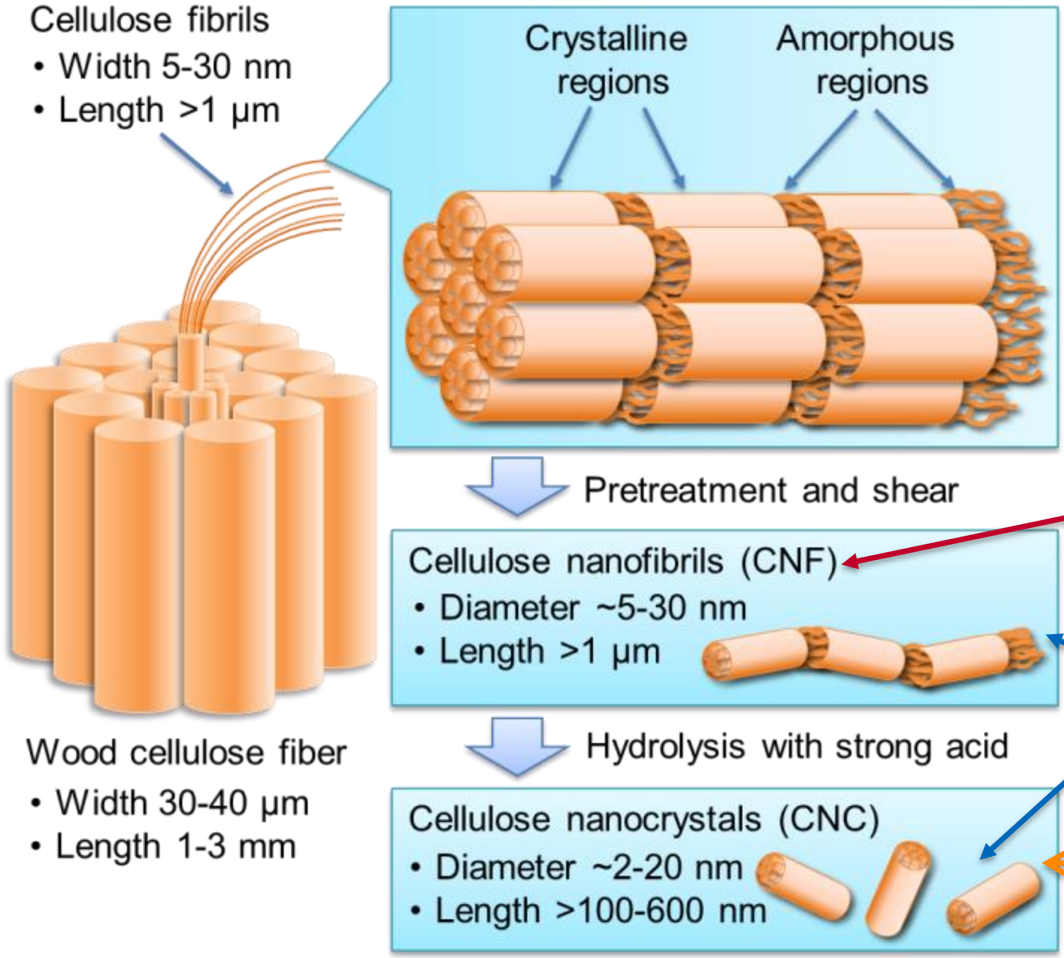
Carboxymethylation



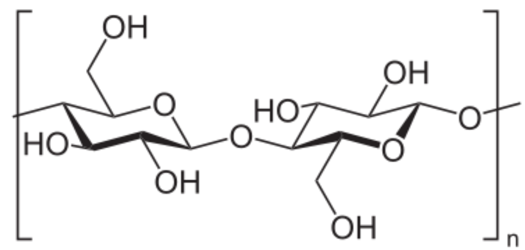
TEMPO -oxidation

[Figure from: Tiina Pöhler et al, 2010 TAPPI International Conference on Nanotechnology for the Forest Product Industry]

Nanocellulose from wood



Chemical structure of cellulose:



Sometimes called also microfibrillated cellulose (MFC), depending on the dimensions

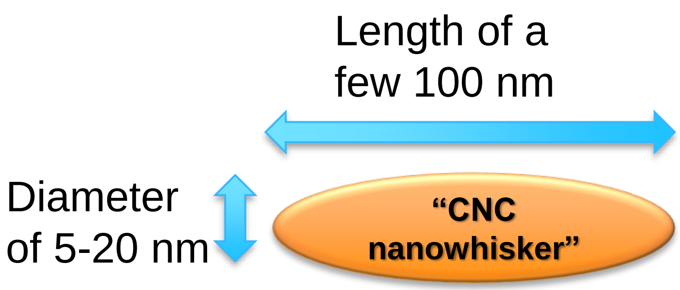
Nanocelluloses

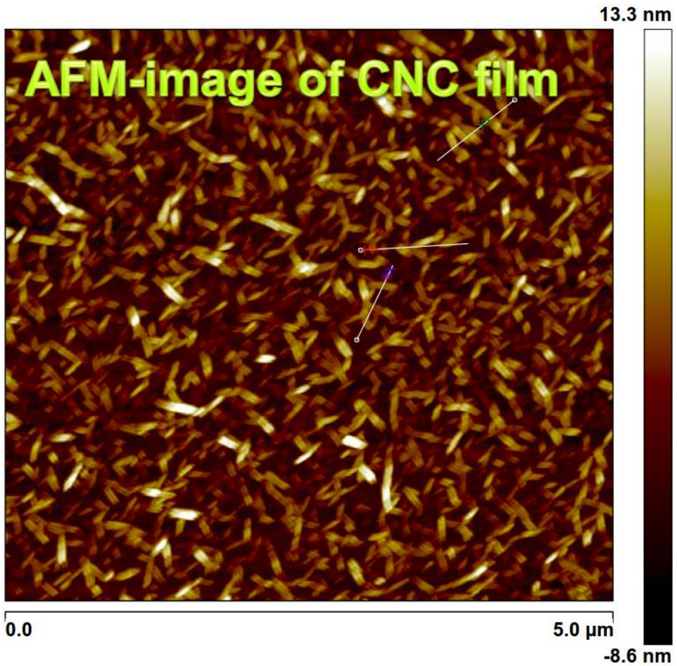
"CNC nanowhisker"

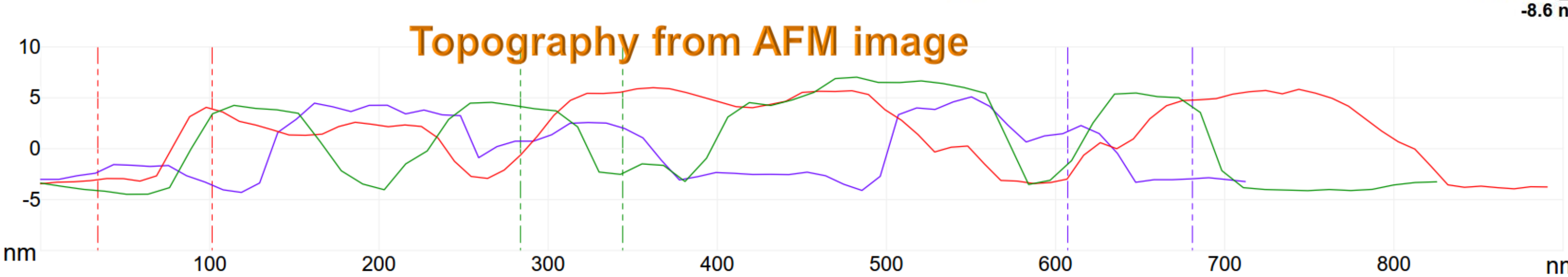
[S. Rajala, T. Siponkoski, E. Sarlin, M. Mettänen, M. Vuoriluoto, A. Pammo, J. Juuti, O. J. Rojas, S. Franssila, and S. Tuukkanen, "Cellulose nanofibril film as a piezoelectric sensor material, *ACS Appl. Mater. Interfaces* **8**(24) (2016) 15607]

Cellulose nanocrystal (CNC)

- AFM (atomic force microscope) image shows that CNCs are **highly crystalline**, rigid, **rod-like** nanoparticles (nanowhiskers) with **a high aspect ratio**



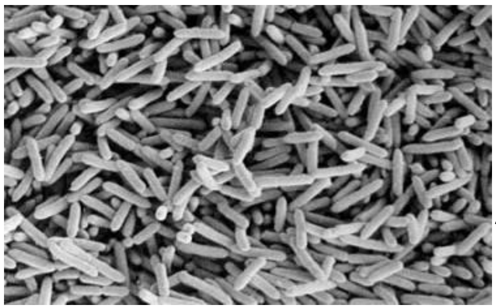




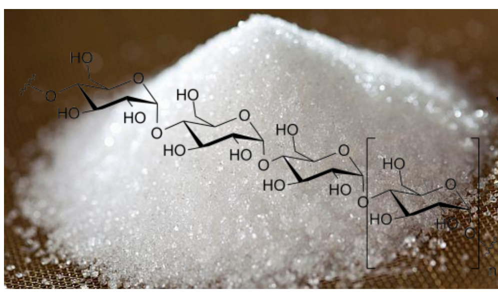
[AFM image by S. Tuukkanen, in 2014 at Nanomicroscopy Center, Aalto University, Espoo, Finland]

Bacterial cellulose films (BC)

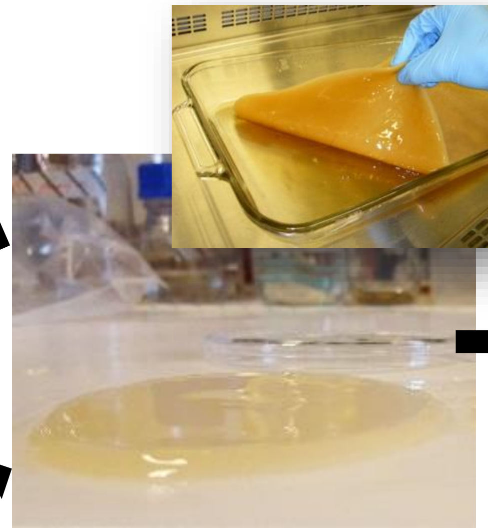
- Certain bacterias can produce high purity nanocellulose films that are robust and flexible



