The role of ligno-nanocellulosics in the biorefinery concept

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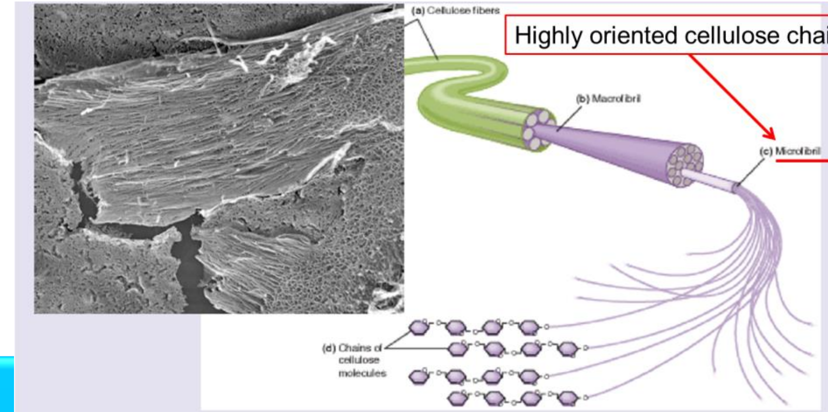
[1]VTT Ltd., Finland; [2]University of Zaragoza; [3]Aalto University, Finland

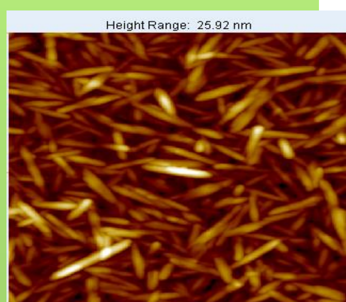
Nanocellulose (man-made) types

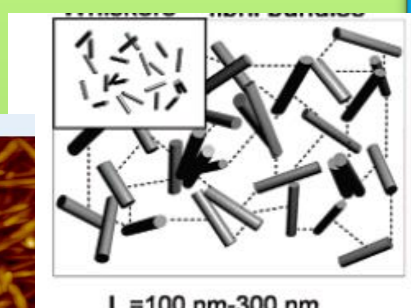


Nanocrystaline cellulose (CNC)

CHEMICAL DESINTEGRATION

- Whiskers – short
- Crystalline
- Chemical process,
  acid hydrolysis
- Self assembly possible
- Defined rheology



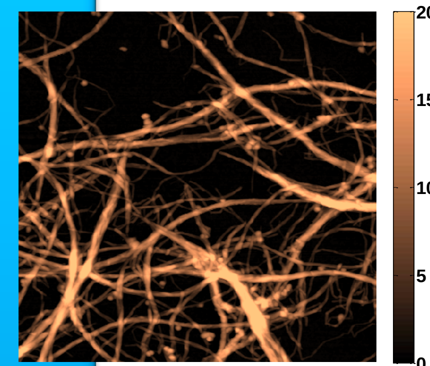


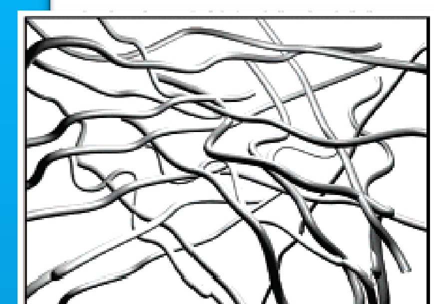
Cellulose nanofibrils (CNF)

MECHANICAL DESINTEGRATION

- Long fibrils
- Amorphous and crystalline parts both in fibrils
- No self assembly
- Strongly shear thinning - rheology *f(*manufacturing process, raw material, etc)

Strong network of fibrils -> gels





Cellulose Nanomaterial Research Strategy

Wood

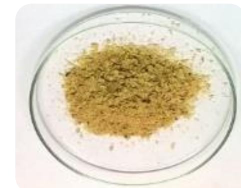
Bran

Bagasse

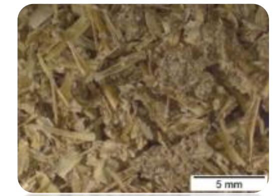
Sugar Beet

Hemp

Soy hulls



BSG



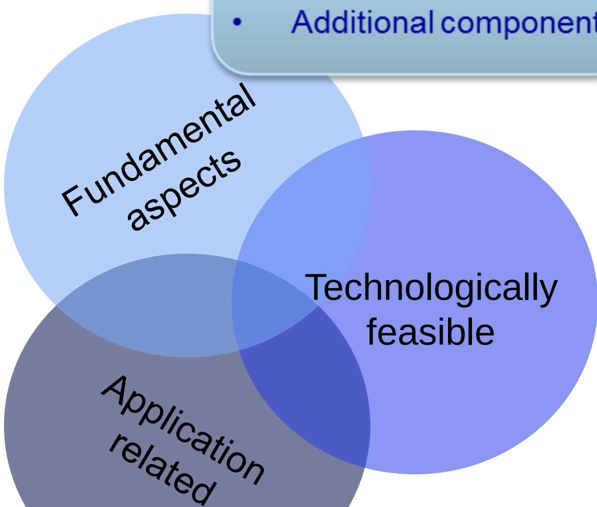
Raw materials
- Composition
- Structure
- Additional components

Pre-treatments
- Mechanical
- Chemical
- Enzymatic

Fibrillation
- Mechanical
- Chemical
- Enzymatic

Structure-function relationships

- Soft matter
- Composites
- Thin films
- Porous materials
- Fibre based materials



