Kraft pulps from Eucalyptus and Pinus radiata - raw materials for nanocellulose production and novel bio-applications

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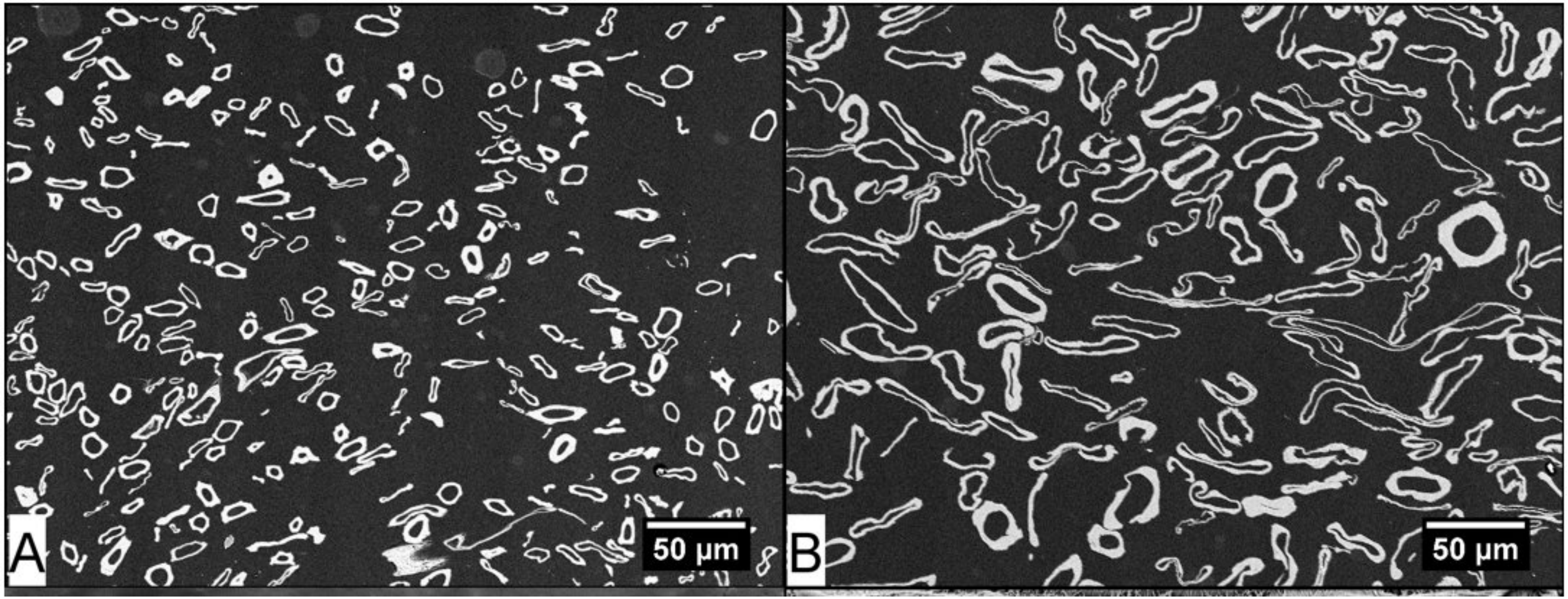
3er Congreso Iberoamericano sobre Biorrefinerías (CIAB)
4to Congreso Latinoamericano sobre Biorrefinerías
2do Simposio Internacional sobre Materiales Lignocelulósicos

Outline

- ❑ Kraft pulp fibres morphology
  - Eucalyptus and Pinus radiata
- ❑ Nanocellulose production
  - Chemical pre-treatments
- ❑ Characteristics of nanocellulose
  - Based on bleached and unbleached fibres
- ❑ Printing
  - Functionalization and 3D printing

Kraft pulp fibres

- Morphology
  - Advanced microscopy and image analysis

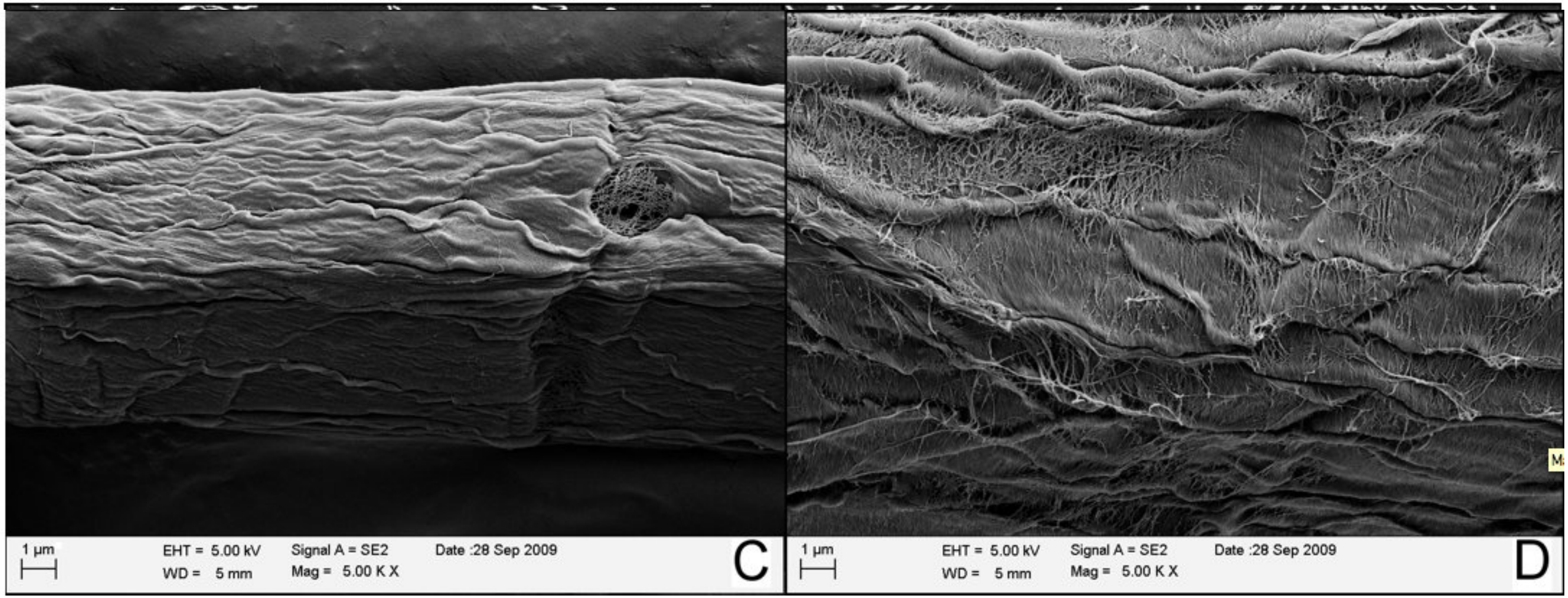


Eucalyptus **Pinus radiata**

Chinga-Carrasco, Yu, Diserud.
Microscopy and Microanalysis 17(4): 563-571 (2011).