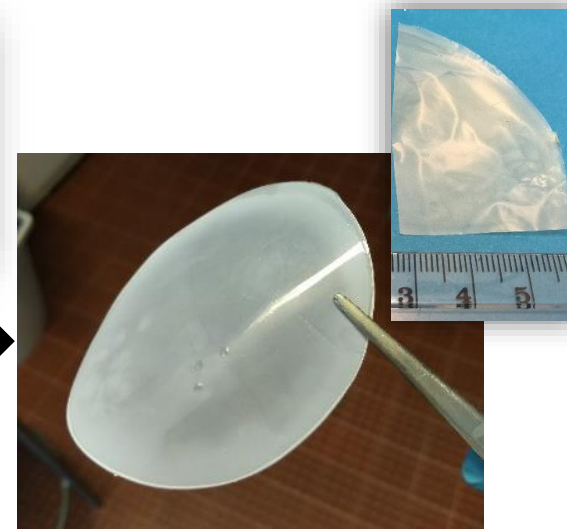
Komagataeibacter xylinus bacterias



Polysaccarides



Bacterial cellulose sheets



Dried bacterial cellulose films

[R. Mangayil, S. Rajala, A. Pammo, E. Sarlin, J. Luo, V. Santala, M. Karp, and S. Tuukkanen, “Engineering and Characterization of Bacterial Nanocellulose Films as Low Cost and Flexible Sensor Material”, *ACS Applied Materials & Interfaces* **9**(22) (2017) 19048]

ADVANTAGES AND APPLICATIONS OF NANOCELLULOSE

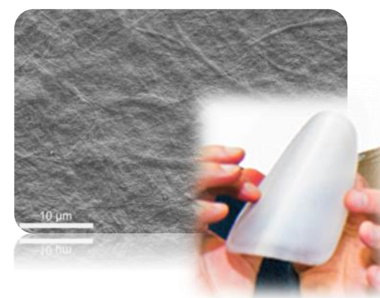
Advantages of nanocellulose

Unique properties of nanocellulose

Manufactured from renewable raw materials
Environmental-friendly biomaterial
Biodegradable
Biocompatible
Strong and elastic networks
High aspect ratio
Large specific surface area
Reactive and chemically modifiable
Good water uptake and up-hold, controlled release (hydroscopic material)
Film formation
Good thermal stability








Applications of nanocellulose

Applications of nanocellulose

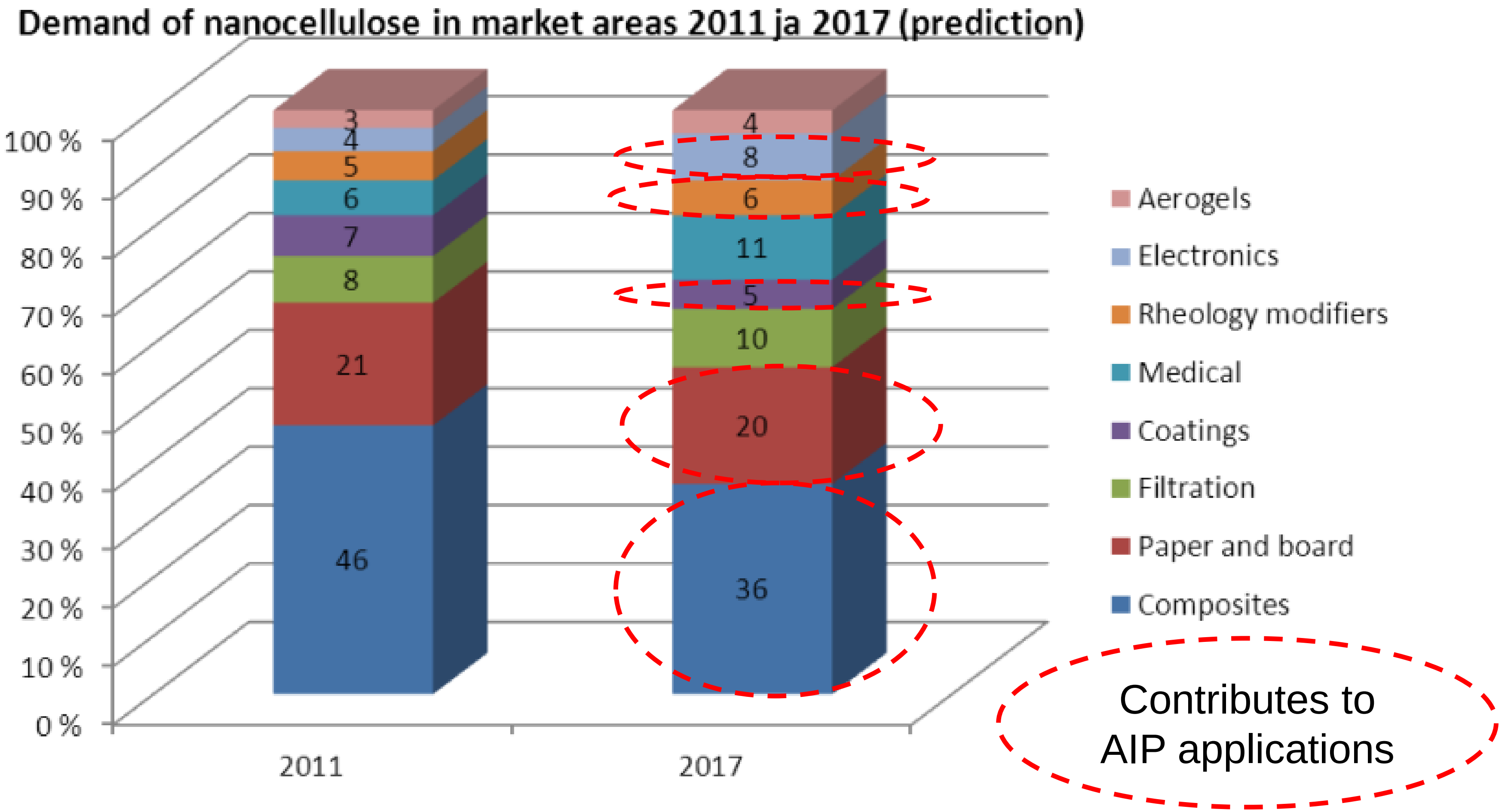
Strong fiber networks (e.g. paper and board)
Strong and light composites (e.g. construction, packages)
Porous materials (aerogels/hydrogels for e.g. tissue scaffolds)
Smooth & transparent films (e.g. barriers, substrates)
Hydroscopic applications (water up-take, hold-up and controlled release)
Rheology modifier (e.g. paints)
Functional surfaces, additives and coatings

Nanocellulose in packaging

- Barrier materials
  - Good grease and oxygen barrier properties
  - Sensitive to moisture – hydrophobization
- Stronger & light-weight packages
  - Robust paperboards with a small nanocellulose filler amount
- Green & disposable piezoelectric sensors
  - A new approach to AIP! Replacing silicon-based intelligence.
  - Nanocellulose as a novel piezoelectric sensor material (discussed below!)

Enabling all-cellulose-based packaging…
One-concept recyclable & disposable packages

Market share



[Source: Nanocellulose, “A technology market study”, Future Markets, Inc. 2012]

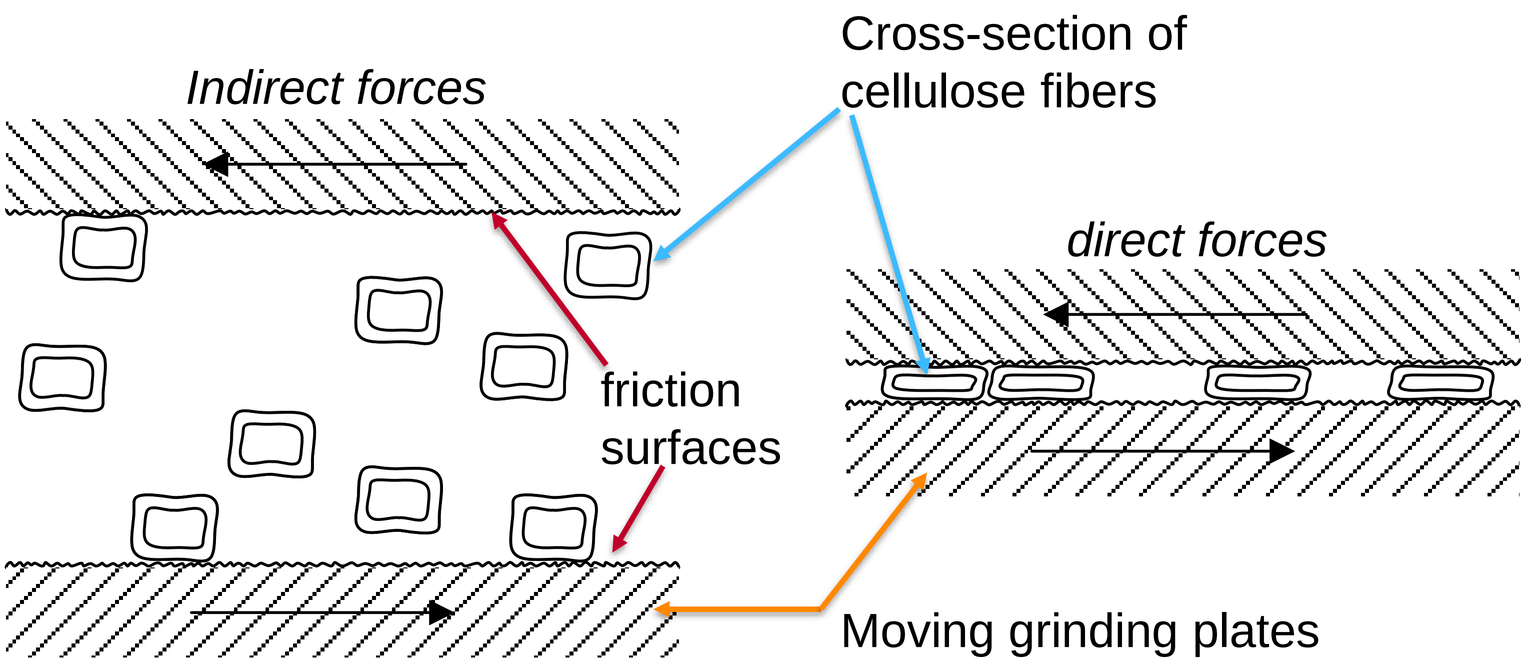
FABRICATION OF NANOCELLULOSE USING A NOVEL MECHANICAL FIBRILLATION METHOD

Challenges of fibrillation

- Ideal mechanical disintegration of fibers (opening of shells) is a challenge
  - Relatively high specific energy consumption (SEC)
  - Low production efficiency
  - Limits the nanocellulose production rate
  - Yields to high costs of micro/nanofibrillated cellulose!
- Lateral dimensions range of nanofibril aggregates between 10 and 30 nm or more
  - Mechanical fibrillation tools (grinding plates etc.) should have dimensions same size-scale to obtain effective disintegration intensity!