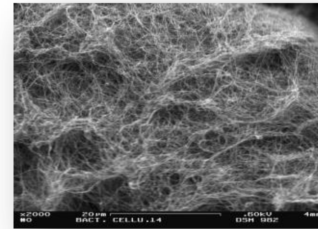
Safety and sustainability

Structure-function relationships

Characterisation

Size/Dimensions/Branching

Bacterial cellulose



Scale bar: 20 µm

Ribbon-like structure

Overall dimensions in macroscale, fine structure in nanoscale

Chain or rod-like structure

All dimensions in nanoscale

Nanocrystals

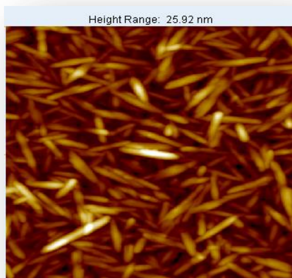


Image area 1x1 µm

Nanofibres

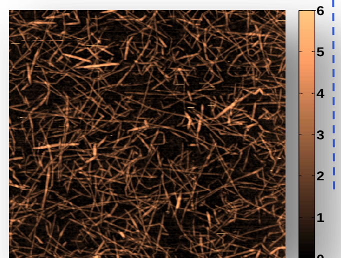


Image area 2x2 µm

Nanofibrillated

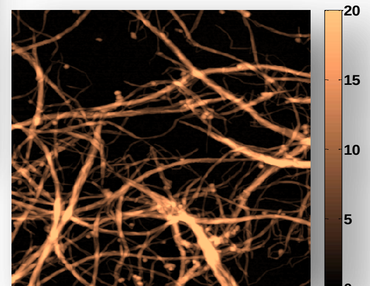


Image area 2x2 µm

Microfibrillated

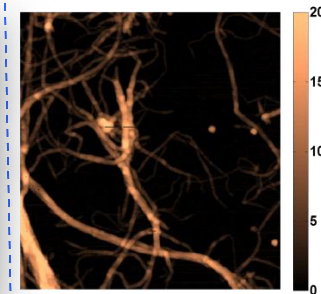


Image area 2x2 µm

Branched structure

Overall dimensions in macroscale, fine structure in nanoscale

Charge/Chemistry

Colloidal dispersion

Polyelectrolyte-like

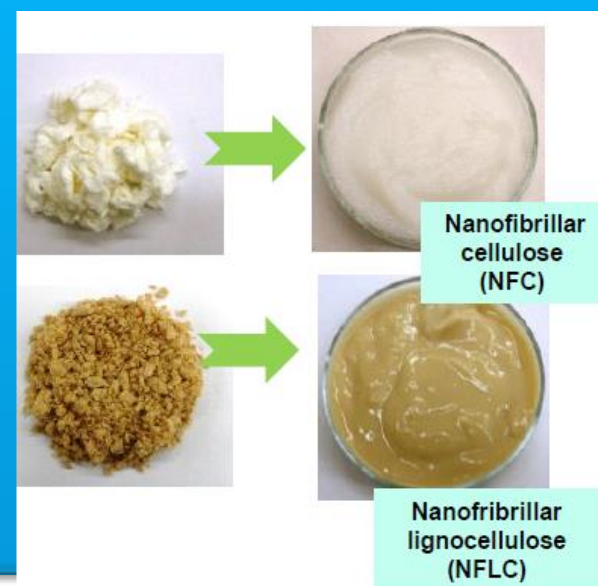
Wood-fibre like

Decreasing surface charge

Pöhler, T., Lappalainen, T., Tammelin, T., Eronen, P., Hiekkataipale, P., Vehniäinen, A., Koskinen, T.M., TAPPI International Conference on Nanotechnology for the Forest Products Industry, Espoo, Sep 27-29, 2010. Tanaka, A., Seppänen, V. Houni, J. Sneck, A. Pirkonen, P., *NPPRJ,* **2012,** *27*, 689-694. Arola S., Malho J.M., Laaksonen P., Lille M., Linder M.B. *Soft Matter*, **2013**, *9*, 1319. Penttilä, P. A., Várnai, A., Pere, J., Tammelin, T., Salmén, L., Siika-aho, M., Viikari, L., Serimaa, R., *Bioresource Technology*, **2013,** *129,* 135. Solala I., Volperts, A., Andersone, A., Dizhbite, T., Mironova-Ulmane, N., Vehniäinen, A., Pere, J., Vuorinen T. *Holzforschung*, **2011**, *66*, 477.

