

2012 TAPPI INTERNATIONAL CONFERENCE ON

Nanotechnology for Renewable Materials

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From Nanocellulose Science towards Applications

Status up-date from Finland

Presented by:

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VTT – Technical Research

Center of Finland



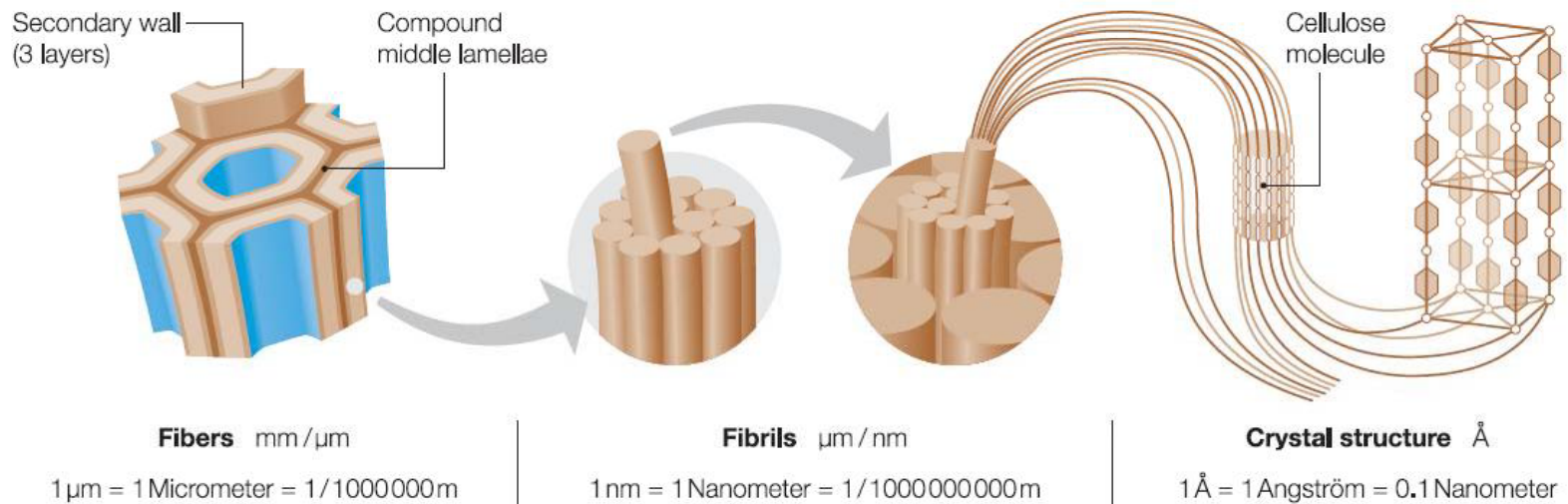
Agenda

- What is Nanocellulose?
- Where is can be used ? – Based on Structure-Properties Relationships
- Towards Applications ? – Based on public research results
- Application studies by Industry
- Standardization

A glass dish containing a white, creamy substance, likely a bio-based material, surrounded by wood shavings. The image is split into two horizontal panels. The top panel shows a close-up of a dollop of the white substance on a wooden surface. The bottom panel shows a glass dish filled with the same substance, with wood shavings scattered around it. A dark green banner with white text is overlaid across the middle of the image.

Nanocellulose research in Finland

A wood-based nanomaterial: nanocellulose



Zimmermann et al. Adv. Eng. Mater. 6 754-761 (2004)

Unique properties

- Mechanical
- Optical
- Surface area

Physical dimensions

- Diameters: $\sim 10\text{-}100\text{nm}$
- Lengths: $\sim 100\ \text{nm}\text{-}100\ \mu\text{m}$
- Different surface functionalities



Nanocelluloses – A Class of Nanomaterials

■ Examples of Raw Materials:

Wood



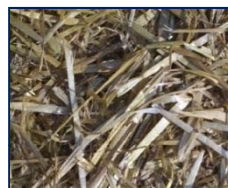
Pulp



Bacteria



Straw



Sugar Beet

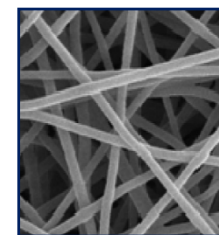
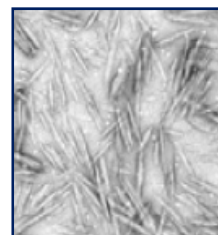
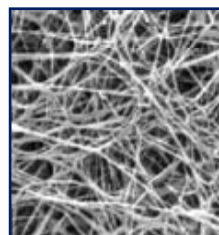
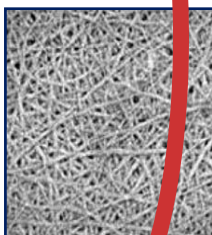


Banana



■ Examples of Production Methods:

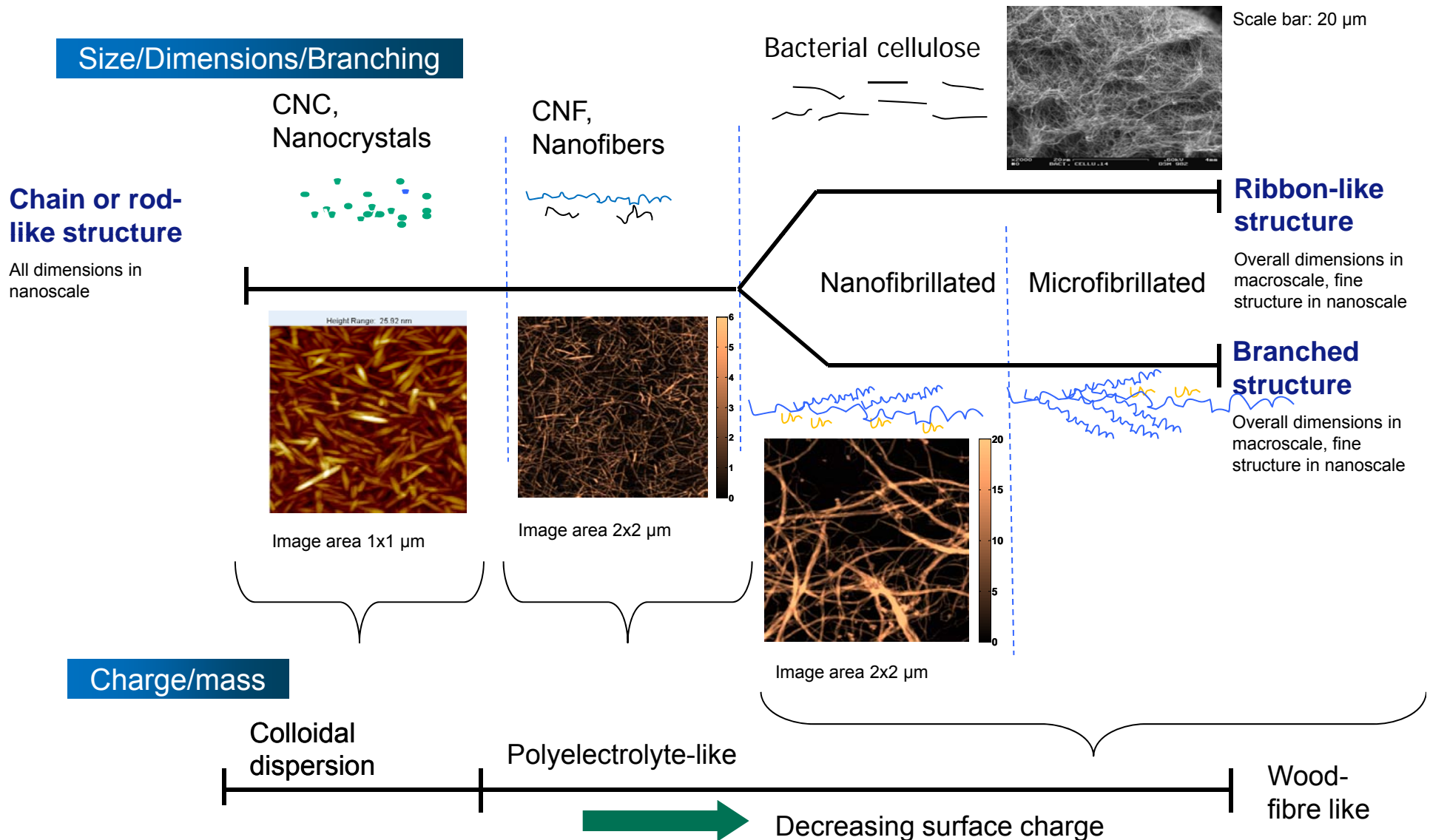
Grinding, Homogenizer, Intensification, Hydrolysis / Electrospinning, Ionic liquids



← Top-Down / Bottom-Up →

Suitable characterization methods depend on fibril type

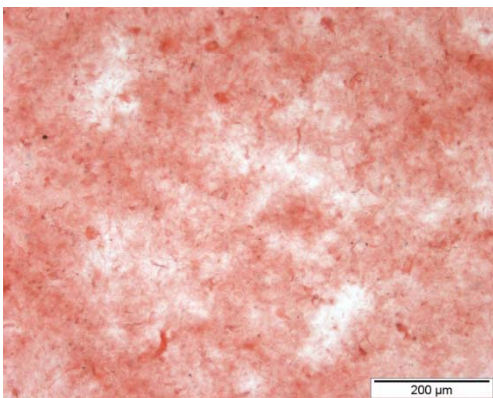
Sneck, A., 2011 TAPPI International Conference on Nanotechnology for Renewable Materials