Indirect vs. direct forces

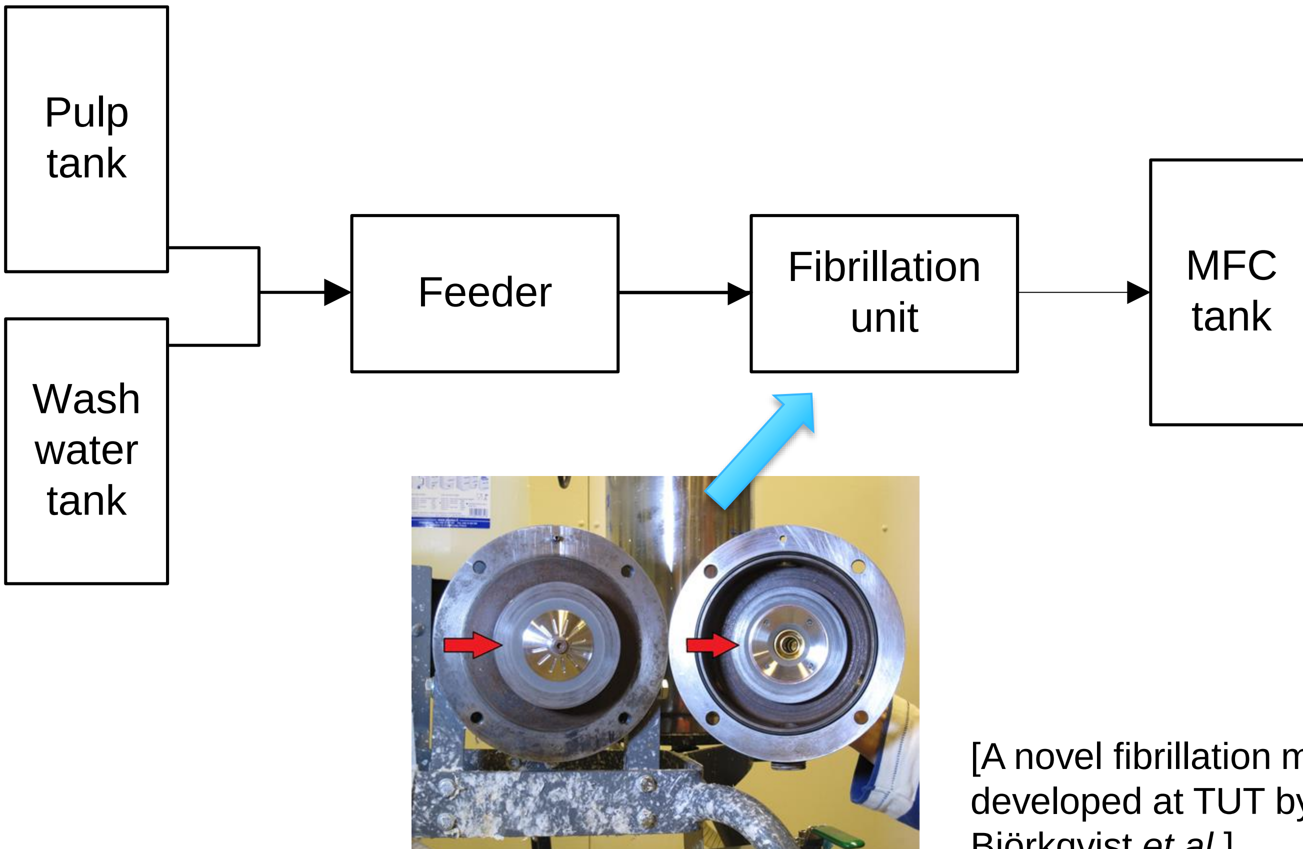
- Bringing mechanical grinding plates close to each other increases the fibrillation efficiency!



Process design goals

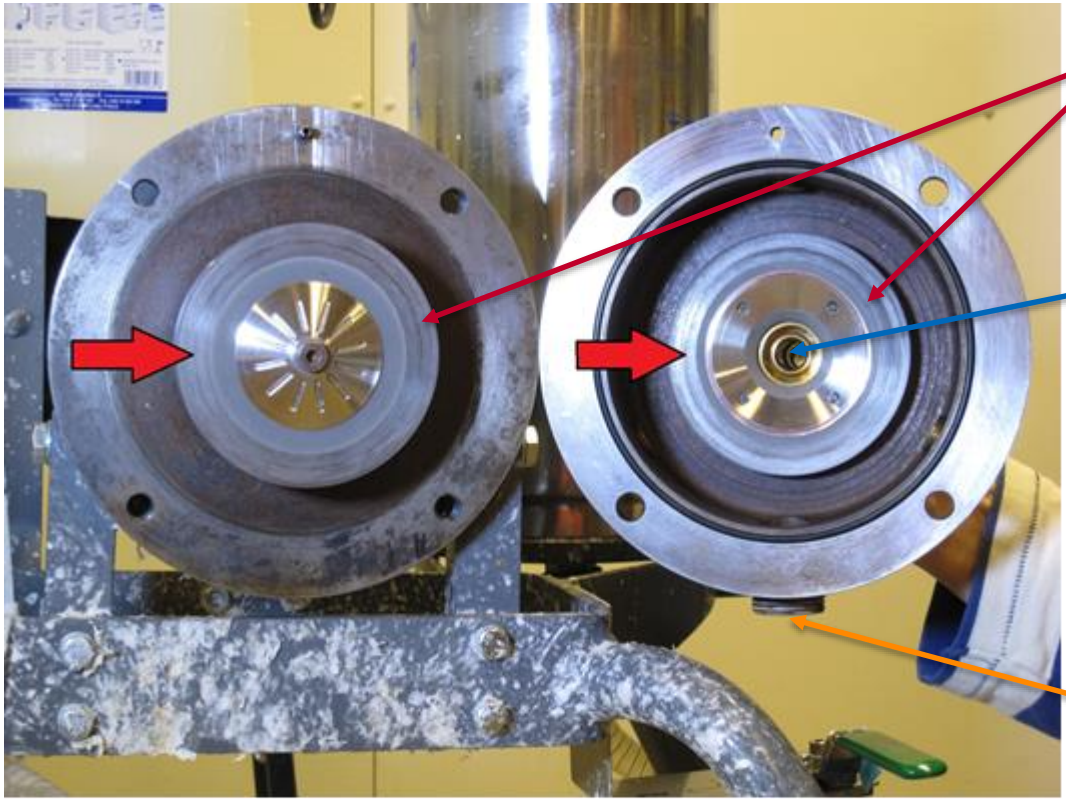
- Challenge of fibrillation of cellulose fibers:
  - A very narrow gap between friction surfaces (grinding plates) moving at high opposite velocity
  - Must prevent a direct contact between the fibrillation surfaces
- Requirements for fibrillation system:
  - Perfectly plane friction surfaces and in-line rotating machinery
  - Microscopic structure of the friction surface in the same order as the fiber diameter
  - Fibrillation gap clearance control

Process flow in fibrillator tool



[A novel fibrillation method developed at TUT by Tomas Björkqvist *et al*.]

Fibrillation tool surfaces



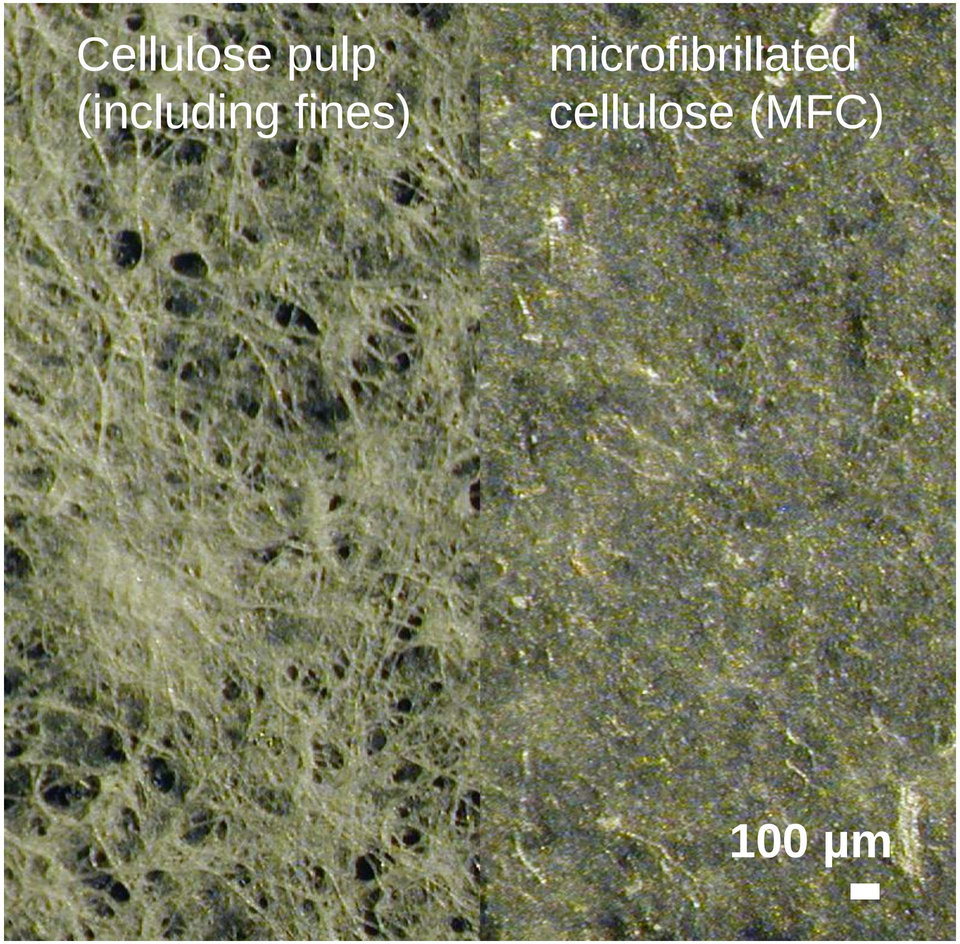
[A novel fibrillation method developed at TUT by Tomas Björkqvist *et al*.]