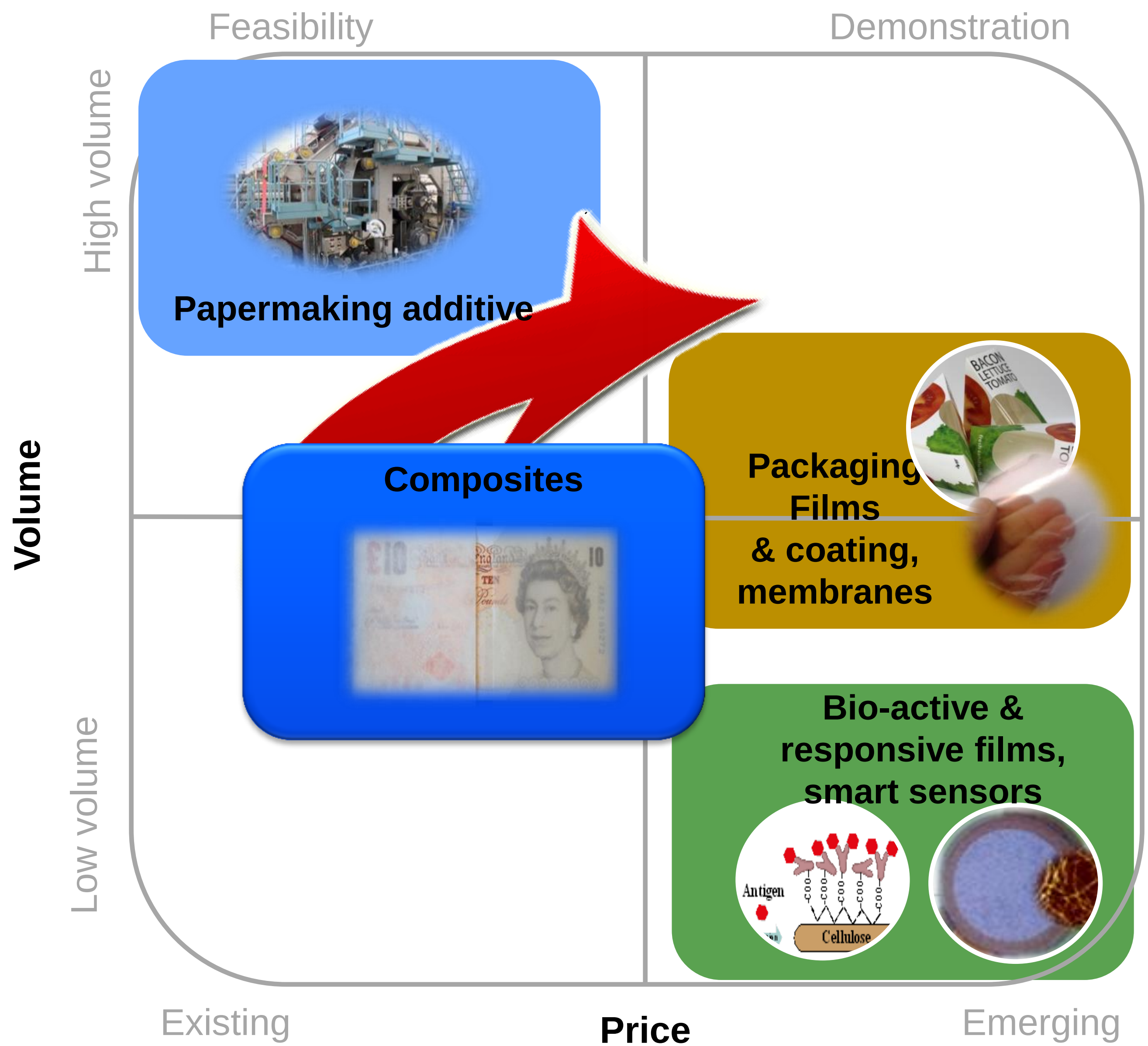
CNF: natural and renewable

- Creamy, viscous gel
- High strength and modulus
- High surface area
- Dimensional and thermal stability
- Biodegradable and biocompatible
- Functionality template
- Can be obtained with original pulp composition
- Moisture absorption/water holding capability



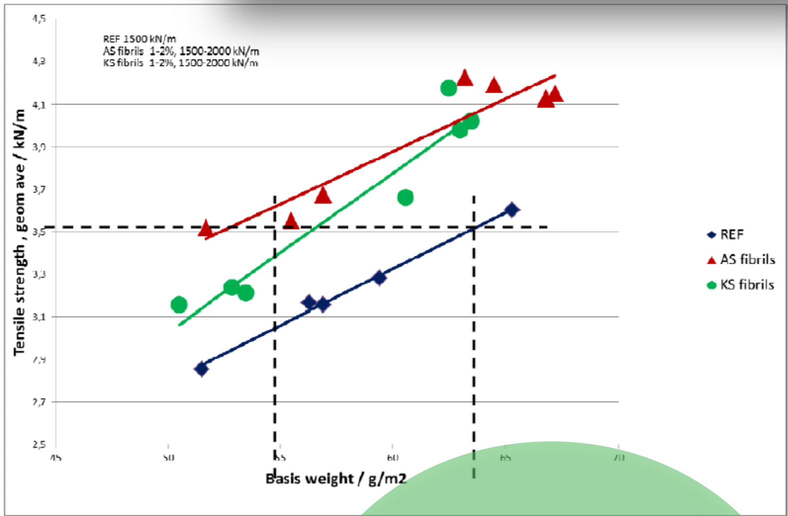
Adapted from Orlando Rojas, Aalto University

Nanocellulose products: Volume vs. Price



Papermaking

- **Denser papers -> OD 1-3%-higher after press section and 20-30% lower porosity**
- No changes in formation or retention
- ***Tensile strength (~8g/m² basis weight reduction) and elastic modulus increase***
- Bending stiffness remains the same
- **Opacity ~4%-units lower**

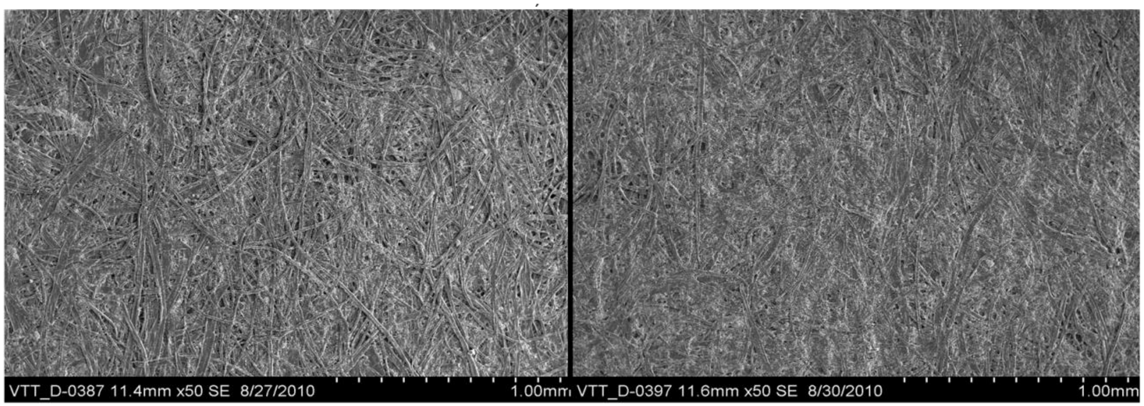


Increased strength without compromising dewatering

Papercoating

SEM x50 SE images from uncalendered paper surfaces

Thin layer of NFC on the paper, below 1 g/m²

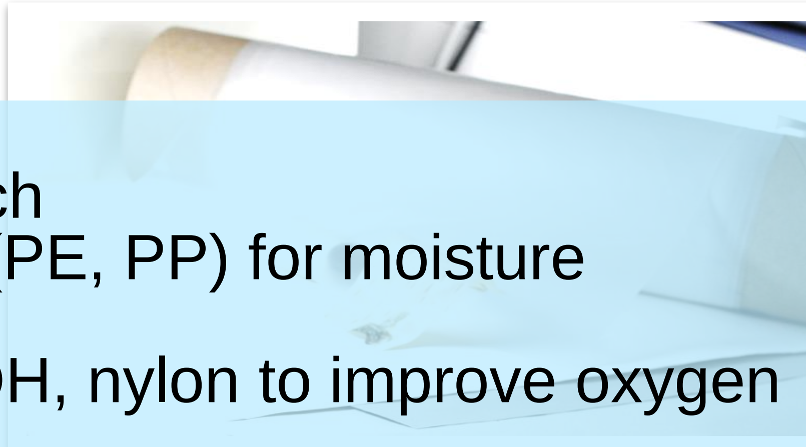


Base paper **CNF coated paper**

Nanofibrillated cellulose film (large scale production)