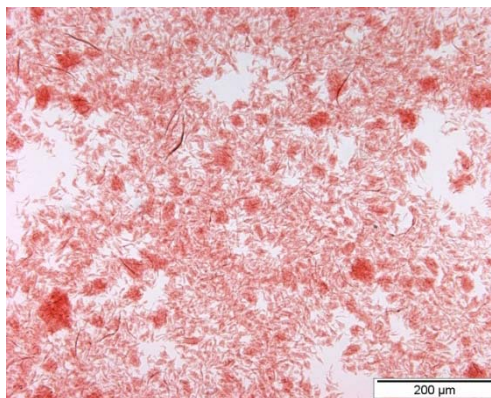
NFC grades vs. commercial MFC

Optical microscope images, macrostructure

Masscolloider



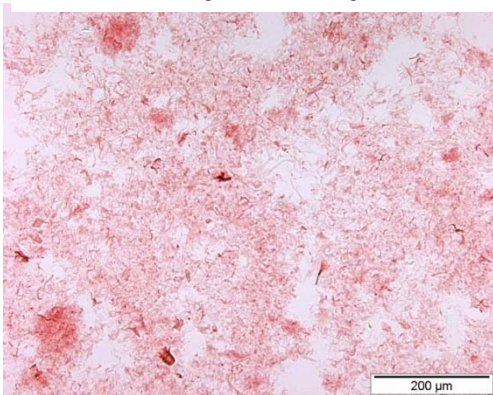
Fluidizer



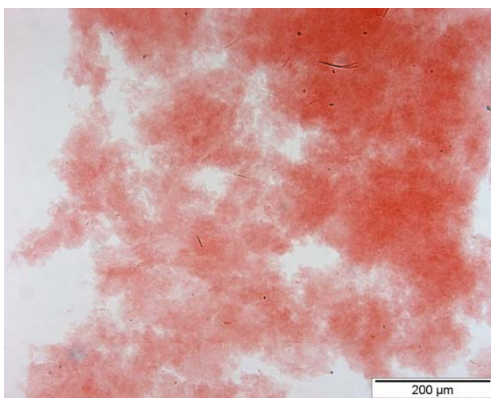
Commercial MFC 1



Carboxymethylation



TEMPO

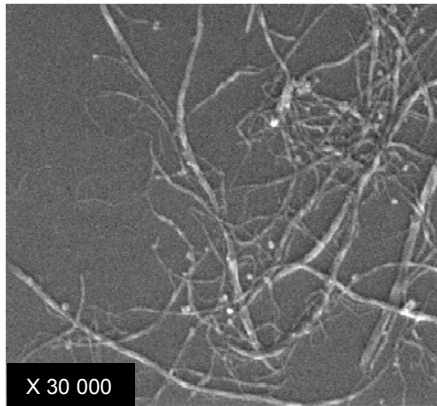


Commercial MFC 2

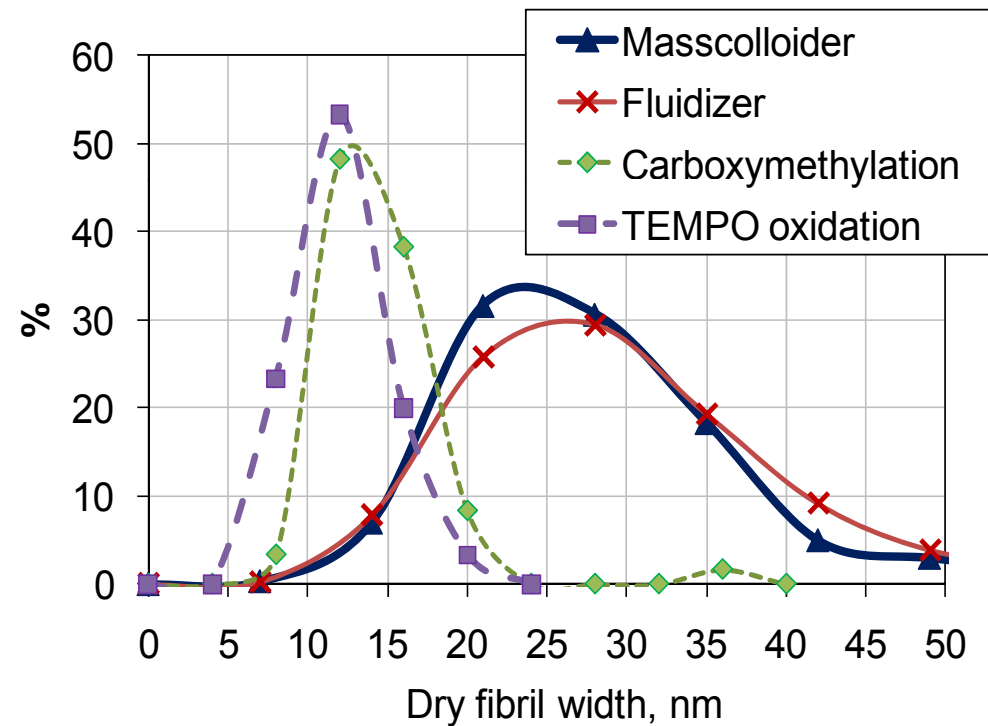
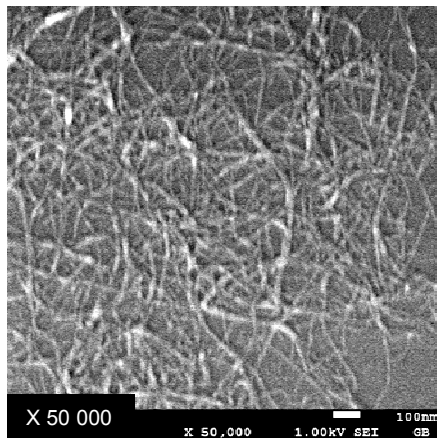