Fibrillation in action

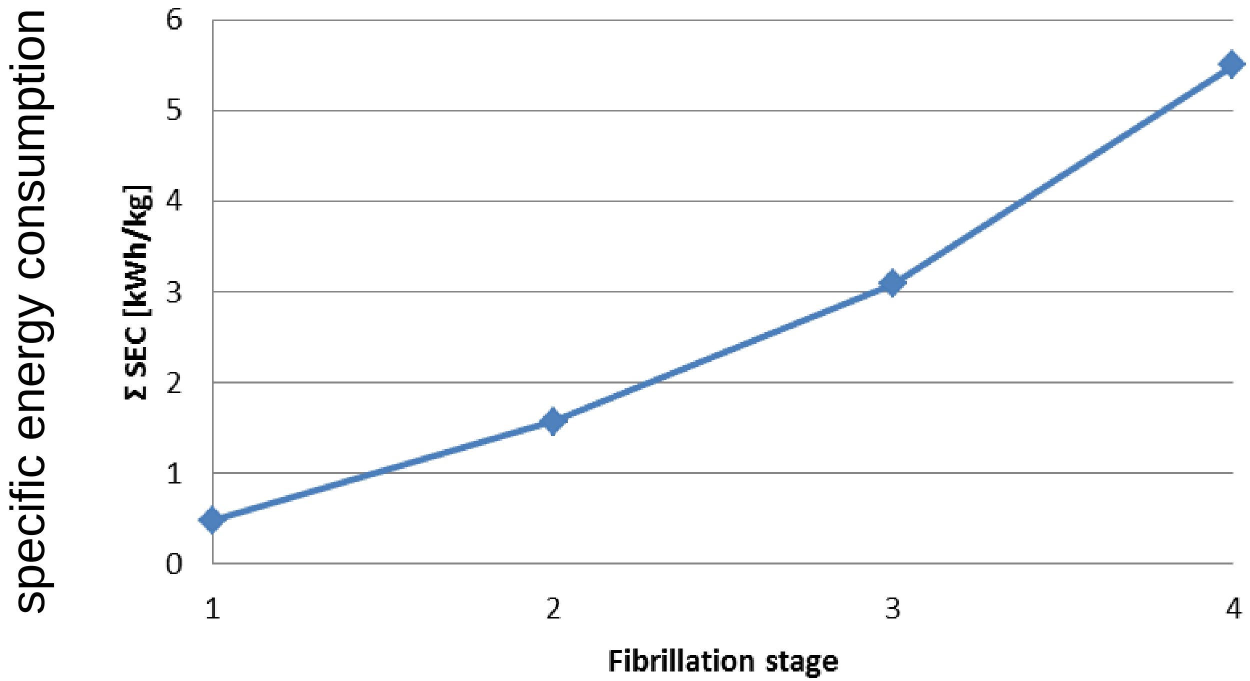
[Video by Tomas Björkqvist, TUT]

Microfibrillated pulp on a tea spoon at 2.0% consistency

Microscope photo of initial and fibrillated dried pulp



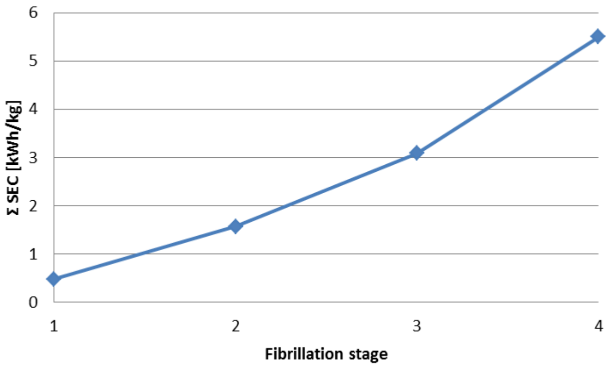
Cumulative specific energy consumption in fibrillation

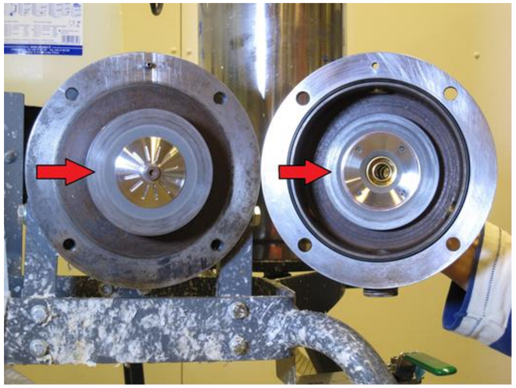


- In comparison, conventional mechanical fibrillation method (Masuko) uses ~20 kWh/kg (vs. ~5.5 kWh/kg in this method)

Advantages of developed fibrillation method

- MFC/NFC at relatively low SEC
  - Lower cost, green production
- Stable process
  - Innovative control strategy
- Enable on-site production
  - No need of “transporting water”
- Chemical free production
  - No harmful residues e.g. for environment (package disposal) or cells (biomedical applications)

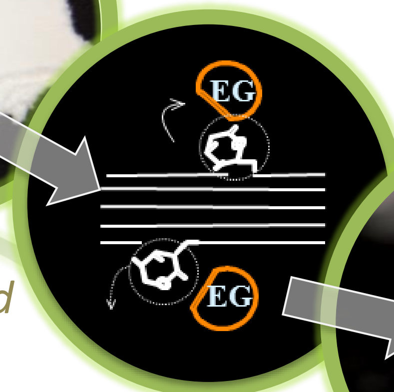




OXYGEN BARRIER PROPERTIES OF CELLULOSE AND MFC FILMS

Wood-cellulose films – Biocelsol-method

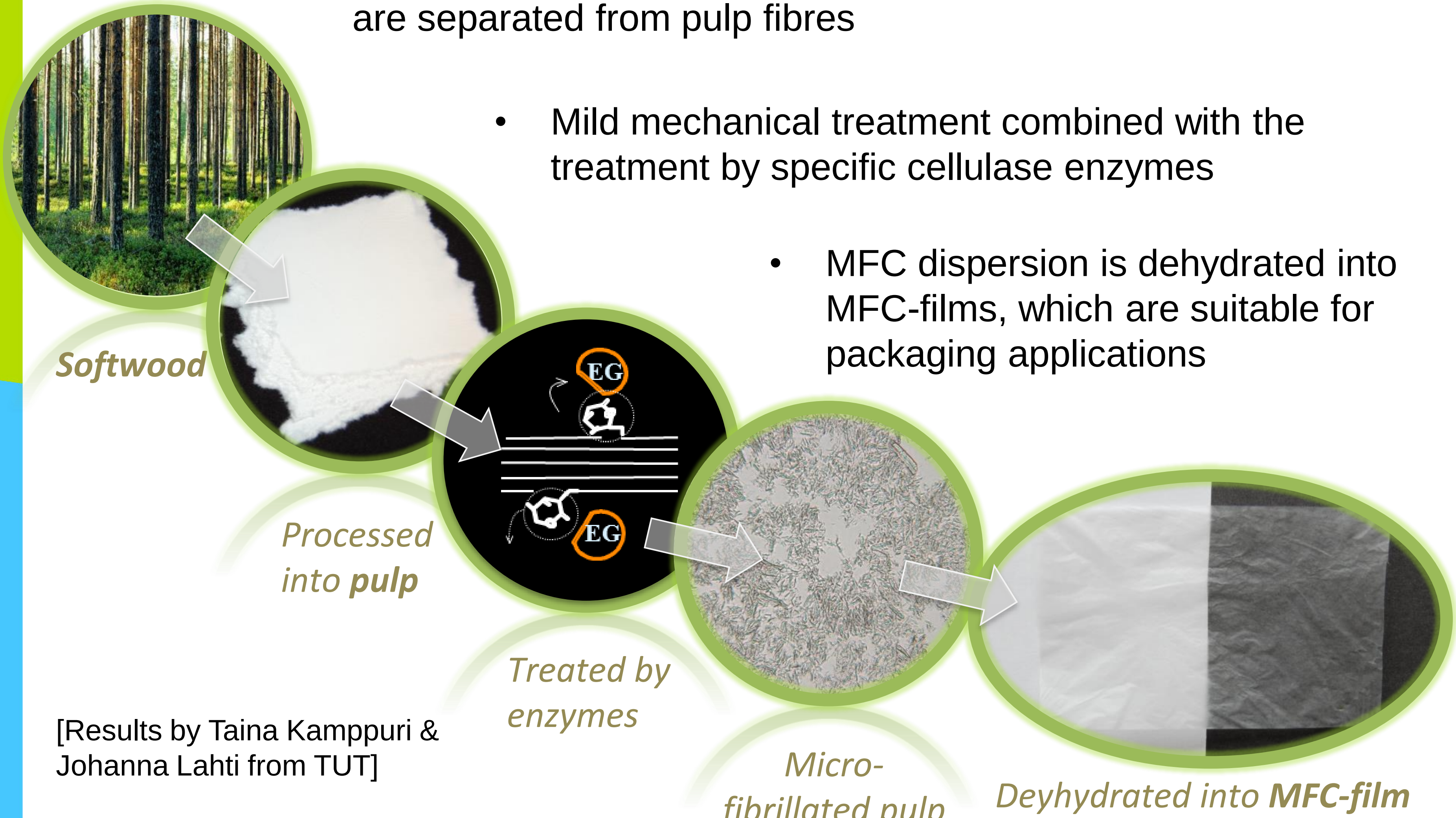
- **Biocelsol-process is an enzyme-catalysed water-based cellulose dissolution method without any hazardous chemicals.**
  - Dissolving pulp is pre-treated with cellulose-specific enzymes
    - Pre-treated cellulose is dissolved into aqueous alkaline solvent
      - Films are coagulated in acidic coagulation bath