Kraft pulp fibres

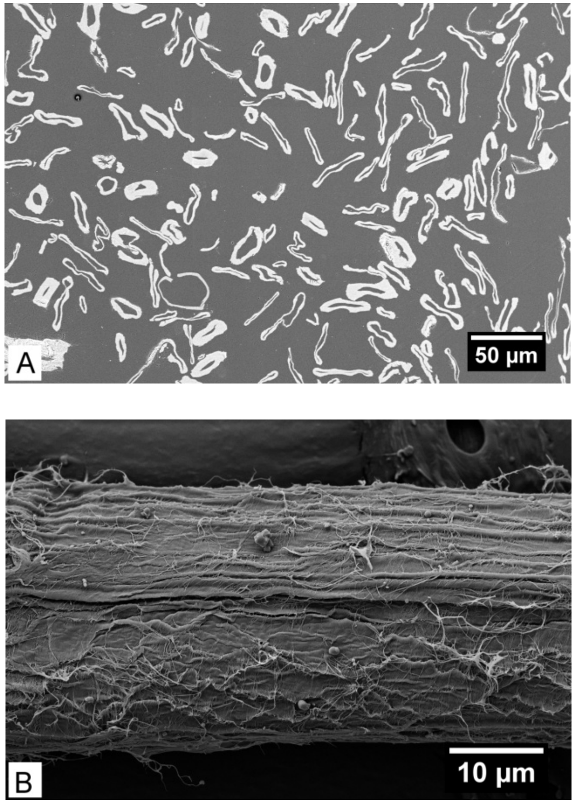
- Morphology
  - Advanced microscopy and image analysis



Eucalyptus **Pinus radiata**

Chinga-Carrasco, Yu, Diserud.
Microscopy and Microanalysis 17(4): 563-571 (2011).

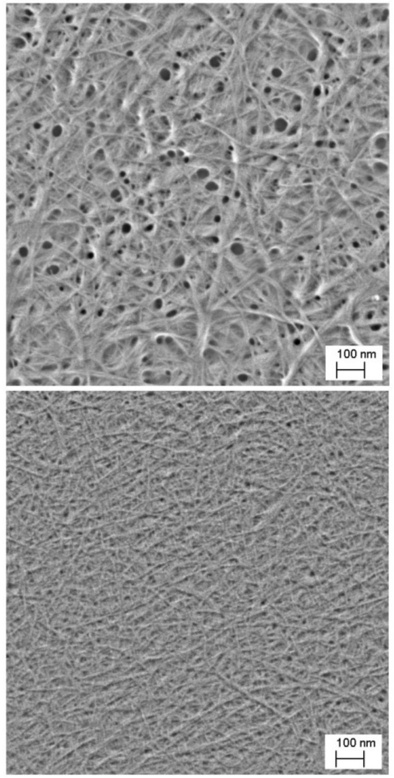
Wood nanocellulose



Cellulose fibres

Fibrillating fibres

- Mechanically
- Chemi-mechanically

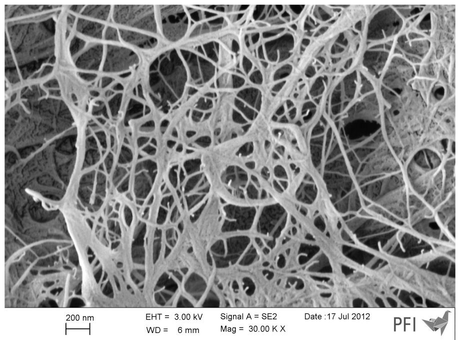


Cellulose nanofibrils

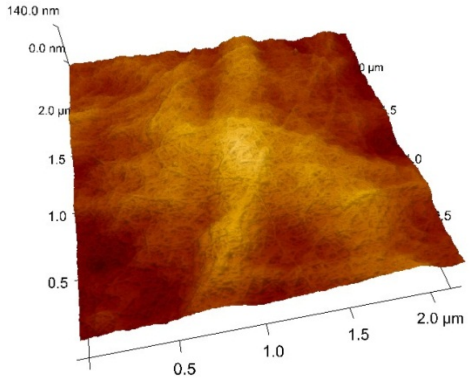
Characterisation

- Proper utilization of a given fibrillated material and its properties requires an extensive understanding of the chemical and structural components and their morphology

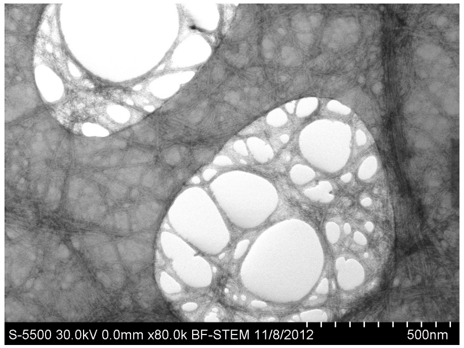
- But how are nanocelluloses characterised?
  - Nano-characterisation?



FESEM



AFM



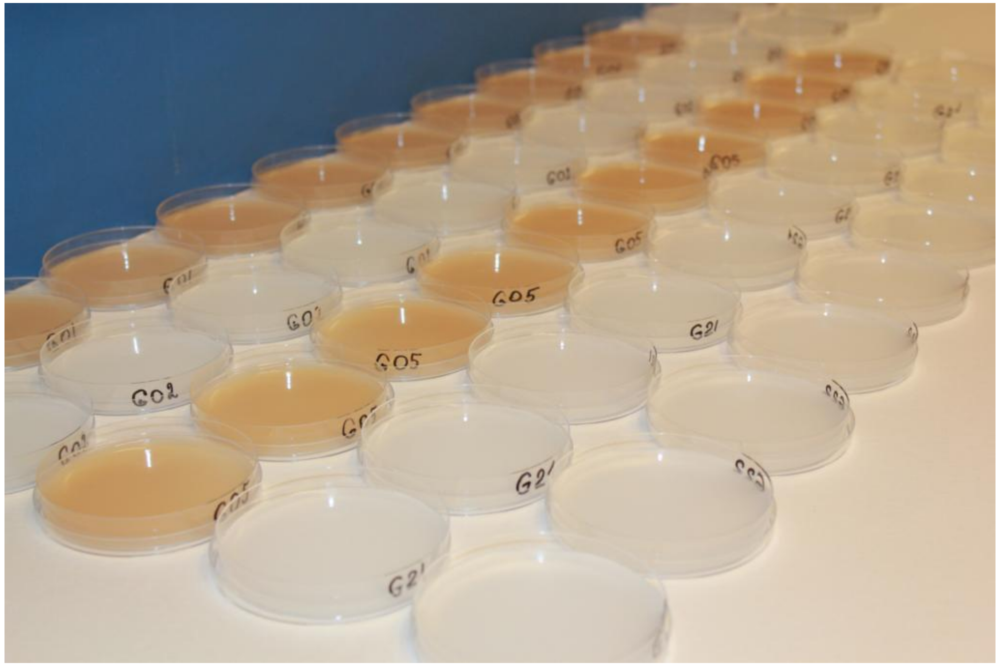
S(T)EM

Images from the PFI advanced nano-characterisation training course 2012

Chinga-Carrasco,, Averianova, Kondalenko, Garaeva, Petrov Leinsvang Karlsen. Micron 56:80-84, 2014