Manual analysis of FE-SEM images: dry fibril width

Fluidizer

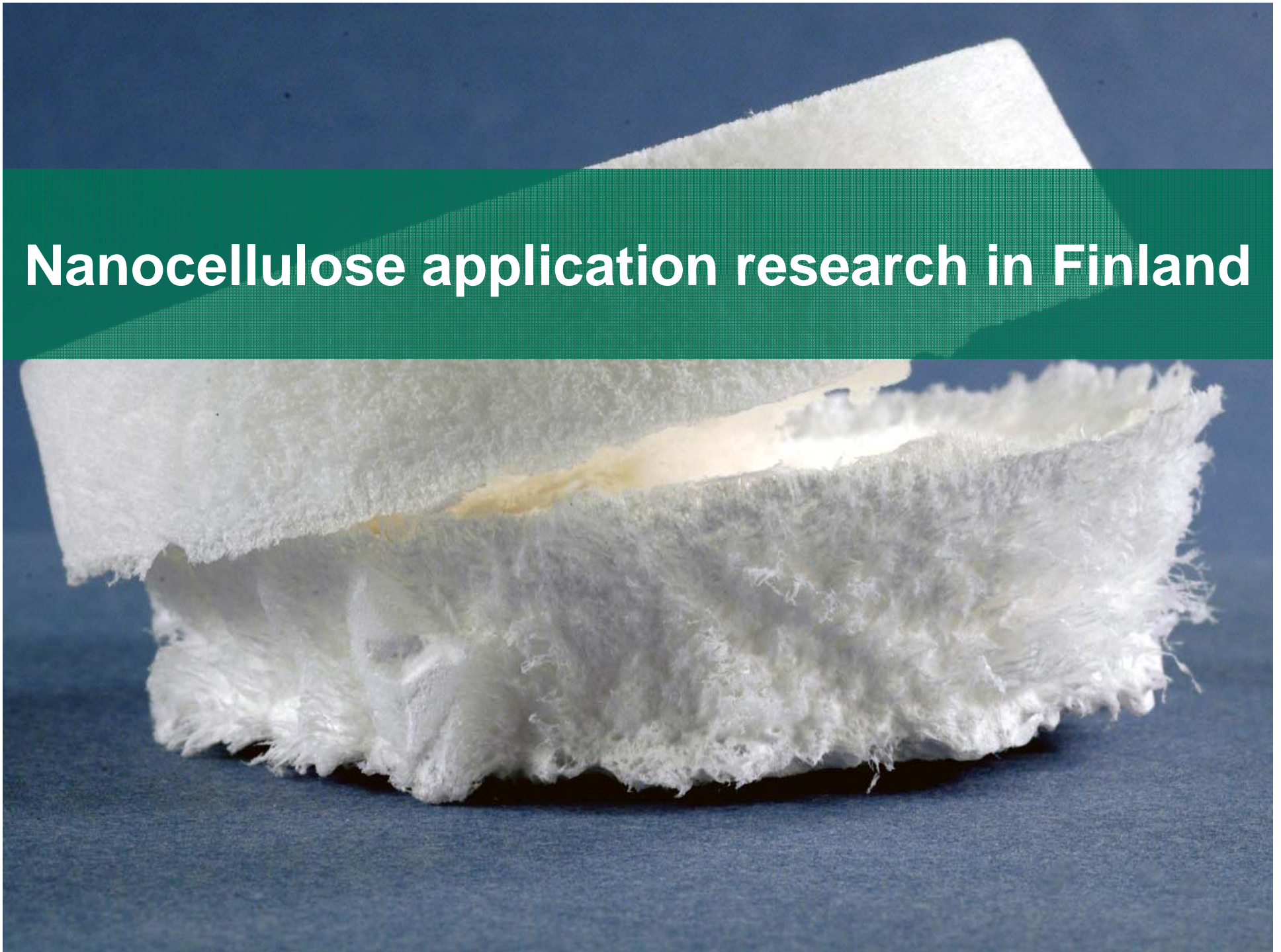


Carboxymethylation



- Similar information than with AFM

Nanocellulose application research in Finland



Potential application areas based on specific advantages of nanocellulose

Properties of nanocellulose

- Natural & renewable
- Biodegradability
- Biocompatibility
- High strength & modulus
- High surface area
- High aspect ratio
- Chemical functionality (e.g. for modification)
- Dimensional stability
- Moisture absorption
- Thermal stability (~200°C)
- Others ...



Potential applications

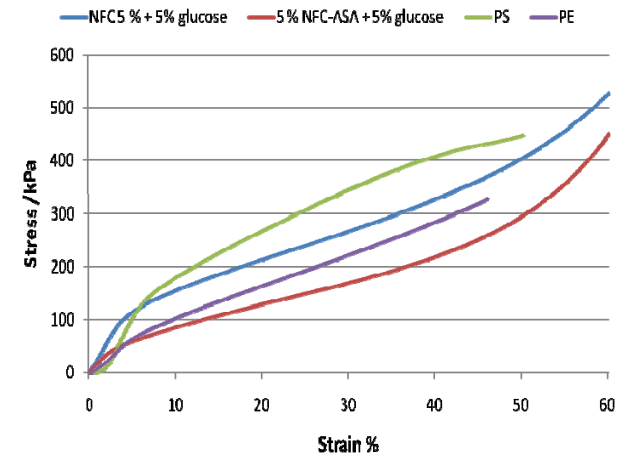
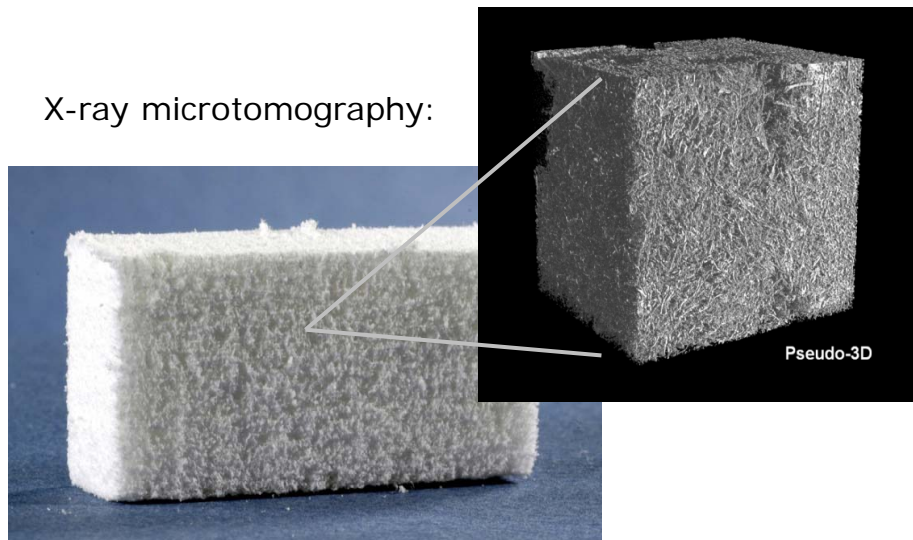
- Composites
- Construction Materials
- Porous Materials
- Fiber Web Structures (e.g. Paper & Board)
- Coatings
- Functional Surfaces
- Functional Additives (e.g. rheological modifiers)
- Others ...

Porous materials & fiber web structures

- **Porous nanocellulosic materials for insulation & packaging**

- Highly porous & strong nanocellulose web structures

(e.g. Svagan *et. al*, *Advanced Materials*, 1263-1269 (2008))

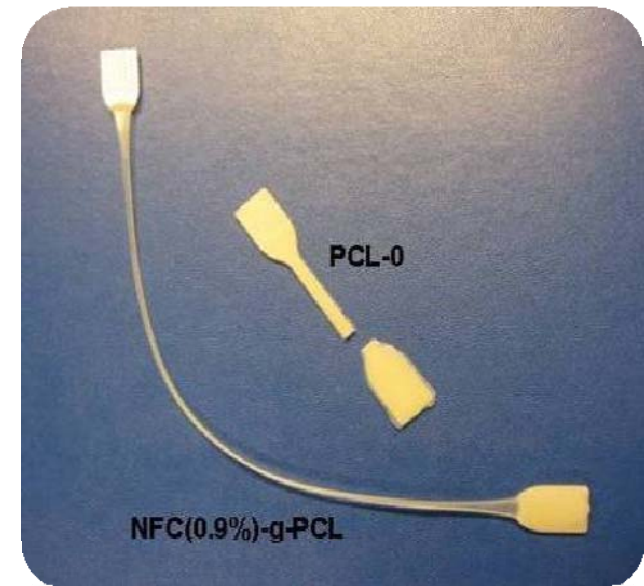


(e.g. Hentze *et. al*, EPNOE Conference 2009)

- Applications: Cellular bioplastics, insulation and packaging, (bio)active membranes & filters

Thermoplastic NFC composites

- In-situ polymerisation of NFC-g-PCL materials (<1% NFC) => Increases in melt strength and mechanical properties. Orientation further improves mechanical properties.