[Results by Taina Kamppuri & Johanna Lahti from TUT]

Wood-cellulose films – MFC-films

- After mechanical fibrillation, the microfibrils are separated from pulp fibres
- Mild mechanical treatment combined with the treatment by specific cellulase enzymes
- MFC dispersion is dehydrated into MFC-films, which are suitable for packaging applications



[Results by Taina Kamppuri & Johanna Lahti from TUT]

Oxygen permeability of the different films

Sample	Thickness, µm	OTR*, ml m^{-2} day^{-1}	Reference
Cellulose	**32 ± 2**	**8***	**This work**
Cellulose	**32 ± 2**	**1****	**This work**
MFC	**58 ± 6**	**3****	**This work**
Cellophane	21	3	a
MFC	21	17	b
Polyester	25	50 – 130	c
EVOH	25	3 – 5	c
Polyethylene LD	25	7800	c
Polyethylene HD	25	2600	c

***Oxygen Transmission Rate**

Measurement conditions: *23°C / 50% RH / 10% O_2
** 23°C / 0% RH / 100% O_2

References:

a) Kjellgren and Engström (2006) Influence of base paper on the barrier properties of chitosan-coated paper. Nordic Pulp Pap Res J 21(5):685–689.

b) Syverud and Stenius (2009) Strength and barrier properties of MFC films. Cellulose 16:75-85. DOI 10.1007/s10570-008-9244-2

c) Parry (1993) Principles and applications of modified atmosphere packaging of foods. Chapman & Hall, Suffolk

[Results by Taina Kamppuri & Johanna Lahti from TUT]

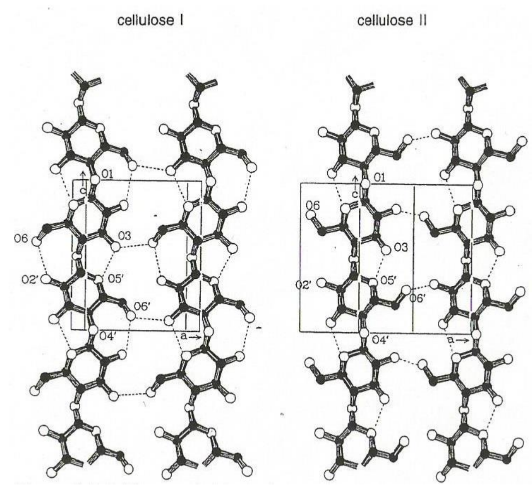
PIEZOELECTRIC SENSORS FROM CNF AND BC FILMS

Origin of piezoelectricity

- **Piezoelectric effect** = Electric charge separation by applied mechanical force
- Piezoelectricity is a fundamental property of cellulose

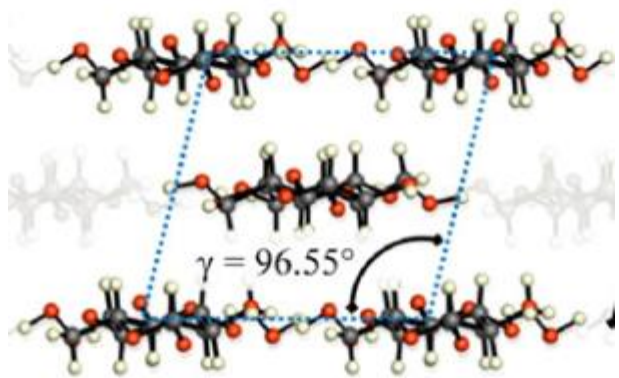
  [E. Fukada, *J. Phys. Soc. Japan* (1955)]

- **Piezoelectricity is arising from a crystal structure lacking center symmetry**
  - At a molecular scale all carbon centers are chiral, but...
  - At a crystal unit cell scale crystals are non-centrosymmetric



Klemm et al.(1998) *Comprehensive Cellulose Chemistry.* Weinheim: Wiley-VCH.

Cellulose crystal [[$C_6H_{10}O_5$]$_n$] unit cell:



Piezoelectric matrix for cellulose

- The piezoelectric tensor d_{mn} is determined by the symmetry of a crystal lattice

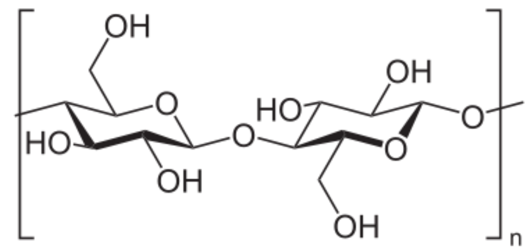
  [E. Fukada, *J. Phys. Soc. Japan* (1955)]

- The monoclinic C2 symmetry and the cancellation effects result into **piezoelectric coefficient matrix**:

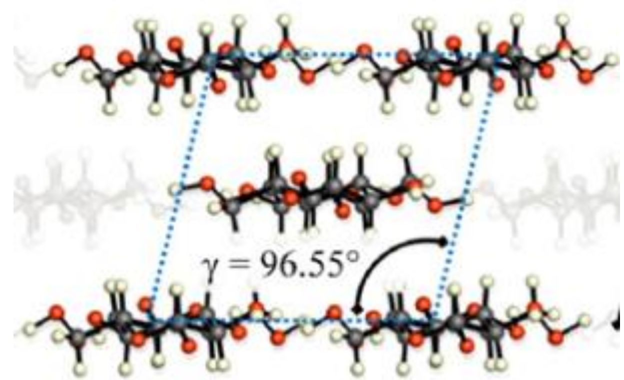
$$d_{mn} = \begin{pmatrix} 0 & 0 & 0 & d_{14} & 0 & 0 \\ 0 & 0 & 0 & 0 & d_{25} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix}$$

where $d_{14} = -d_{25}$

Chemical structure of cellulose:



Cellulose crystal $[[C_6H_{10}O_5]_n]$ unit cell:

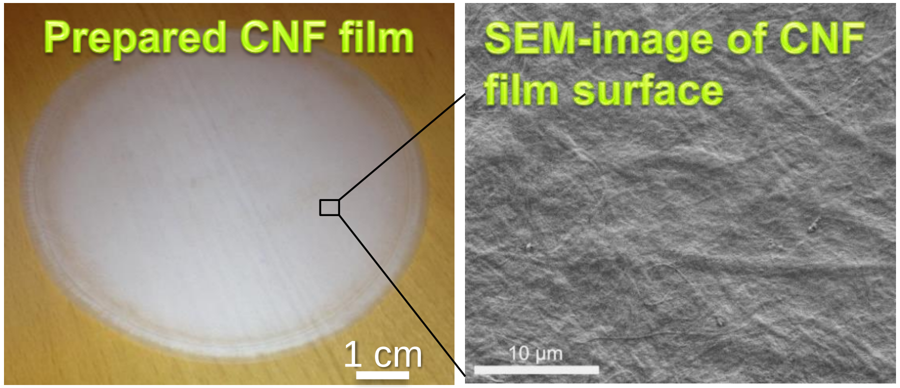


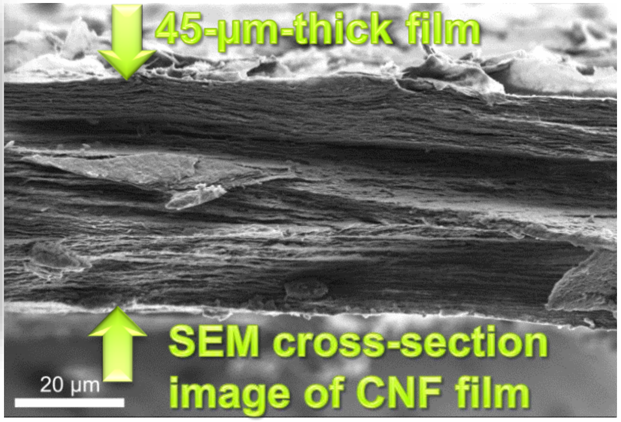
[Zuluaga et al. (2013)]

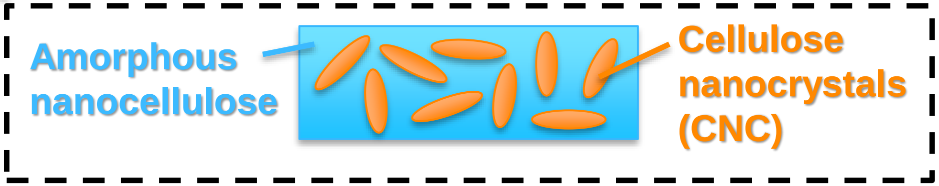
CNF-film fabrication

- Aqueous dispersion of CNF material (bleached birch cellulose mass) produced by a mechanical homogenizing process (6 passes through a **microfibrillator**)
- CNF film was prepared by pressure **filtering**, followed by pressing and drying in **hot-press** (2 h @ 100 C), resulting a **bendable CNF film** containing amorphous areas and non-aligned CNC crystals areas

[S. Rajala, T. Siponkoski, E. Sarlin, M. Mettänen, M. Vuoriluoto, A. Pammo, J. Juuti, O. J. Rojas, S. Franssila, and S. Tuukkanen, “Cellulose nanofibril film as a piezoelectric sensor material, *ACS Appl. Mater. Interfaces* **8**(24) (2016) 15607]