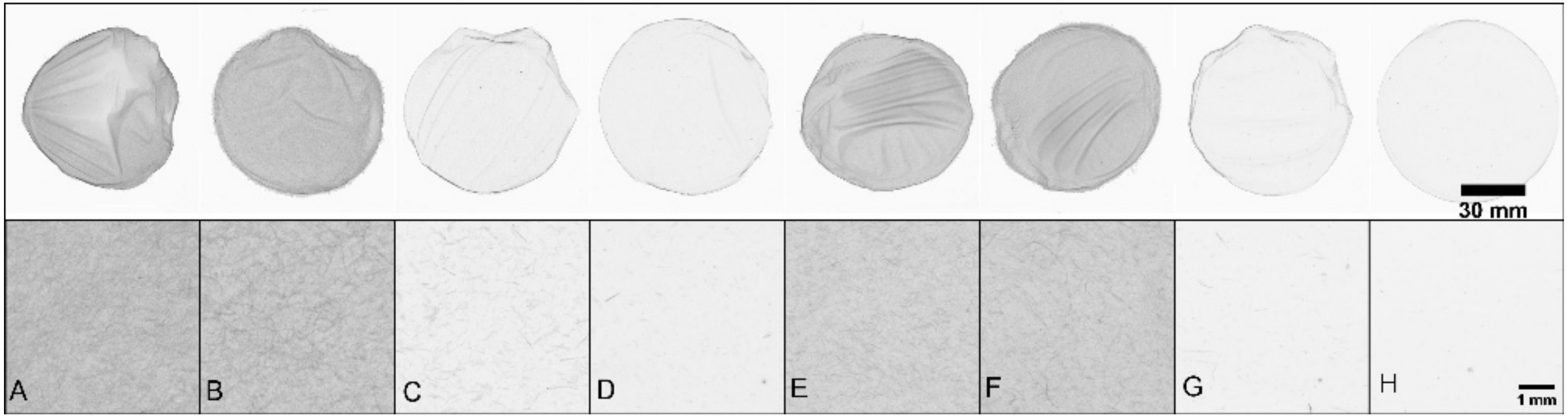
Optical quantification

- Samples for structural assessments
  - Suspensions/casting, 0.2 %
  - Grammage 20 g/m2
  - Drying 3-5 days



Optical quantification

- Digital images of nanocellulose films
  - Acquired with a conventional desktop scanner

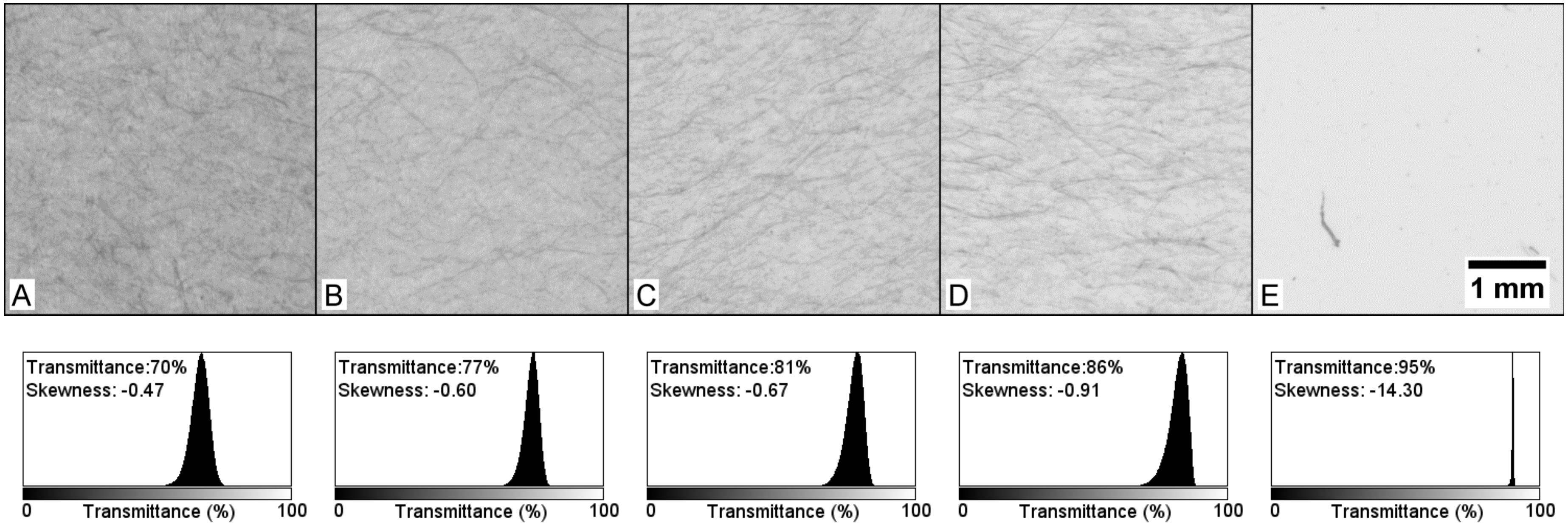


Eucalyptus	*P. Radiata*	*Eucalyptus*	*P. Radiata*	*Eucalyptus*	*P. Radiata*	*Eucalyptus*	*P. Radiata*
No pretreatment		Tempo		No pretreatment		Tempo	
3 passes		3 passes		5 passes		5 passes	

Syverud, Chinga-Carrasco, Toledo, Toledo. (2011). Carbohydrate polymers, 85(3):1033-1038.

Optical quantification

- Light transmittance measured with scanners
  - The higher the fibrillation the higher the light transmittance
  - Residual fibres clearly observed in digital images



No-pretreatment **70/30** **50/50** **30/70** **TEMPO**

Chinga-Carrasco, Micron 48: 42-48, 2013

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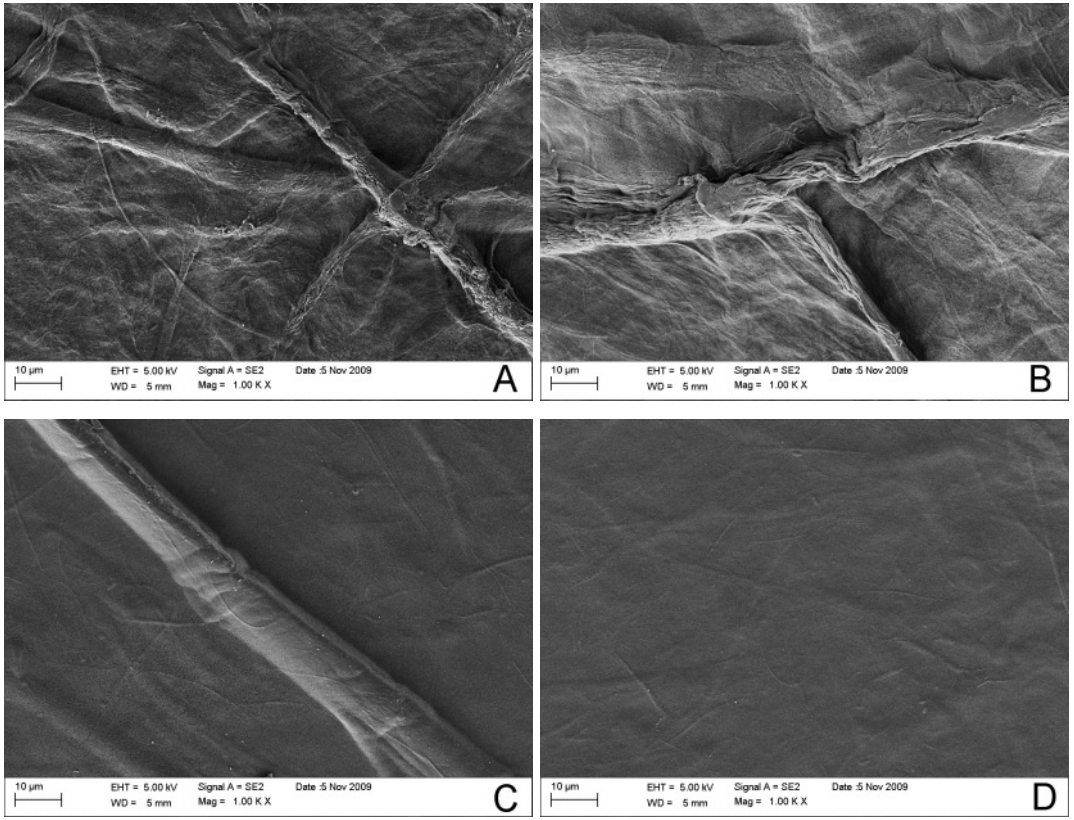
Nanofibrils