Patent pending technology e.g. WO2013/060934

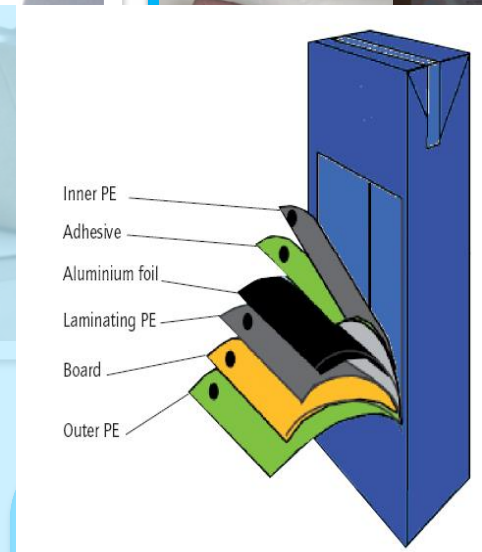
Low roughness

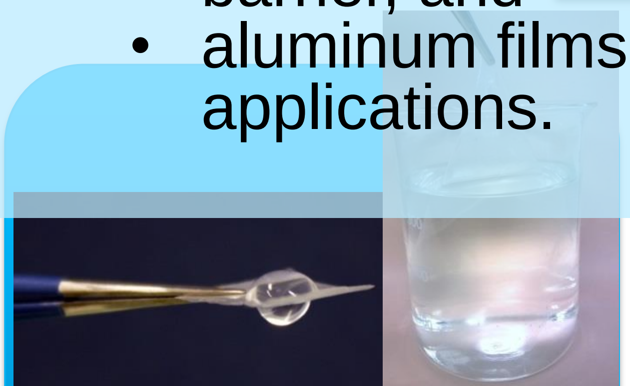


quality

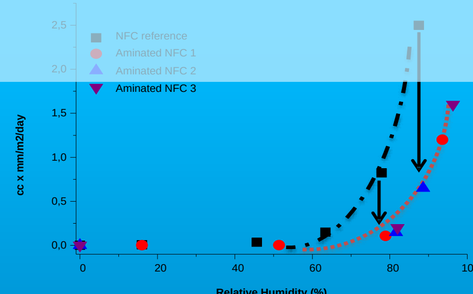
Multilayer approach

- Polyolefins (PE, PP) for moisture barrier,
- EVOH, PVOH, nylon to improve oxygen barrier, and
- aluminum films for high barrier applications.

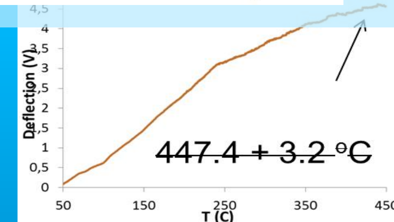




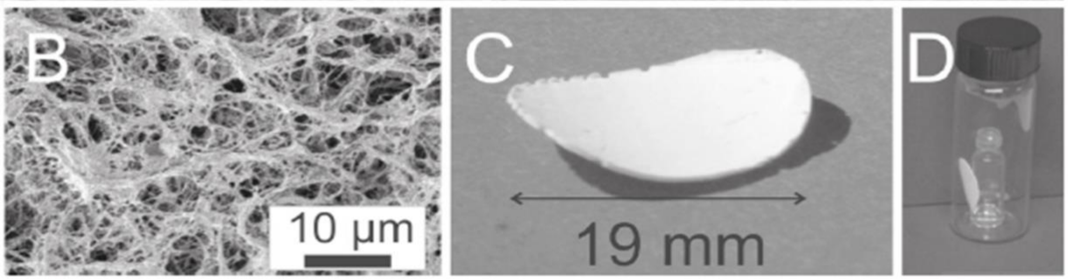
Dimensionally stable



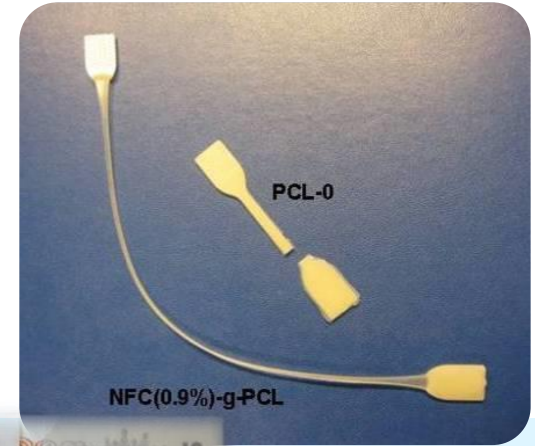
Oxygen barrier

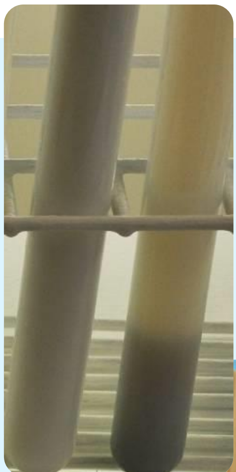


Thermal stability



Jin et al. *Langmuir* **2011**, *27*, 1930.





Other applications

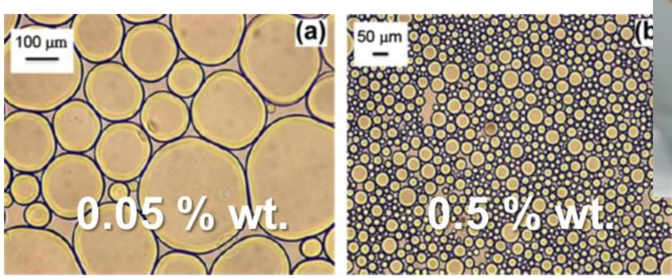
Aerogels
Composite materials
Rheology modifier
Emulsion stabilizer
3D printing

	v_f (vol.-%)	E (GPa)	$E_{norm} = (E / v_f)\times 0.6$ (GPa)	σ (MPa)
	0	3.0	-	71
es	58 ± 1	8.5 ± 0.2	8.8 ± 0.2	96 ± 1
es	49 ± 2	7.1 ± 0.1	8.7 ± 0.2	102 ± 1

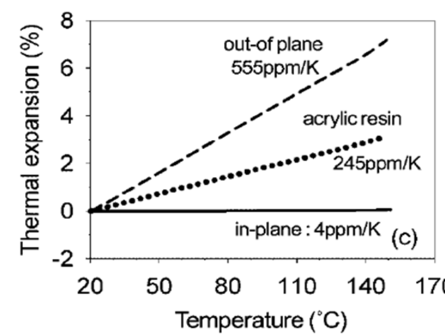
K.-Y. Lee, et al **2012**.