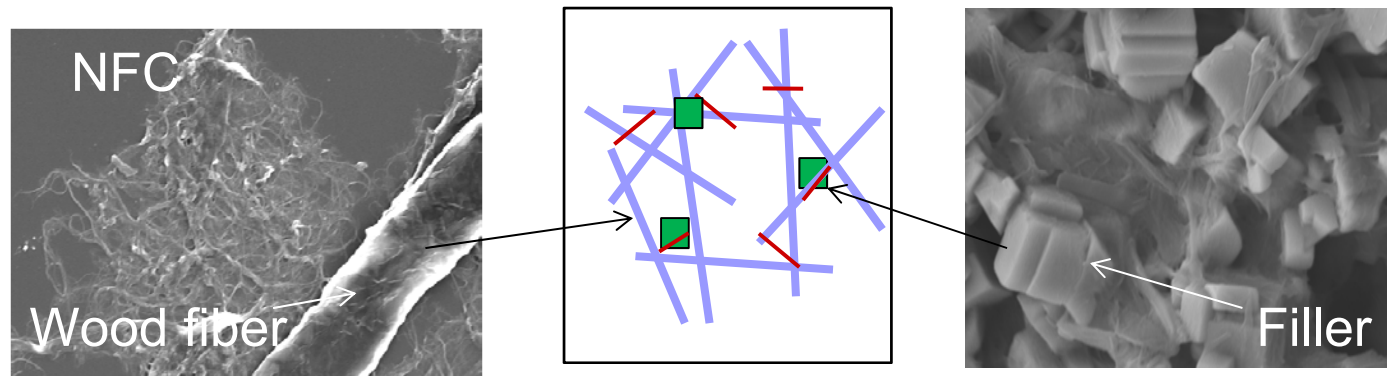


Porous Materials & Fiber Web Structures

■ Paper & Board Strength Enhancement

Wood fiber web structures – Paper as a porous nanocomposite

(e.g. Gardner *et. al*, J. Adhesion Sci. and Tech. (2008) 545–567,
Eriksen *et. al*, Nordic Pulp & Paper Research Journal, 299-304 (2008))



**NFC increased both:
binding area and binding strength ($S_{tot} \sim A_B \cdot S_B$)**

Applications: High strength /high bulk /high filler

A jump towards raw material and energy-efficient papers

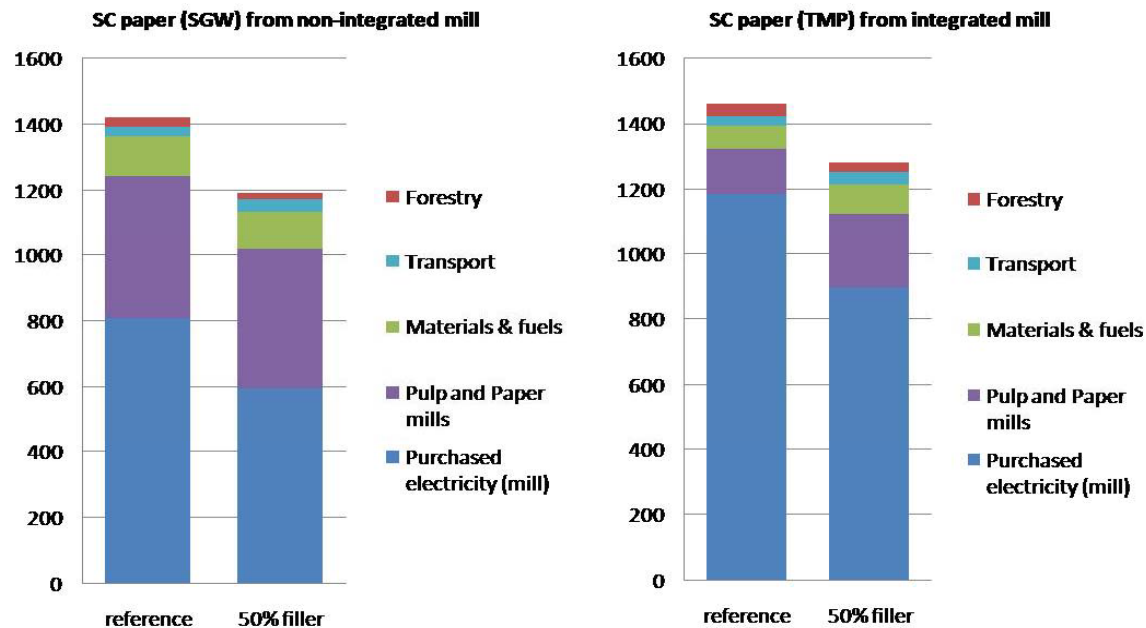
NFC-based filler containing SC paper

CO2 eq. of 1000kg SC paper

2 – 4% NFC addition:

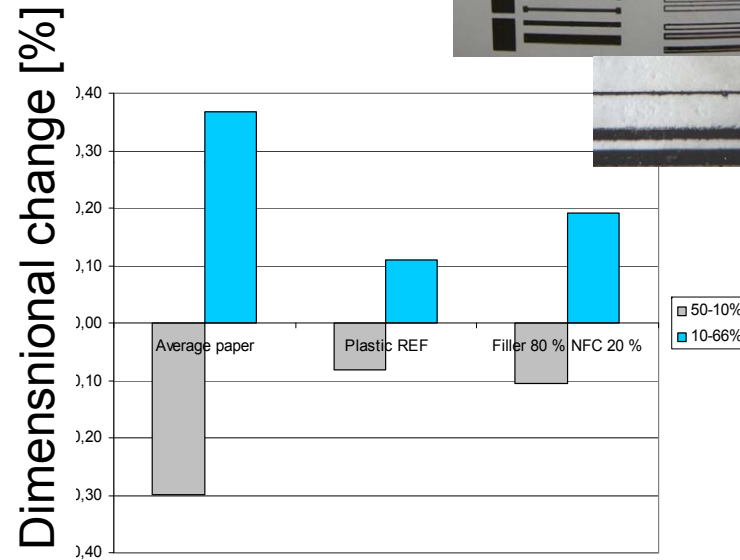
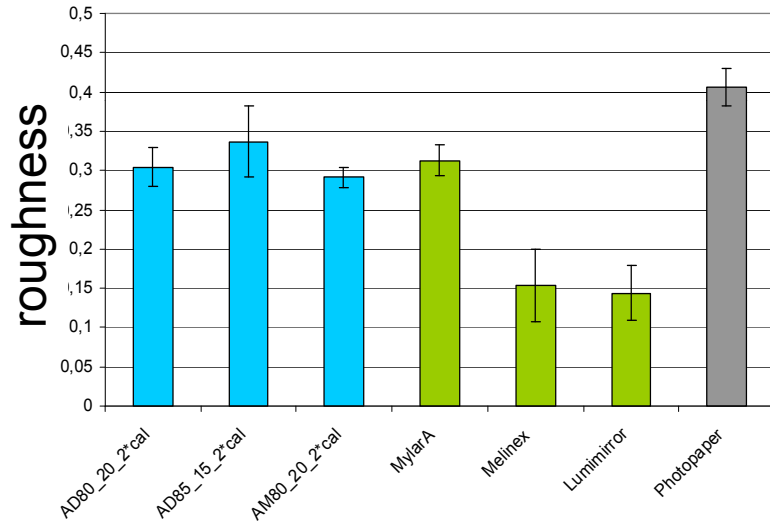
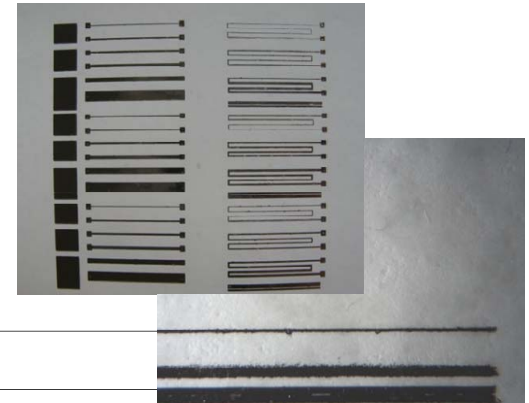
- Filler content increased from 24% to 50%
- 15% decrease in carbon footprint
- 30% less drying energy
- Good wet strength
- Better optical properties
- Cost saving potential