- The yield depends on the fiber type

Mechanical

TEMPO Pretreatment

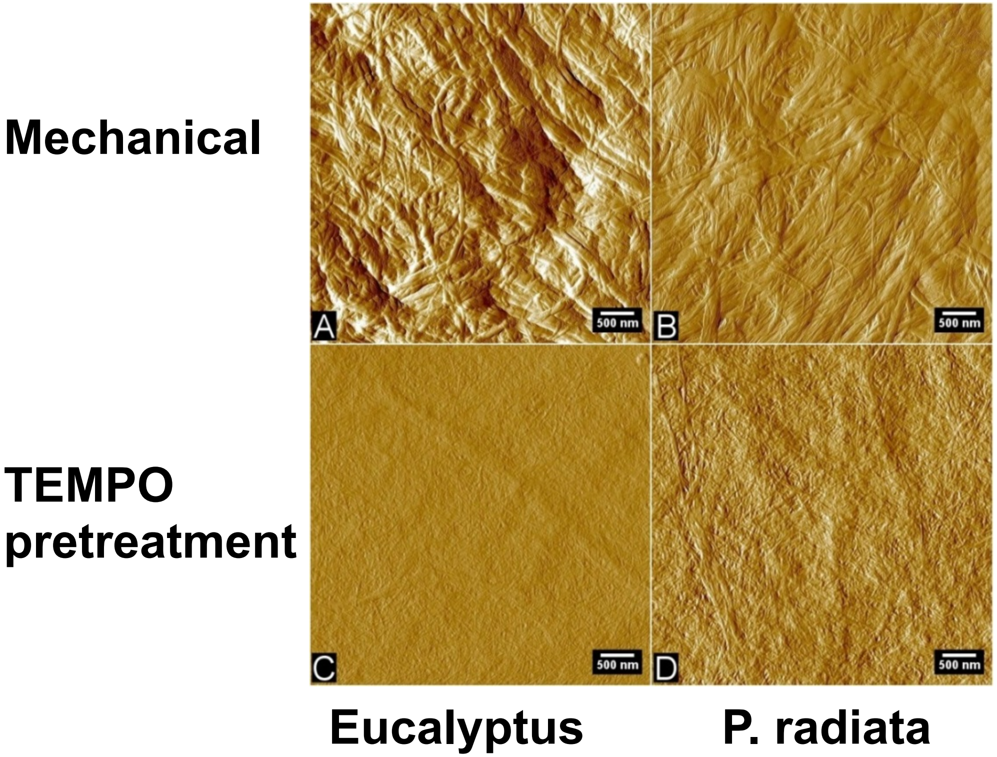


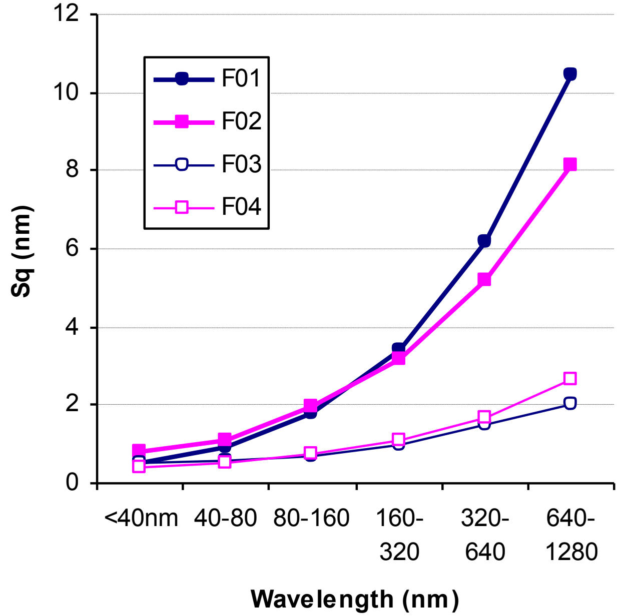
Eucalyptus **P. radiata**

Chinga-Carrasco, Yu, Diserud.
Microscopy and Microanalysis 17(4): 563-571 (2011).

Nanofibrils

- Nanofibrils are revealed by nano-characterization methods
  - AFM
  - Chemical pre-treatment yields an homogeneous surface





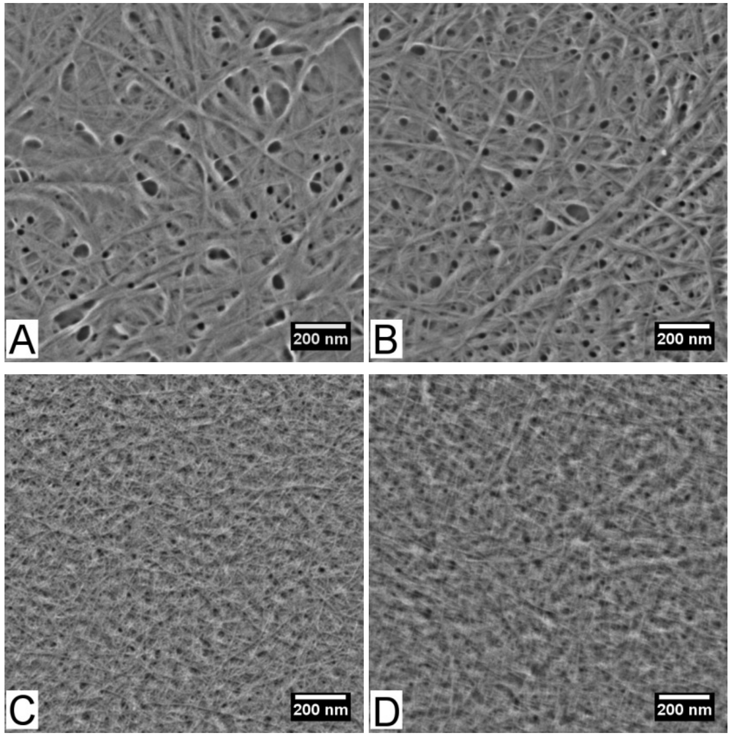
Syverud, Chinga-Carrasco, Toledo, Toledo. (2011). Carbohydrate polymers, 85(3):1033-1038.

Nanofibrils

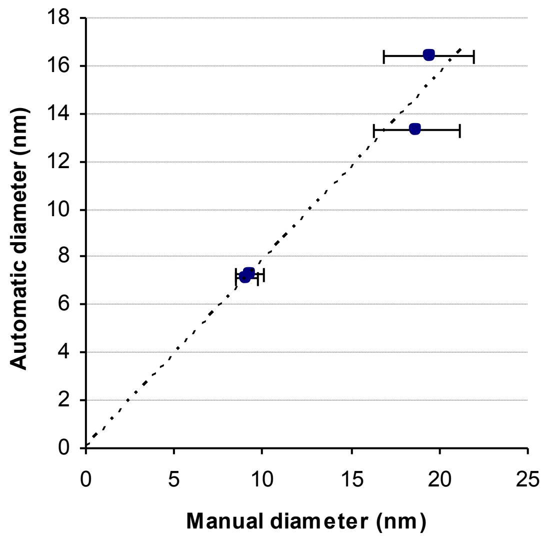
- Nano-porous structures
  - FE-SEM - Quantification of nanofibril width and porosity
  - Resolution, 1 nm. Surfaces without coating!