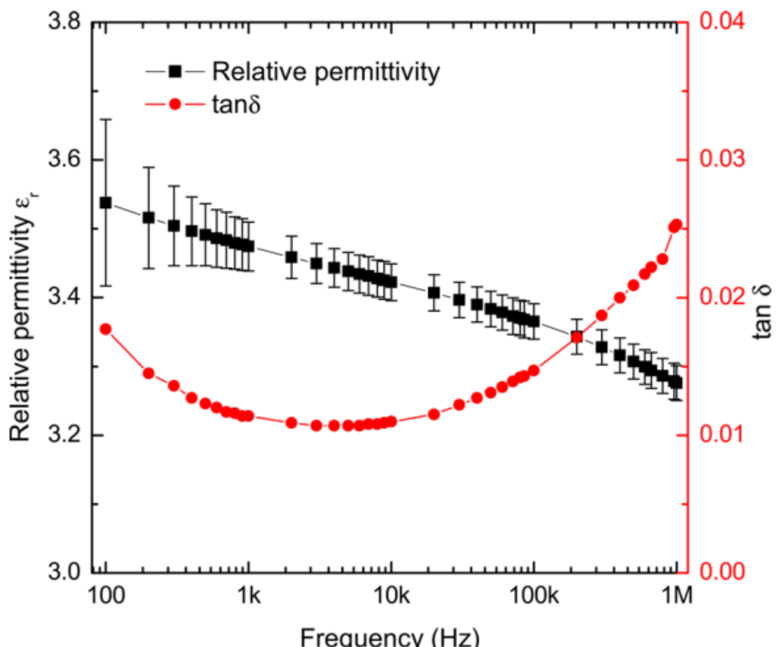


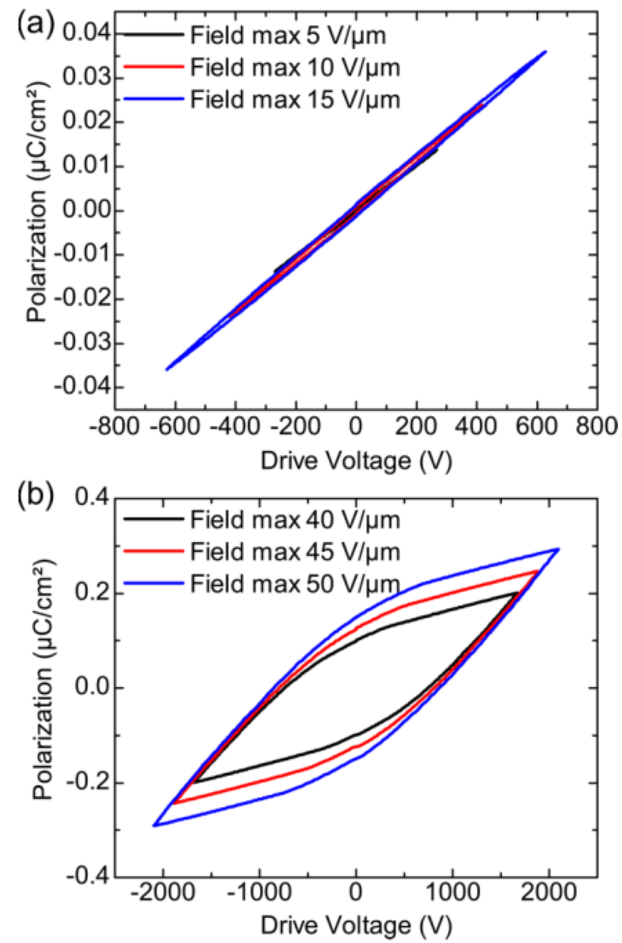




Permittivity and hysteresis

- Relative permittivity and loss tangent were similar to **typical dielectric polymers**
- Polarization-voltage hysteresis curves for CNF film showed has **<u>some level of ferroelectric properties</u>** <u>at high electric fields</u>



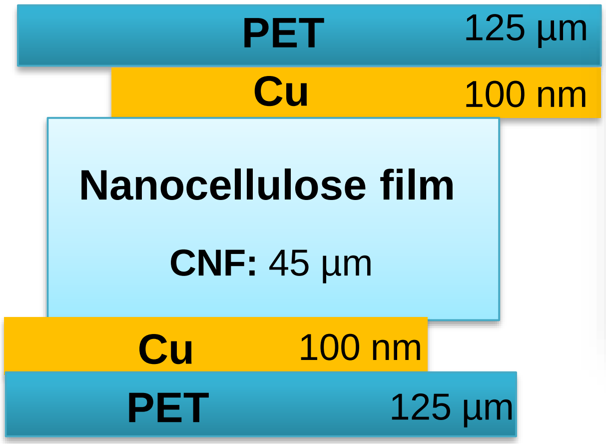


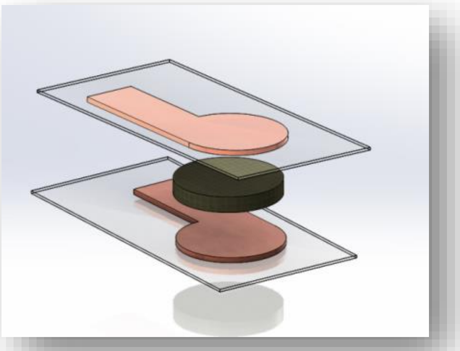
[S. Rajala *et al*, ACS Applied Materials and Interfaces (2016)]

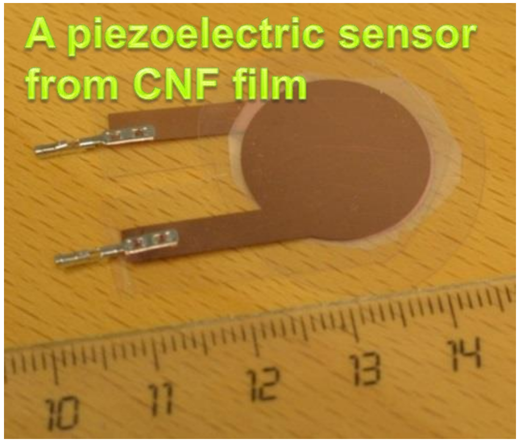
CNF-film sensor assembly

- For piezoelectric sensitivity measurements, five nominally identical CNF-film sensors were assembled
  - CNF films assembled between two evaporated copper electrodes on polyethylene terephthalate (PET) substrate using adhesive film
  - Crimp connectors (Nicomatic Crimpflex) were used for getting a reliable contacts to the copper electrode on flexible PET substrate

Sensor structure side-view and 3D illustration





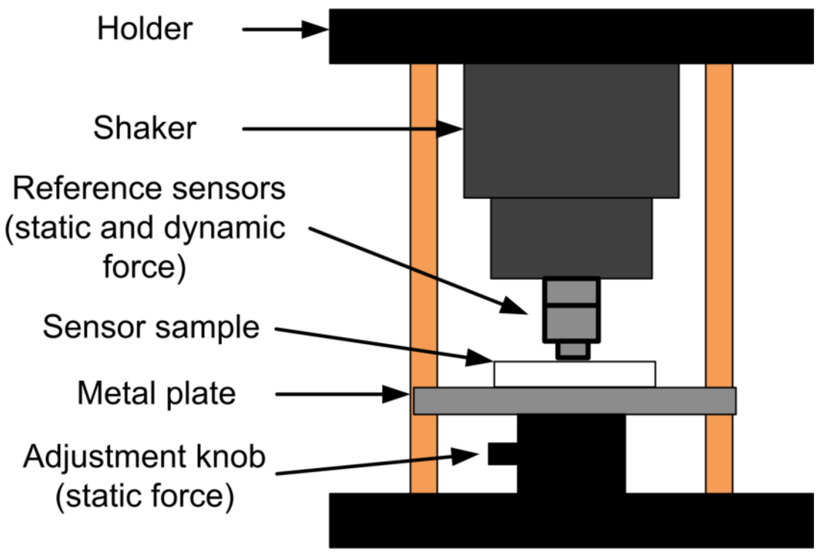


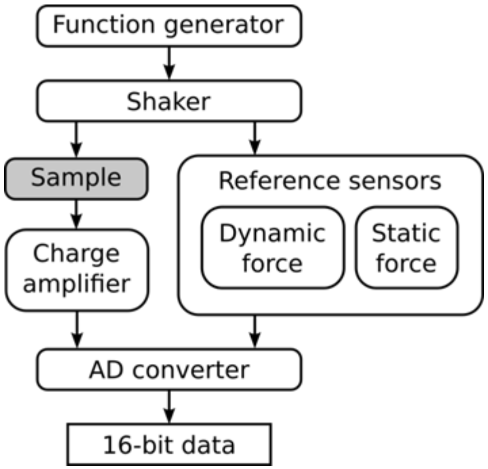
[S. Rajala *et al*, ACS Applied Materials and Interfaces (2016)]

Measurement setup

- **Mini-Shaker** (Brüel & Kjaer type 4810) used for sensitivity measurements
- **Reference sensors** for dynamic and static forces (normal direction)
- **Charge amplifier** for measuring the produced charge
- DUT (device-under-test) placed horizontally on the metal plate
- The **sensor sensitivity** measure here is closely related to **transverse piezoelectric coefficient d_{33}** (from piezoelectric tensor)

Piezoelectric sensitivity measurement setup





[For details see: S. Tuukkanen *et al.*, Synthetic Metals (2012) or IEEE Sensors (2015)]