National project



New product opportunities

High filler content (80%) substrates for printed electronics applications, printed conductors



Two most essential properties:

- smoothness
- dimensional stability

Potential:

- Rapidly growing markets
- Sustainable electronics (printing with water-based inks demanding on plastics)

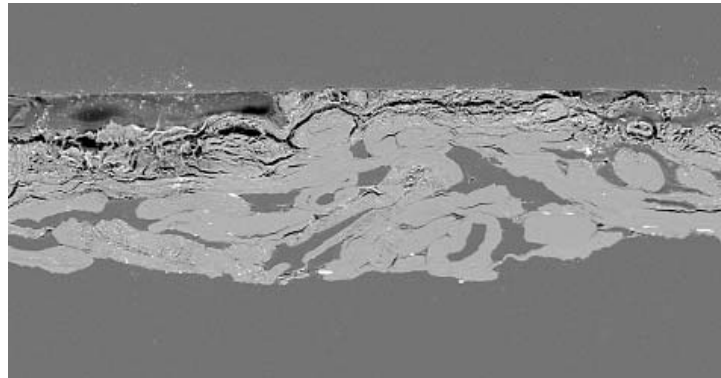
National project

Coatings & Functional Surfaces

■ Nanocelluloses for Coating Applications

- Nanocelluloses as barrier materials
- Specific advantages: high oxygen barrier, affinity to wood fibers
Disadvantage: Moisture sensitive (hydrophobic compound required)

**Multilayered coating
with oxygen and
water
vapor barrier
properties**



Shellac
NFC
Paper

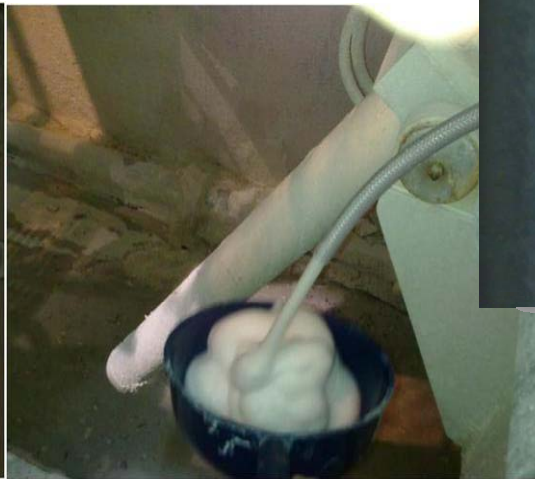
(Hult *et. al*, Cellulose, 575-586 (2010))

- Application: Food packaging, printing papers
(smooth surfaces, NFC as an organic pigment)

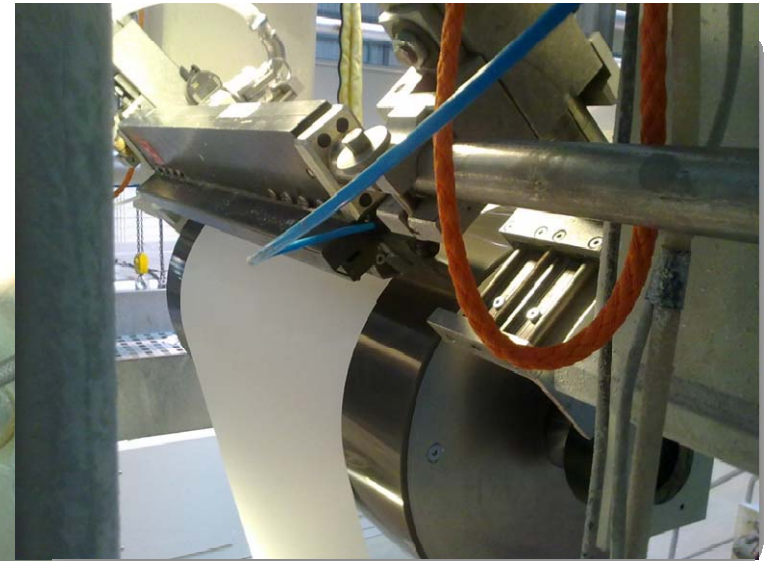
EU SUNPAP: Foam application of nanofibrillated cellulose Thin layers 0.5-2 g/m² applied