Mechanical

TEMPO pretreatment



Eucalyptus **P. radiata**

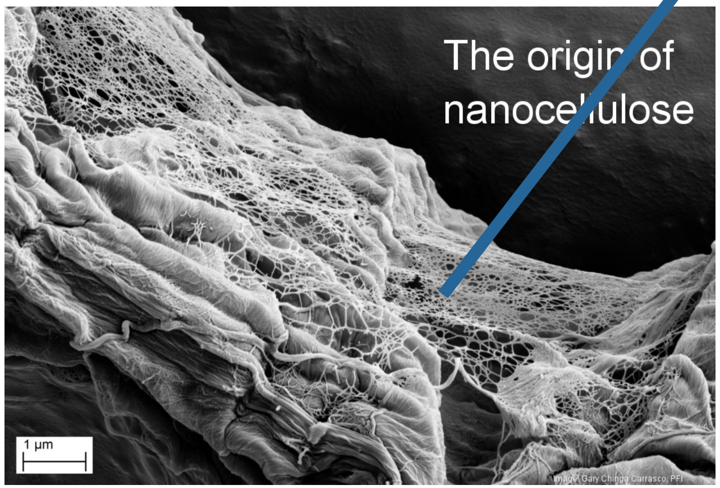


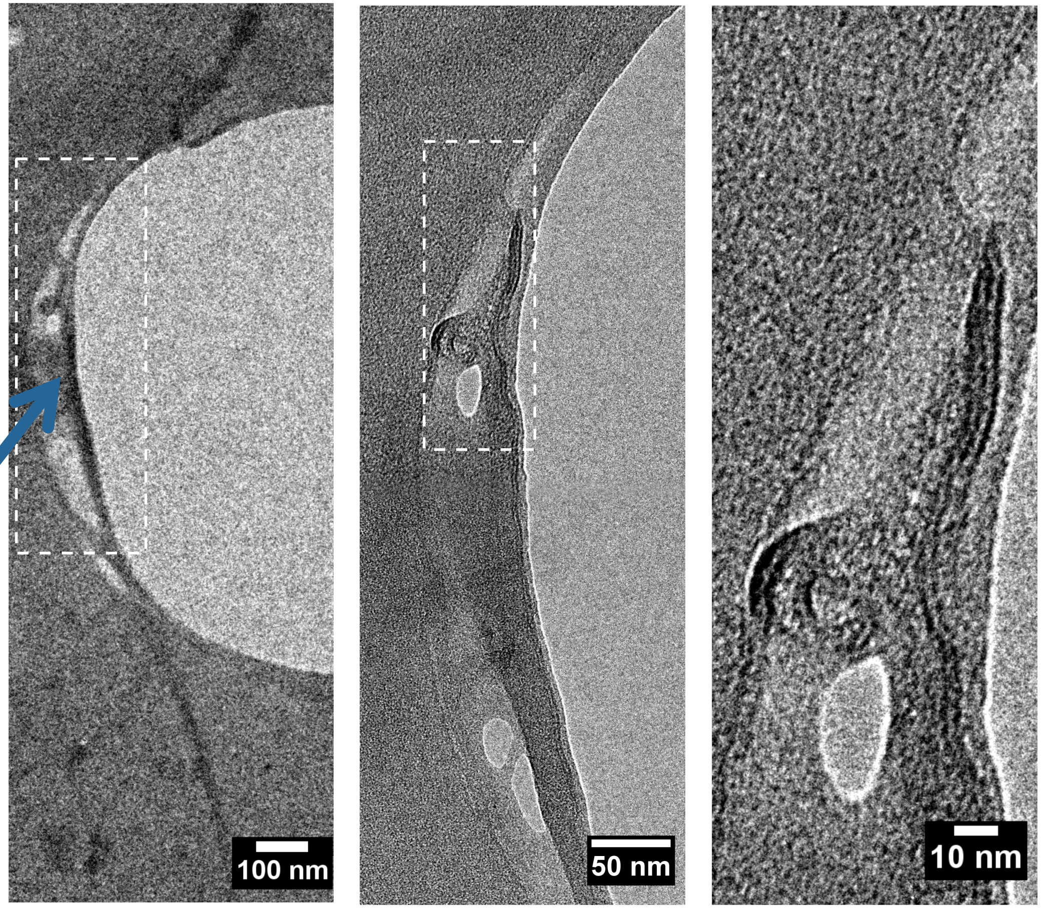
TEMPO pre-treatment yields homogeneous nanofibrils

Chinga-Carrasco, Yu, Diserud.
Microscopy and Microanalysis 17(4): 563-571 (2011).

Nanofibrils

- TEM assessment
  - Ultimate technique for nano-characterisation
  - Visualization of elementary fibrils



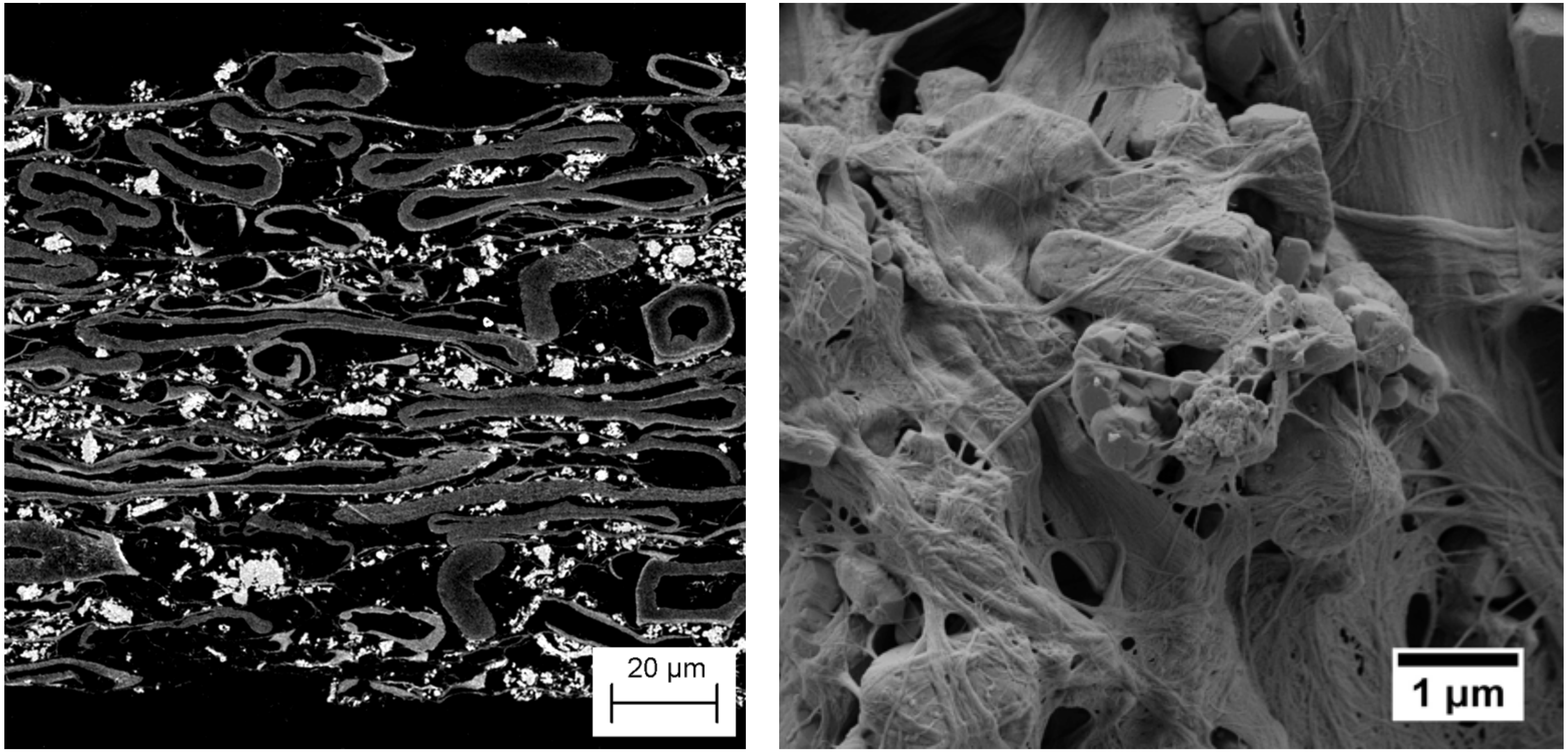


Adjacent elementary fibrils
Width 3.5 nm

Chinga-Carrasco, Yu, Diserud.
Microscopy and Microanalysis 17(4): 563-571 (2011).