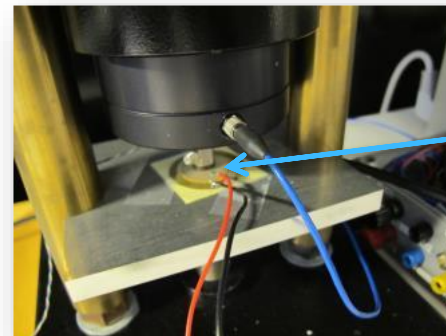
Sensitivity measurements

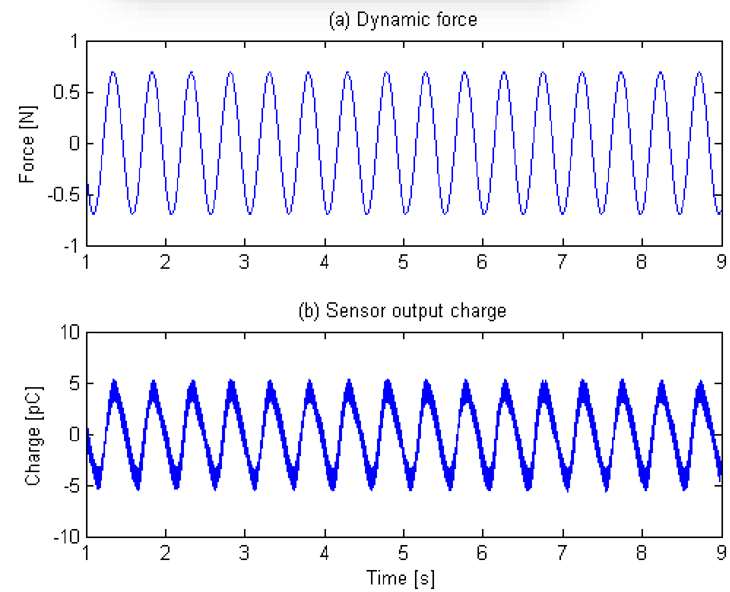
- **Static force of ~3 N** was used to keep sample steady
- Excitation with **2 Hz sinusoidal** input signal of 1 V (peak to peak) results in a **dynamic force of ~1.3 N**
- Excitation by applying the force in the middle of the sensor; measurement repeated 3-9 times from both sides, resulting in a total of **6-18 excitations per sensor**
- The sensor sensitivity by dividing the generated charge by the dynamic force

$$Sensitivity = \frac{Q_{sensor}}{F_{dynamic}}$$

- The unit of sensitivity is **pC/N**

Sensor in the shaker setup





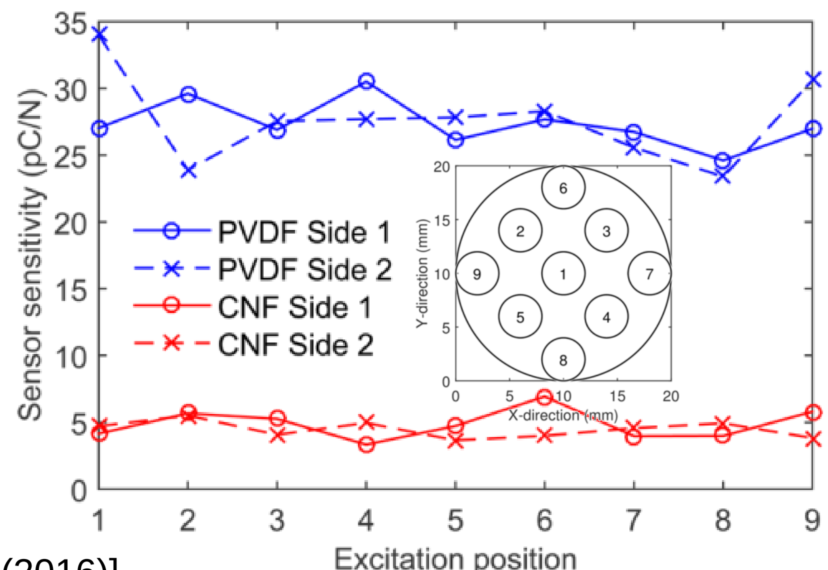
Piezoelectric sensitivity results

- **Mean piezoelectric sensitivity ± standard deviation** for excitations from each side of the CNF-sensors.

- Sensitivity from **different excitation positions** for the CNF sensor and a polyvinylidene fluoride (PVDF) reference sensor shows only small variations.
- The **average sensitivity for the CNF-film sensor was 4.7 pC/N**, while for the reference PVDF sensor was 27.5 pC/N.

Table 1. Average Force Sensitivities for Each Sensor Side

sensor name	electrode diameter (mm)	sensitivity (pC/N), side 1	sensitivity (pC/N), side 2	sensitivity (pC/N), average
S1	15	4.7 ± 1.1	5.8 ± 1.6	5.3 ± 1.4
S2	15	5.9 ± 0.9	4.5 ± 0.5	5.2 ± 1.0
S3	15	4.6 ± 0.4	7.4 ± 1.6	6.0 ± 1.9
S4	15	6.1 ± 1.3	6.7 ± 1.2	6.5 ± 1.3
S5	20	4.9 ± 1.1	4.5 ± 0.6	4.7 ± 0.9



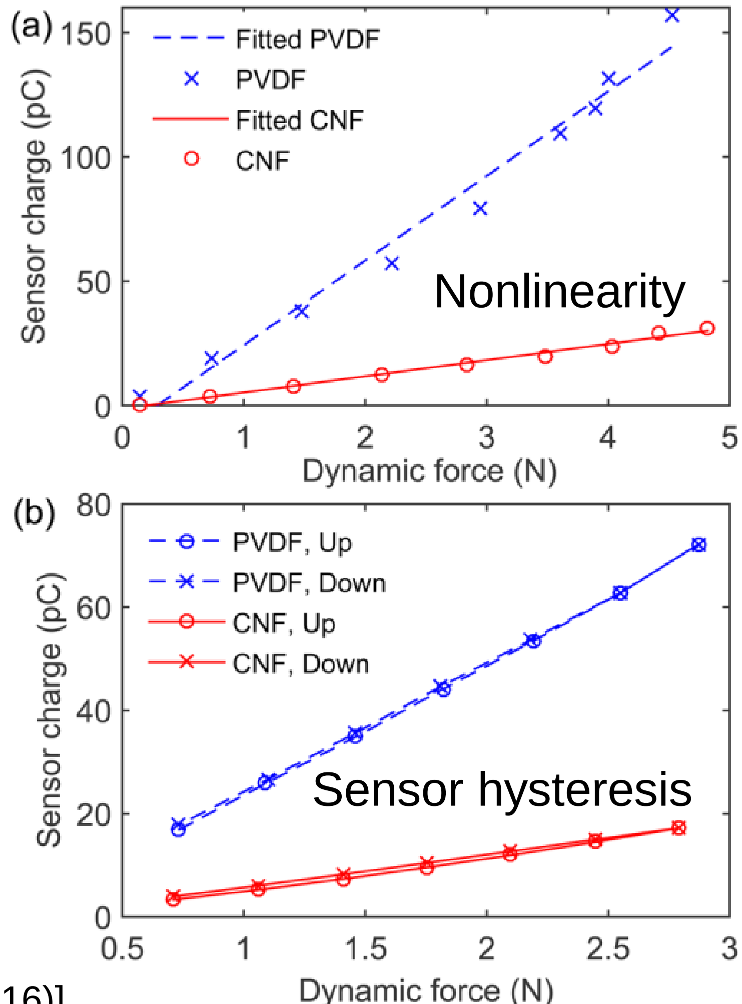
[S. Rajala *et al*, ACS Applied Materials and Interfaces (2016)]

Sensor linearity and hysteresis

- Plots show (a) nonlinearity and (b) hysteresis curves for the CNF and the PVDF reference sensor

- **Nonlinearity** (charge vs. force curve by fitting a first degree polynomial via least-squares minimization) was found to be (0.86 ± 0.48) pC for CNF and (6.47 ± 3.76) pC for PVDF

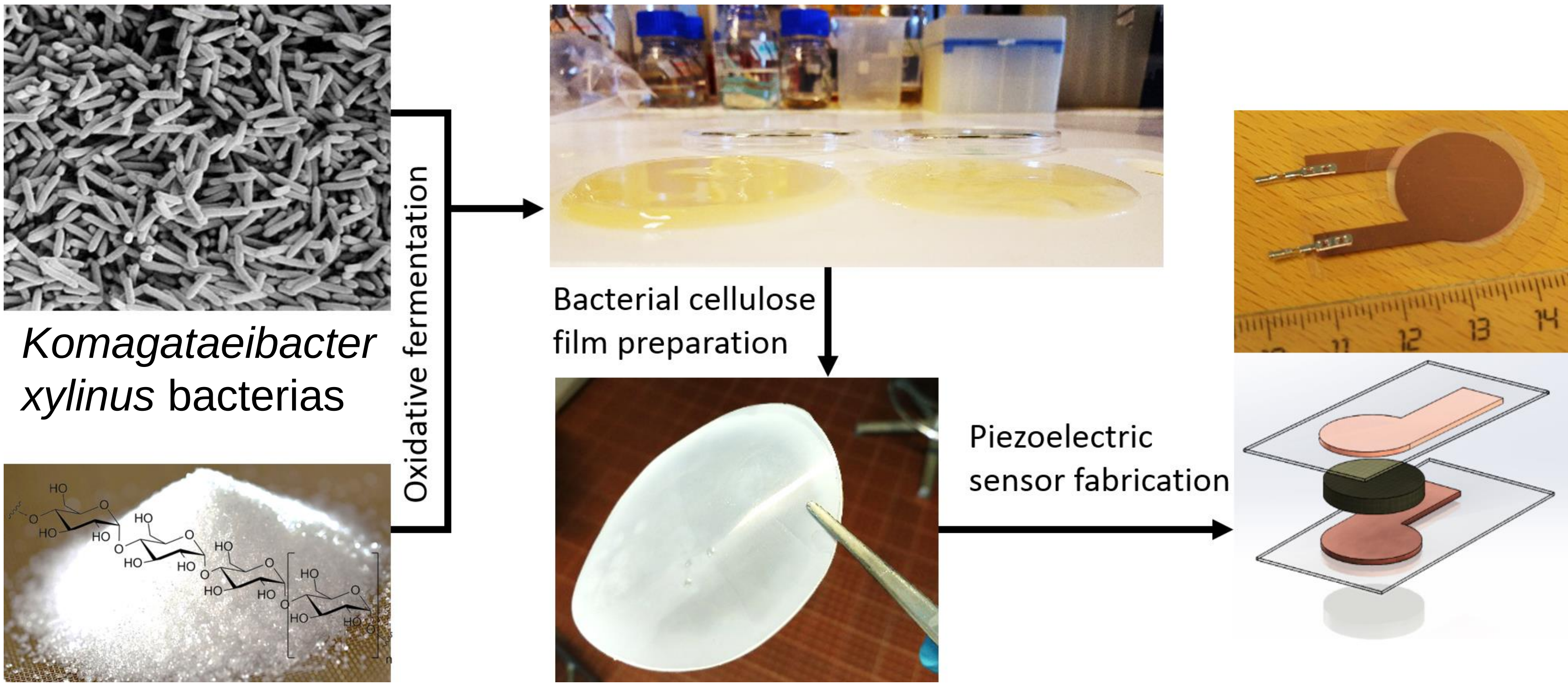
- **Sensor hysteresis** (with increasing vs. descreasing force) was **below 1 pC** in maximum for both sensors



[S. Rajala *et al*, ACS Applied Materials and Interfaces (2016)]

Piezoelectricity of bacterial cellulose films

- Freestanding BC-films were fabricated, and sensors were assembled and characterized similarly to CNF-film sensors.