Jämsä, et al. 2010

Printed structures before and after freeze-drying

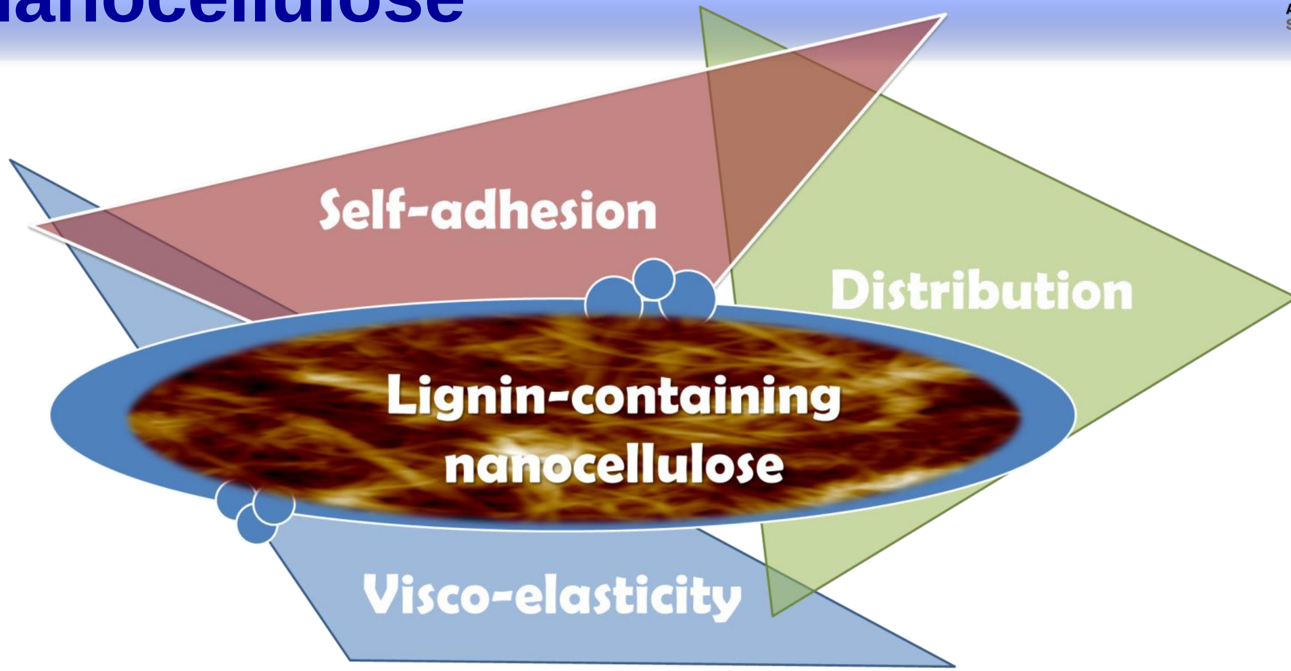


Zoppe, et al., 2011



Nogi and Yano *Adv. Mater.* **2008**, *20*, 1849.

Ligno-nanocellulose



- Higher yield
- Lower production costs
- Lower environmental impact

- Lignin can adjust cellulose polarity and hydrophilicity

AVAP® (American Value Added Pulping)

- Kraft pulp mill: 50-60% of the wood is burned for Energy and chemical recovery

AVAP® utilizes SO2-EtOH-water cooking technology

1) Pulp
2) Volatile cooking chemicals are stripped and reused
3) Lignosulfonates are precipitated and burned (Energy)
4) Sugar rich solution is fermented (22.6M Ga/bioethanol/year)

- Ethanol processing occurs concurrently with pulping: heat and chemical input are split between the two products, without sacrificing the yield of each product

- Additional components are obtained

*American Process Incorporated, Atlanta, GA

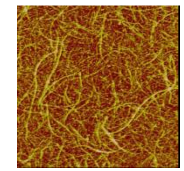
LCNF and nanopapers manufacture

SO2–EtOH–H2O
(SEW *)

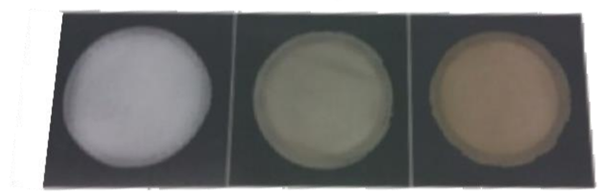
0, 2, 4 and 14% L

Microfluidizer

6 passes



1. Filtration
2. Cold press
3. Hot press



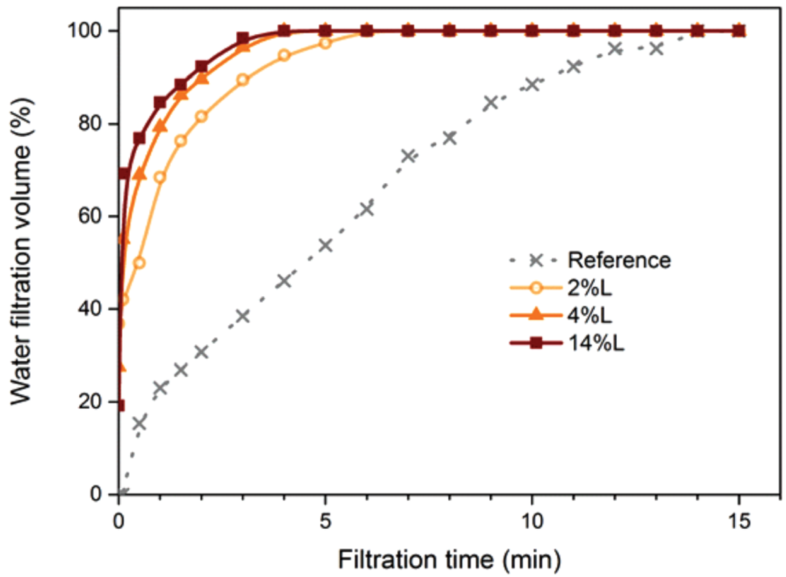
*American Process Inc,
AVAP® (American Value Added Pulping)