Nanofibrils

- Cellulose nanofibrils from *P. radiata,* used as reinforcement in paper filled with $CaCO_3$



Hii, Gregersen, Chinga-Carrasco and Eriksen.
Nordic pulp and Paper Research J. 27(2): 388-396 (2012).

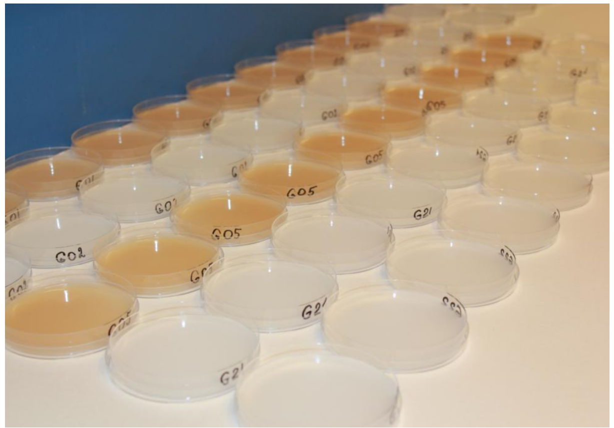
Characteristics of nanocellulose films

- Based on bleached and unbleached pulp fibres

Characteristics of nanocellulose films

- Lignin-containing fibres yield a higher nanofibrillation
  - Form smoother films
  - Are less hydrophilic

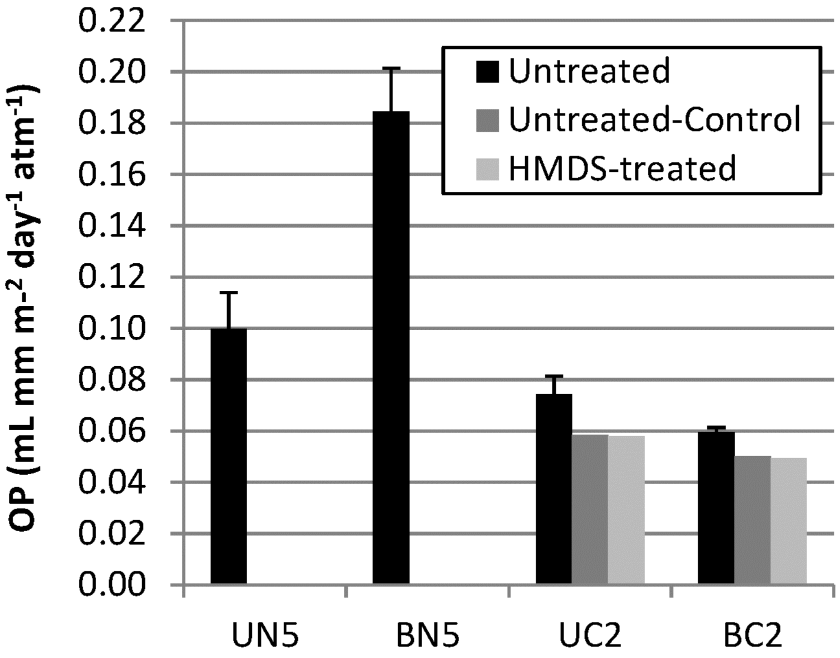
	Contact angle (degrees)	LP-roughness (µm)
Unbleached, 3 passes	**61 ±4**	**0.33 ±0.07**
Bleached, 3 passes	40 ±3	0.56 ±0.08
Unbleached, 5 passes	**58 ±3**	**0.26 ±0.06**
Bleached, 5 passes	38 ±2	0.63 ±0.05
Unbleached carboxymethylation, 2 passes	**74 ±4**	**0.24 ±0.05**
Bleached carboxymethylation, 2 passes	54 ±3	0.16 ±0.01

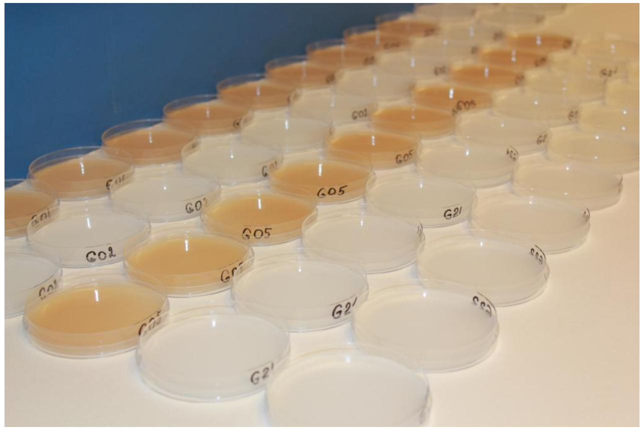


Chinga-Carrasco, Kuznetsova, Garaeva, Leirset, Galiullina, Kostochko, Syverud.
J. Nanoparticle research 14:1280 (2012)

Characteristics of nanocellulose films

- Lignin-containing fibres yield a higher nanofibrillation
  - Form dense films with low oxygen permeability
  - But the chemical-pretreatment has a larger effect on bleached fibres



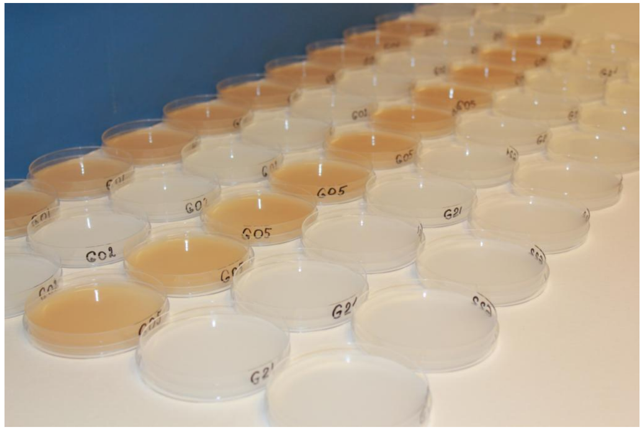


Chinga-Carrasco, Kuznetsova, Garaeva, Leirset, Galiullina, Kostochko, Syverud. J. Nanoparticle research 14:1280 (2012)

Characteristics of nanocellulose films

- Lignin-containing fibres yield a higher nanofibrillation
  - Form stronger films
  - But the chemical-pretreatment has a larger effect on bleached fibres

Series	Tensile strength (MPa)	Elongation (%)
Unbleached, 3 passes	**145 ±13**	**12.2 ±1.6**
Bleached, 3 passes	118 ±10	12.3 ±1.2
Unbleached, 5 passes	**163 ±16**	**13.9 ±3.3**
Bleached, 5 passes	137 ±18	17.8 ±1.2
Unbleached carboxymethylation, 2 passes	**162 ±31**	**9.9 ±4.8**
Bleached carboxymethylation, 2 passes	239 ±25	17.1 ±7.5