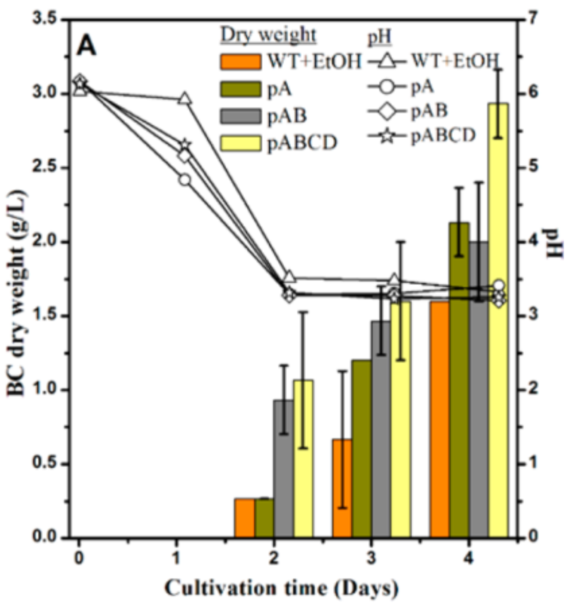


[R. Mangayil, S. Rajala, A. Pammo, E. Sarlin, J. Luo, V. Santala, M. Karp, and S. Tuukkanen, “Engineering and Characterization of Bacterial Nanocellulose Films as Low Cost and Flexible Sensor Material”, *ACS Applied Materials & Interfaces* **9**(22) (2017) 19048]

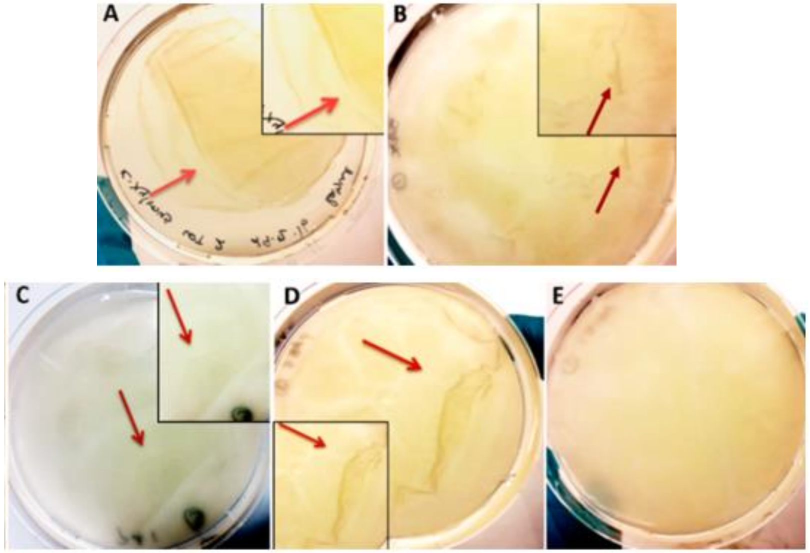
BC film production

- Aiming at improved BC production and tailored crystallinity of BC films, we **engineered *K. xylinus* to overexpress** partial and complete bacterial cellulose synthase operon that encodes activities for **BC production**.
  - Highest observed titer (~test solution content) was obtained with K. xylinus-bcsABCD strain producing 4.3 ± 0.46 g/L BC in 4 days, which is 2−4-fold higher than for wild type K. xylinus.

BC production and the drop in medium pH:



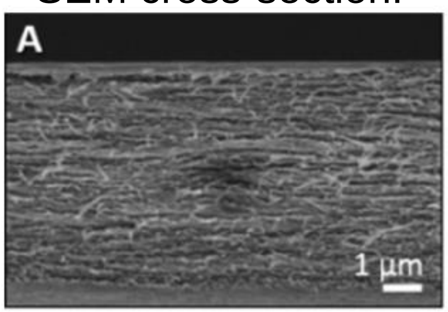
Morphologies of untreated BC pellicles produced by WT and engineered K. xylinus strains in cultivation plates:



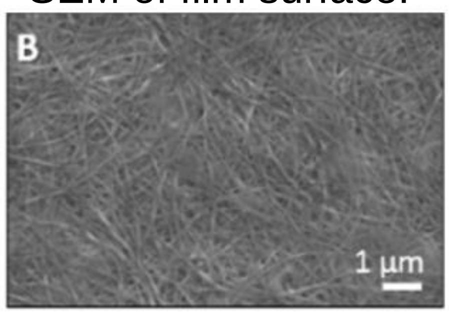
BC film production

- BC-films were analyzed with a stylus profilometer, tensile strength measurement system, scanning electron microscope (SEM), and X-ray diffractometer (XRD).
  - The engineered K. xylinus strains produced **thicker BC films**: Wild type, 5.1 μm, and engineered K. xylinus strains, 6.2−10.2 μm.
  - SEM did not revealed principal difference in the structures of BC-films grown from different bacterial strains.
  - The crystallinity index of all films was high (from 88.6 to 97.5%).

SEM cross-section:



SEM of film surface:



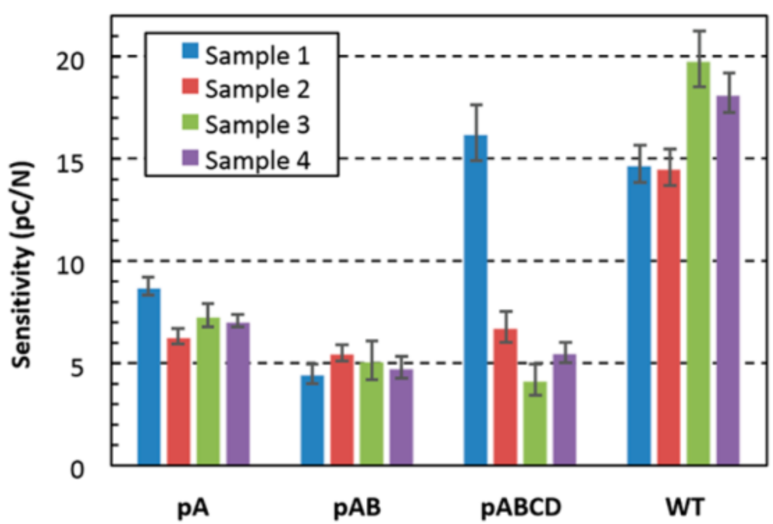
Profilometer, stretching and XRD results:

BC film produced from the tested *K. xylinus* strains	film thickness (μm)	crystallinity index (%)	stress at break (MPa)
WT	4.8 ± 0.8	92 ± 4	47.9
pA	7.4 ± 0.3	97 ± 10	40.7
pAB	6.2 ± 0.3	91 ± 6	80.9
pABCD	10.3 ± 0.6	89 ± 3	48.5

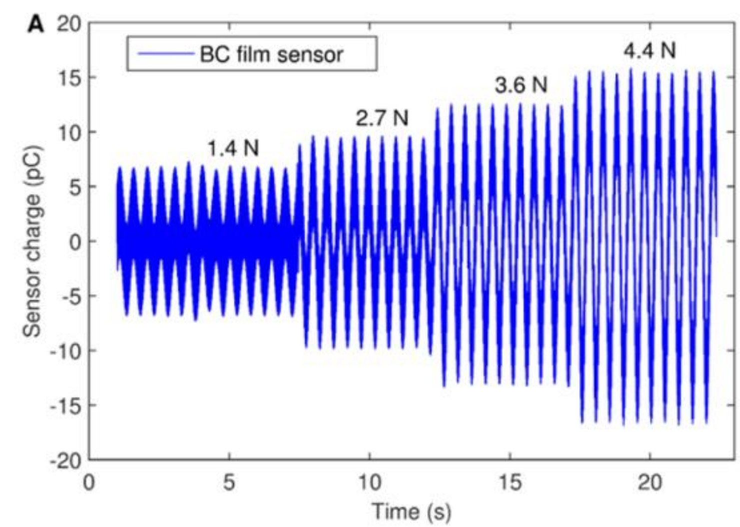
Sensitivity of BC-sensors

- All BC films showed significant piezoelectric response (5.0−20 pC/N), indicating BC as a promising sensor material.
- The alterations in the measured piezoelectric sensitivities for different BC film types cannot be explained by the used characterization methods… → There is room for further research!

Piezoelectric sensitivity
of prepared BC films:



Sensor response under
increased mechanical load:



Summary

- Most common type nanocellulose:
  - Wood-based MFC, CNF and CNC, as well as bacterial cellulose
- Nanocellulose is a renewable, biodegradable, biocompatible, strong, elastic, high surface area, and hydroscopic material
- Energy-efficient mechanical fibrillation method developed at TUT
- Piezoelectric properties of CNF and BC film studies at TUT
- Applications of nanocellulose in Active and Intelligent Packaging:
  - Light-weight mechanical reinforcement material
  - Barrier films for oxygen and moisture
  - Piezoelectric sensor material

Questions & Research interests?
Contact: Sampo.Tuukkanen@tut.fi