Rojo et al. Green Chem., 2015, **17**, 1853

Filtration time in LCNF nanopapers

Lower energy consumption for LCNF production was reported

K. L. Spence et al, Cellulose, 2010, 17, 835 and Cellulose, 2011, 18, 1097.

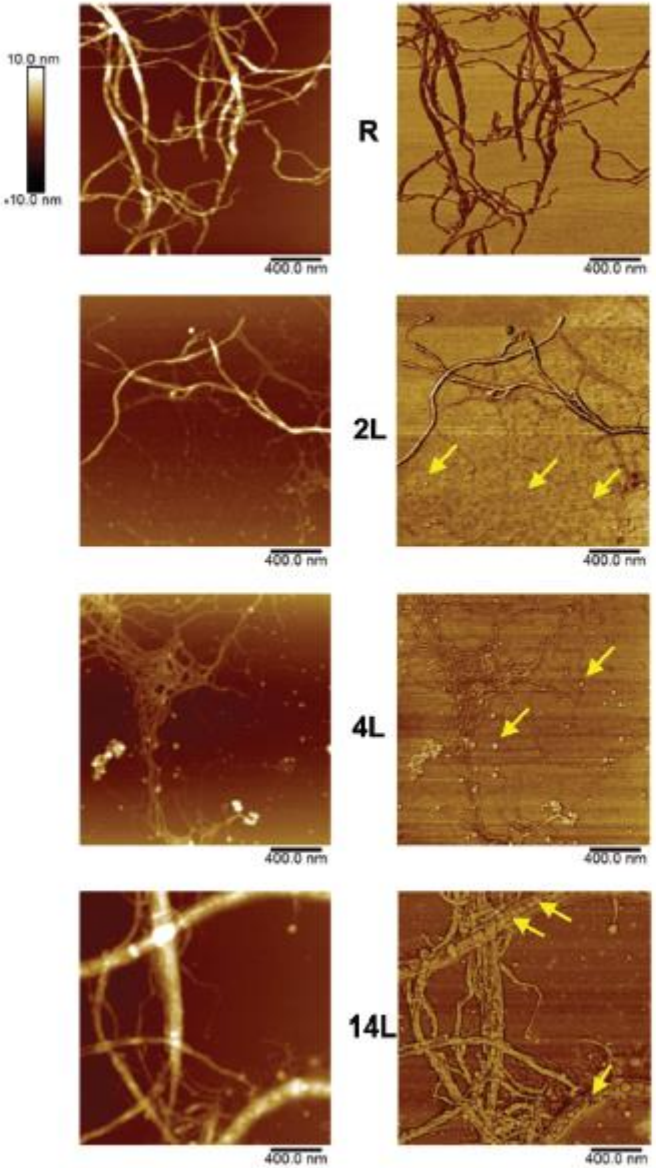


Filtration time decreases ~70 % with lignin → Energy savings!

- ❑ Stiffer fibrils
- ❑ More open structure

Rojo et al. Green Chem., 2015, **17**, 1853

Morphological investigation (AFM)



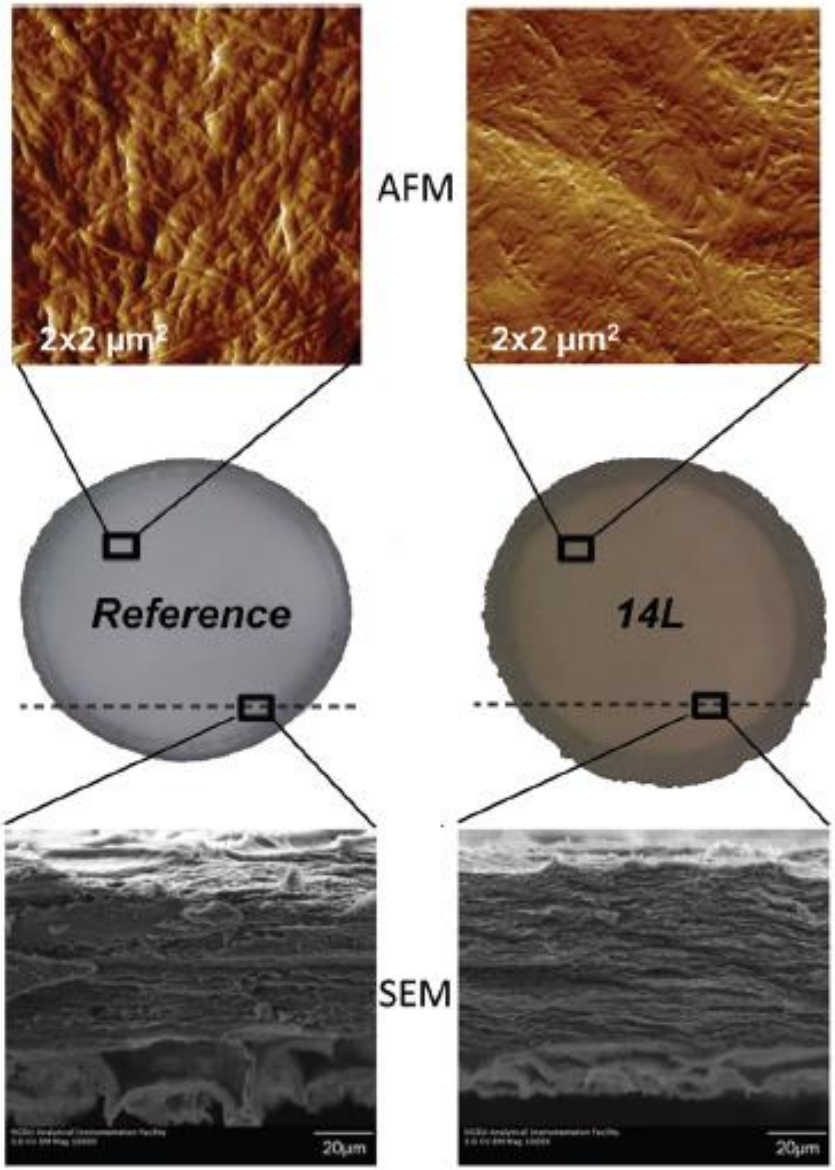
- Globular-shape lignin nanoparticles within the fibrils

	Diameter (nm)
Reference	44 ± 3
2L	25 ± 1
4L	20 ± 2
14L	16 ± 2

- Smaller fibril diameter with higher lignin content

Rojo et al. Green Chem., 2015, **17**, 1853

Morphological investigation (AFM&SEM)



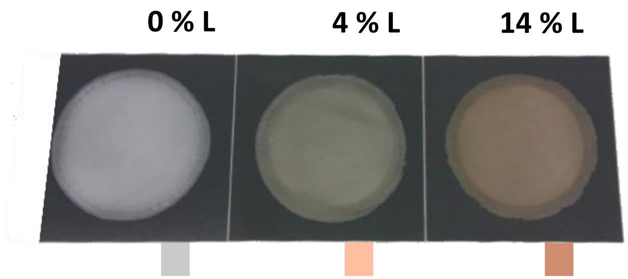
- ❑ Consolidated structures
- ❑ More pronounced laminar structure
- ❑ Lower roughness

AFM roughness:

- Reference -> 17.1 nm
- 14% -> 8.6 nm

Rojo et al. Green Chem., 2015, **17**, 1853

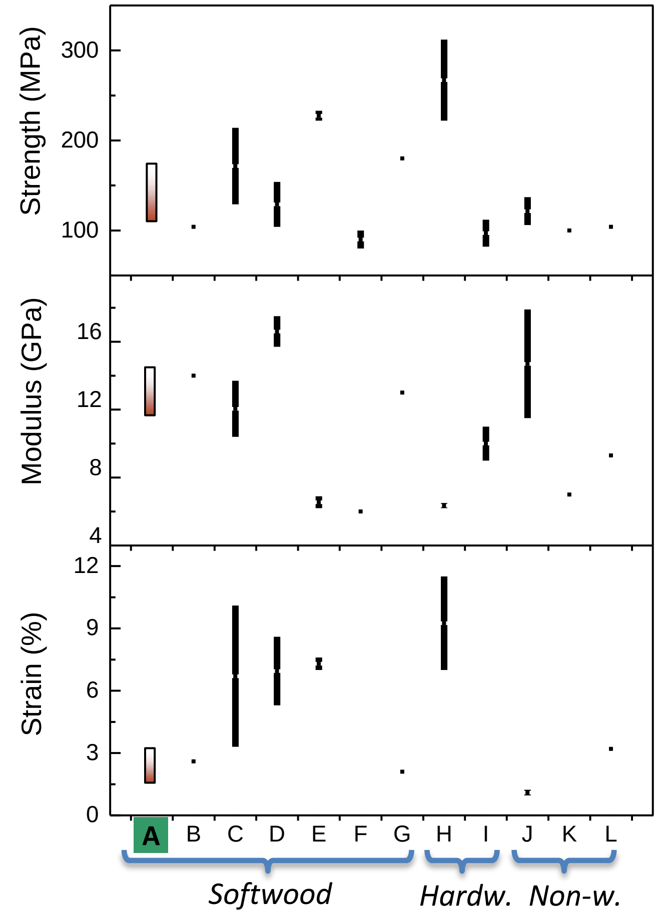
Mechanical properties



	Reference	2L	4L	14L
Density (g cm^{-3})	1.24 ± 0.03	1.10 ± 0.03	1.18 ± 0.05	1.20 ± 0.02
Tensile strength (MPa)	164 ± 17	123 ± 8	156 ± 17	116 ± 7
Tensile index (kN m kg^{-1})	132 ± 14	112 ± 7	132 ± 15	97 ± 6
Breaking strain (%)	2.9 ± 0.1	3.5 ± 0.5	2.8 ± 0.4	1.7 ± 0.3
Elastic modulus (GPa)	14.3 ± 0.5	10.5 ± 0.1	13.4 ± 0.9	12.2 ± 0.2
Specific elastic modulus (MN m kg^{-1})	11.5 ± 0.4	9.5 ± 0.1	11.4 ± 0.8	10.1 ± 0.2
Specific TEA (kJ g^{-1})	1.9± 0.3	2.0 ± 0.4	1.6 ± 0.3	0.7 ± 0.2

A: Present work

B-L: Lit values



Competitive mechanical properties of all the nanopapers

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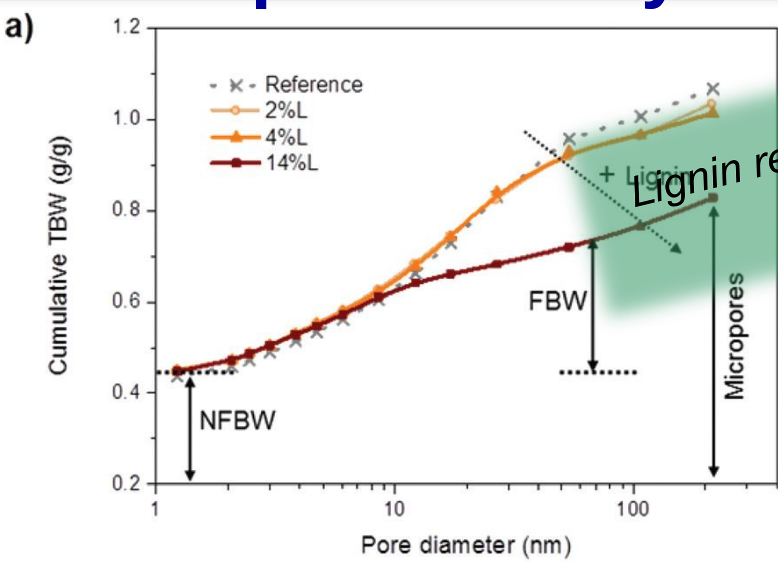
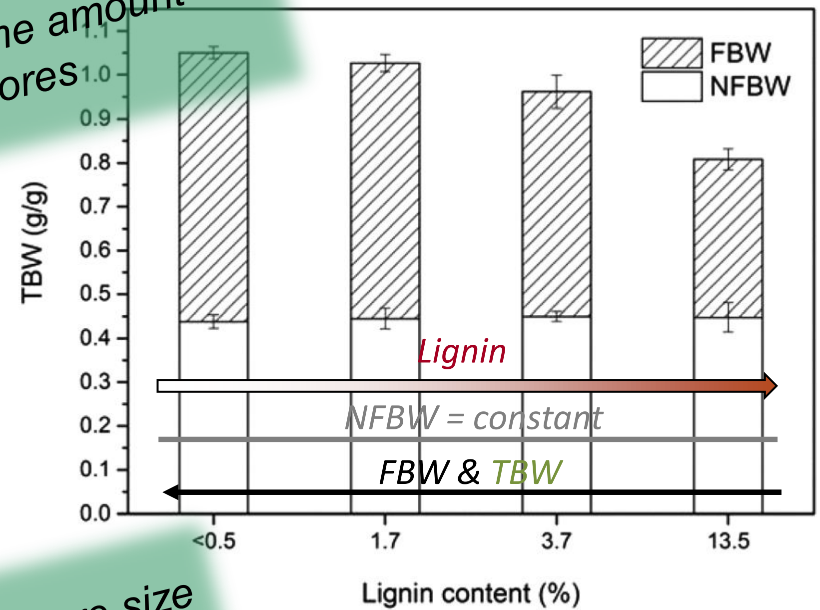
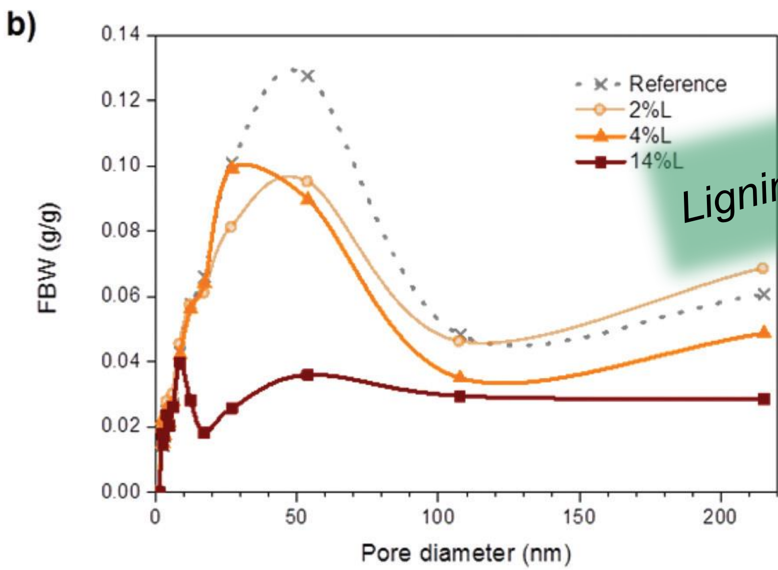
Thermoporosimetry