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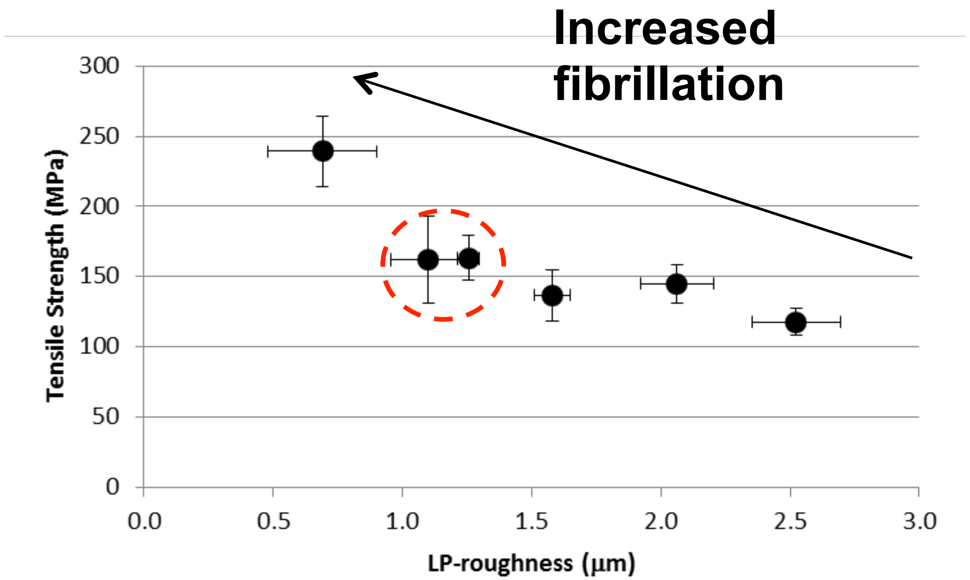
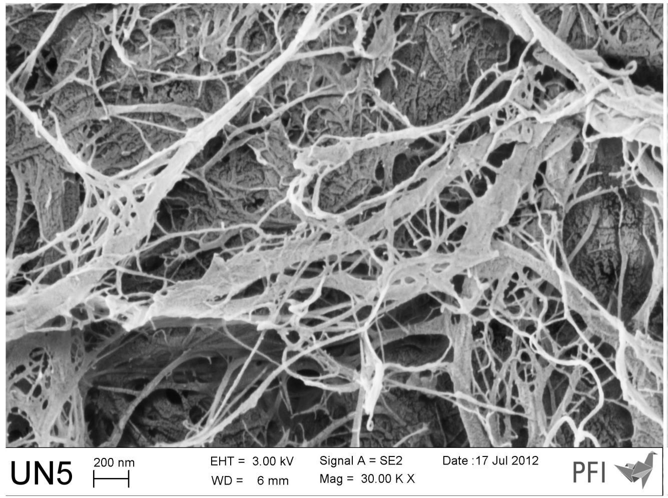
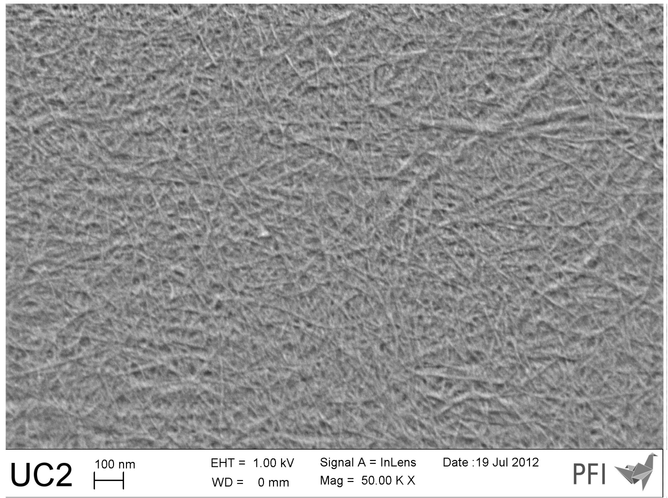
Chinga-Carrasco, Kuznetsova, Garaeva, Leirset, Galiullina, Kostochko, Syverud.
J. Nanoparticle research 14:1280 (2012)

Characteristics of nanocellulose films

- Nanocellulose films
  - The more fibrillated the material is the higher the strength







Chinga-Carrasco, Kuznetsova, Garaeva, Leirset, Galiullina, Kostochko, Syverud.
J. Nanoparticle research 14:1280 (2012)

Biomedical applications

- ❑ Nanocellulose from wood has potential in wound dressings

- ❑ The assessment of biocompatibility requires direct contact with living tissue
  - Cytotoxicity and biocompatibility
  - Requires ultrapure nanocellulose materials
    - LPS levels lower than 100 endotoxin units/g

- ❑ LPS < 50 EU/g

- ❑ Non-cytotoxic material

Nordli, Chinga-Carrasco, Rogstad, Pukstad.
Submitted.

Biomedical applications

- Microbiological testing
  - A set of nanocellulose materials have been tested, including
    - Neat nanocellulose
    - Chemically-pretreated nanocellulose
  - Nanocellulose may impair bacterial growth
  - Further studies are being performed to explore the bacteria-nanocellulose interactions and biofilm formation

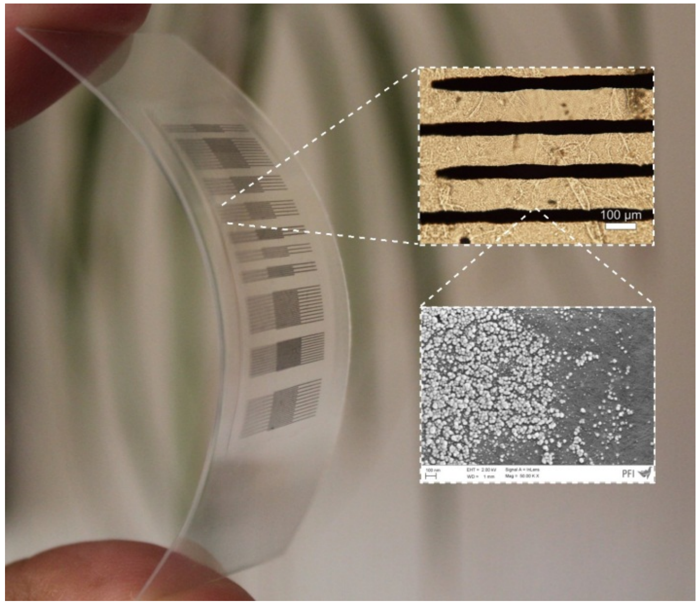
Powell, Khan, Chinga-Carrasco, Wright, Hill, Thomas.
Carbohydrate polymers 137: 191-197 (2016)

Functionalization by printing

- Nanocellulose films
  - high oxygen barrier properties
  - Strong
  - Translucent
  - **Smooth**

  - Surface modification by printing

- Great potential for adding functionality

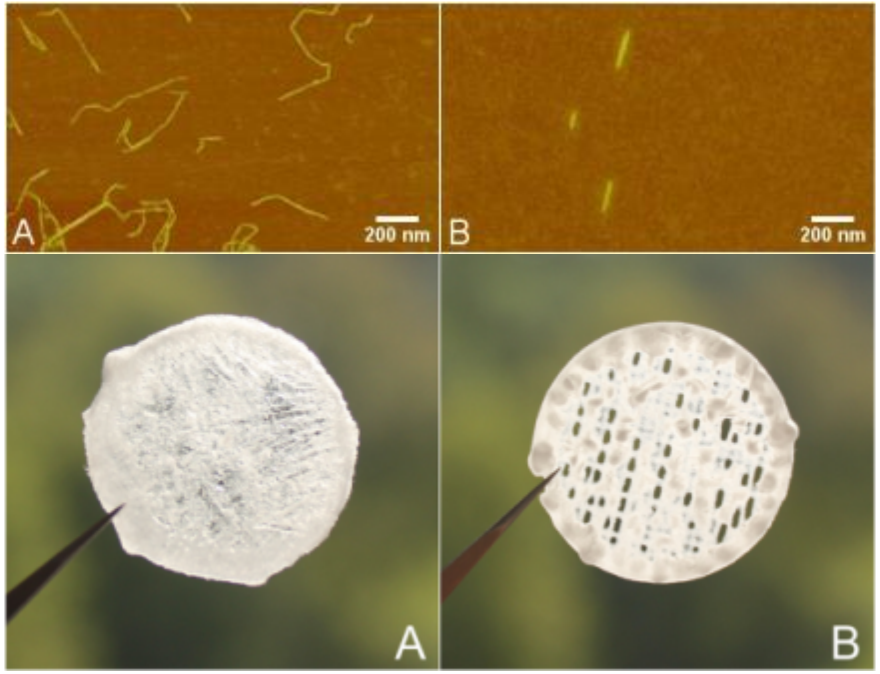


Conductive structures printed on nanocellulose surfaces

Chinga-Carrasco, Tobjörk, Österbackä (2012)
J. Nanoparticle research 14:213

Hydrogels

- ❑ Nanocellulose can be modified to form functional structures
  - 3D bioprinting of nanocellulose constructs