NFC, solids
content 2.98%

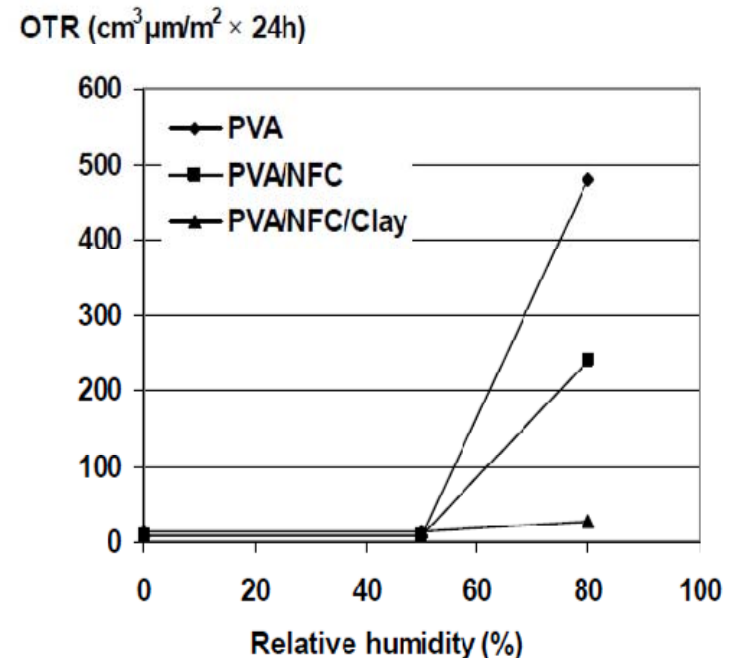


Foamed NFC,
90% air



NFC films

- Unmodified NFC films in dry conditions are good oxygen barriers
- Combination of NFC with well-known barrier materials and additives (PVA and nanoclay) significantly enhance the barrier properties at high humidity.



National project

NFC films

- Printed film of nanocellulose manufactured in pilot scale through controlled adhesion, spreading and drying of NFC with excellent smoothness without any wiremarkings.



National project

Functional Additives

- **Nanocelluloses as rheology modifiers**
 - NFC as a thixotropic, biodegradable, dimensionally stable thickener (stable against temperature and salt addition)
 - Low-calories **food** applications
 - Thickener in **cosmetics**
 - **Pharma** (tablet binder, diagnostics: bioactive paper)
 - Pickering stabilizer for **emulsions** & particle stabilized **foams**
 - **Paint** formulations
 - Enhanced **oil recovery**



NFC as additives in paints and resins

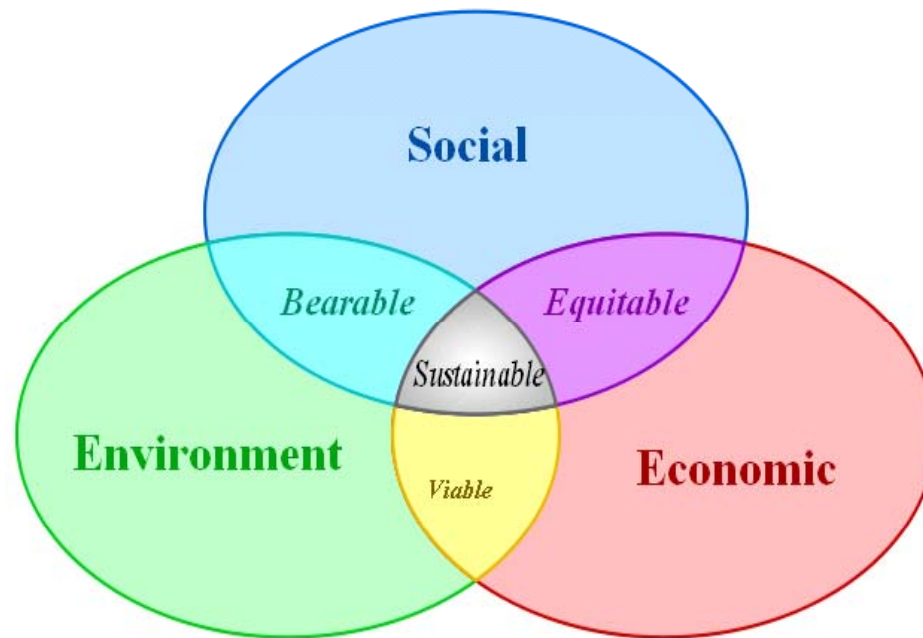
- Homogeneous distribution of nanoparticles and prevention of deposition of the additives in paint and resin applications.
- NFC network acts also as rheology modifier, less sensitive to temperature changes.



Effect of NFC on nanoparticle sedimentation in a lacquer.