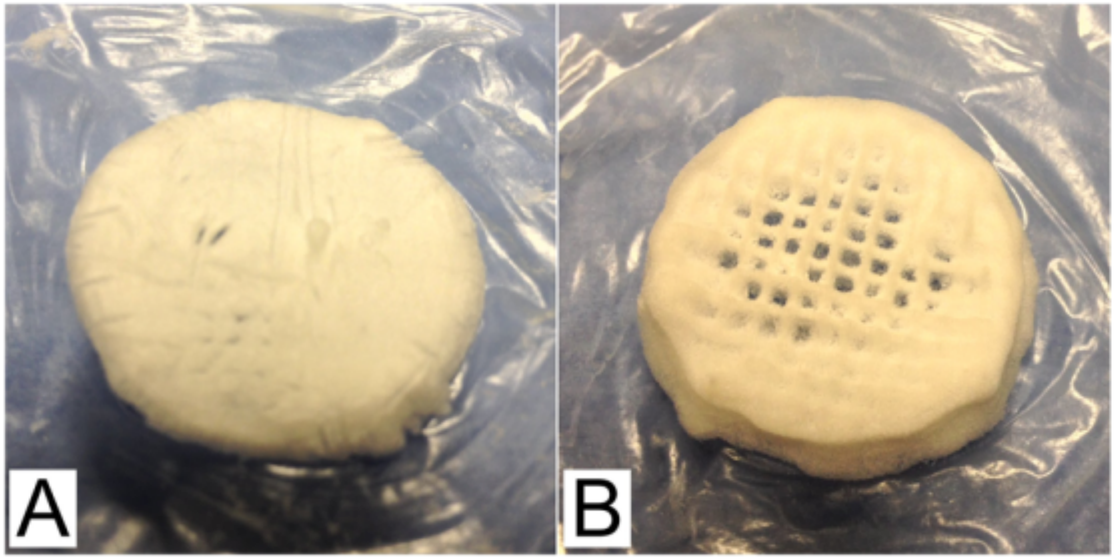
TEMPO
1%

Carboxymethylated
+Periodate
3.9%

Rees, Powell, Chinga-Carrasco, Gethin, Syverud, Hill, Thomas
BioMed Research International. Article ID 925757 2014.

Hydrogels

- Nanocellulose can be modified to form functional structures
  - 3D bioprinting of nanocellulose constructs
  - Tailor-made biocomposites for wound healing



Rees, Powell, Chinga-Carrasco, Gethin, Syverud, Hill, Thomas
BioMed Research International. Article ID 925757 2014.

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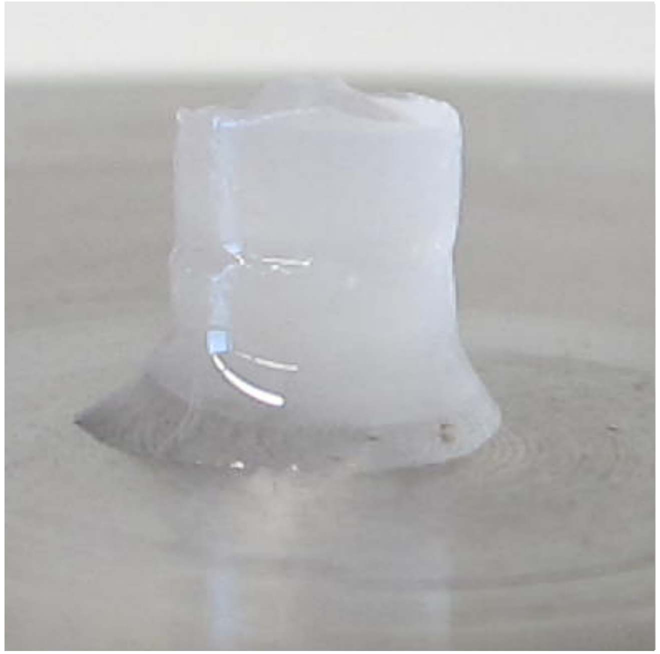
Hydrogels

- Macro-porous structures can be created through cryo-gelation and cross-linking

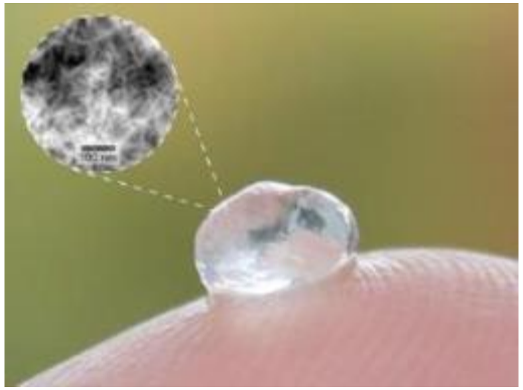


- The gels are elastic and spongy
- Regain the shape

Syverud, K., Kirsebom, H., Hajizadeh, S., Chinga-Carrasco, G.
Nanoscale research letters 6:626 (2011)

Conclusions

- A set of structural and chemical characterization methods have been established
- Various chemical pre-treatments have been applied to tailor-make the nanofibril morphology and surface chemistry
- New printing techniques have been demonstrated to functionalize nanocellulose
- Nanocellulose has great potential for biomedical applications



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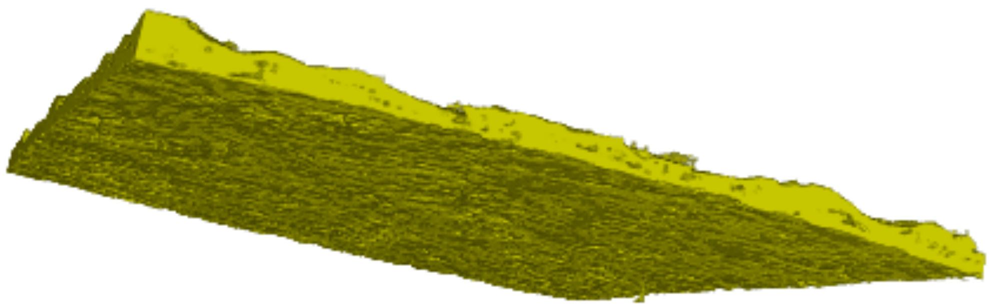
- The Research Council of Norway is acknowledged for funding part of this work through the Grants
  - 193706 - A Norwegian-Chilean Cooperation project as a step to develop novel bio-based materials and sustainable energetic solutions in Latin America;
  - 196119 - Nanofibril filters for environmental nanoparticles: Development of innovative protection against Nano-pollution;
  - 219733 - NanoHeal: Bio-Compatible Cellulose Nanostructures for Advanced Wound Healing Applications.



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