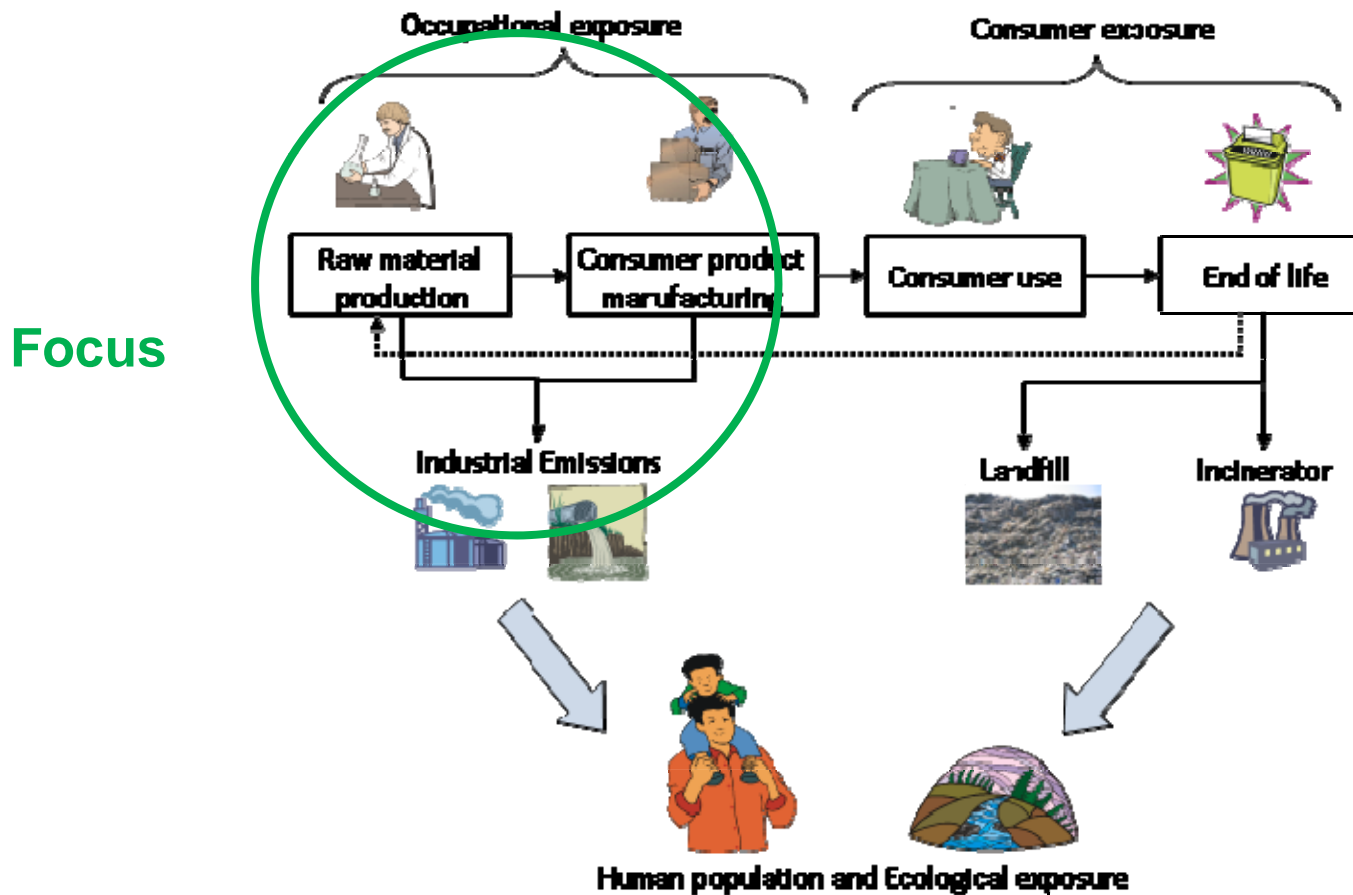
National project

“Three pillars of sustainable development” - not only economic, but also environmental and social impacts



Source: Adams, W.M. 2006.

EU SUNPAP: Risk assessment focused on NFC and occupational exposure, toxicity in vitro and in vivo



Source: Pöyry

A wide-angle photograph of a large industrial facility, likely a paper mill, showing a long, complex production line. The machinery is multi-tiered with numerous metal walkways, railings, and stairs. The floor is a light-colored, polished concrete. The ceiling is high with recessed lighting. A green semi-transparent banner with white text is overlaid across the middle of the image.

**Finnish forest companies – global
frontrunners
in bringing nanocellulose to business**

UPM-Kymmene Ltd

UPM started pre-commercial production of fibril cellulose and is developing new fibril cellulose applications with industrial partners.



- Objective to create the preconditions needed for industrial-scale production of fibril cellulose.
- The first stage mainly consists of developing products used in paper and packaging materials and the concrete and paint industries.
- UPM's fibril cellulose provides new properties and design opportunities for traditional materials; it can be used to make products tougher, lighter or thinner, depending on the application. (UPM 15 November 2011)

Stora Enso Ltd

Stora Enso is building a pre-commercial plant at Imatra for the production of microfibrillated cellulose.

- New type of renewable material will be used in existing and new unique fibre-based paper and board products, barrier materials.
- With MFC it is possible to develop lighter, stronger renewable packaging materials. In the longer term, the applications of the material may well extend to replacing today's fossil-based materials such as plastics and some speciality chemicals, and aluminium. (Stora Enso 31 May 2011)



Standardization/ Roadmap → ISO TC 229

Draft III Roadmap for Nanocellulose Standards 10-10-11-1ECT_UF2.pdf - Adobe Reader

File Edit View Document Tools Window Help

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Roadmap for the Development of International Standards for Nanocellulose

Third Draft – October 10, 2011

This is a collaborative document prepared by an international community of scientists and professionals to chart the path forward in developing international standards.

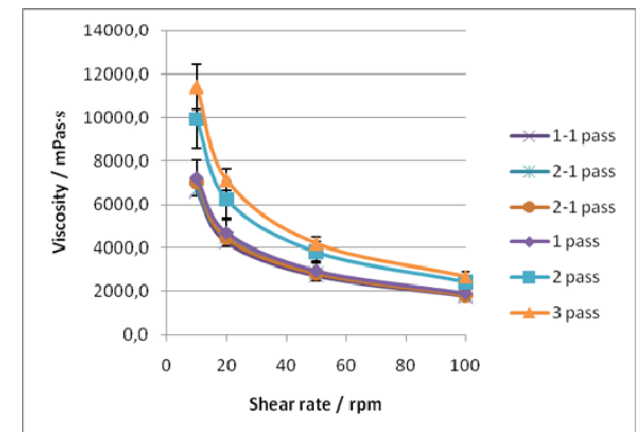
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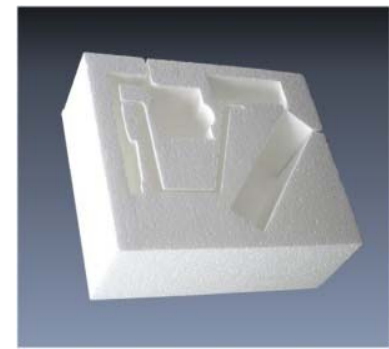
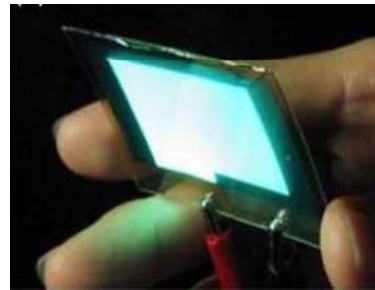
Standardization



- Roadmap work for ISO autumn 2011
- Companies in Finland started last year to measure viscosity of NFC/MFC
 - ✓ with the selected procedure that includes sample-taking, measurement, and computation and processing of results.
- Terminology discussions difficult without knowing characteristics



Multiple industrial products, consumer and well being applications



Acknowledgements

- My coworkers Pia Qvintus, Hans-Peter Hentze, Markus Linder, Ali Harlin, Tekla Tammelin, Mika Härkönen, Erkki Hellen at VTT



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Thank you

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