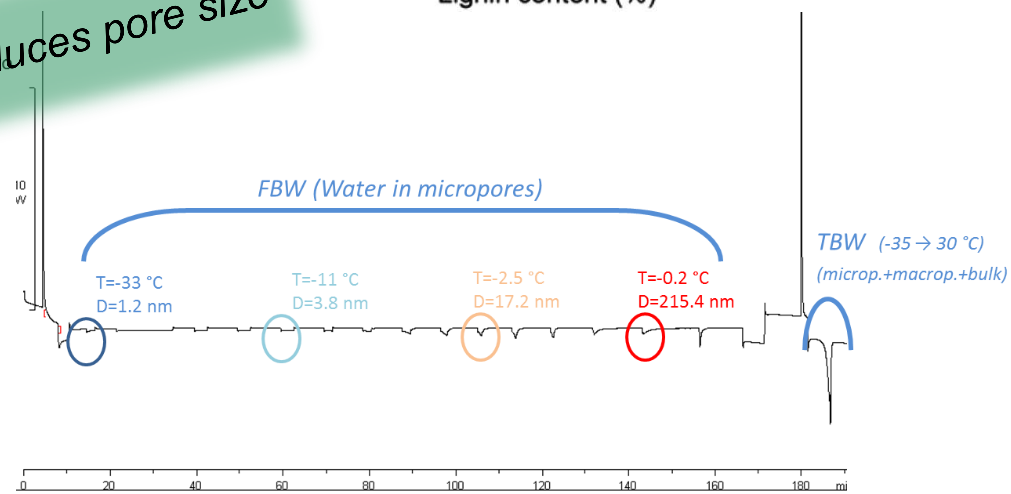


Lignin reduces the amount of micropores





Lignin reduces pore size



Rojo et al. Green Chem., 2015, **17**, 1853

Static water contact angle and surface energy

Aalto University School of Science | VTT

Acid-base theory

$$(1+cos\theta)\cdot\gamma_{lv} = 2\cdot\left(\sqrt{\gamma^{LW}{}_{l}\cdot\gamma^{LW}{}_{s}}+\sqrt{\gamma^{-}{}_{l}\cdot\gamma^{+}{}_{s}}+\sqrt{\gamma^{+}{}_{l}\cdot\gamma^{-}{}_{s}}\right)$$

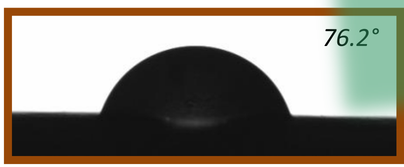
$$\gamma_s = \gamma^{LW} + 2\sqrt{\gamma^+\gamma^-}$$

γ^{AB}

0 % L

4 % L

14 % L



WCA increases ~ 40° with lignin

	$\gamma^{TOT a}$	γ^{LW}	γ^{AB}	γ^-	γ^+	γ^-/γ^+	ΔG^{IF}_{SWS}
Test liquids							
Water	72.8	21.8	51	25.5	25.5	—	—
Formamide	58	39	19	39.6	2.28	—	—
Diiodomethane	50.8	50.8	0	0	0	—	—
Ethylene glycol	48	29	19	47	1.9	—	—
Nanopaper							
Reference	52.6	48.6	4	40.2	0.1	400	13.8
2L	53.9	45.5	8.5	24	0.7	32	−11.0
4L	52.3	44.5	7.8	11.8	1.3	9	−33.3
14L	46.7	43.2	3.5	2.3	1.4	2	−62.2

[a] $\gamma^{TOT} = \gamma_L$ for the test liquids and $\gamma^{TOT} = \gamma_S$ for the nanopapers.

Liquid	Contact angle (°) of different nanopapers: Reference	2L	4L	14L
Water	35	49	61	78
Formamide	15	16	21	36
Diiodomethane	20	29	31	34
Ethylene glycol	18	13	20	34

[a] Standard deviation of the contact angle values was less than 2°.

Surface energy decreases with lignin (reduction of base component)

Hydrophobicity increased 6-fold with highest lignin content

“hydrophobic” vs “hydrophilic”

03/12/2015

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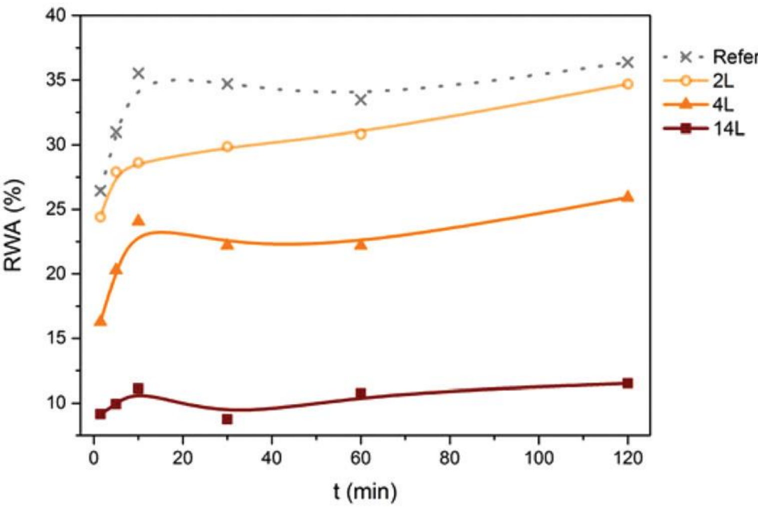
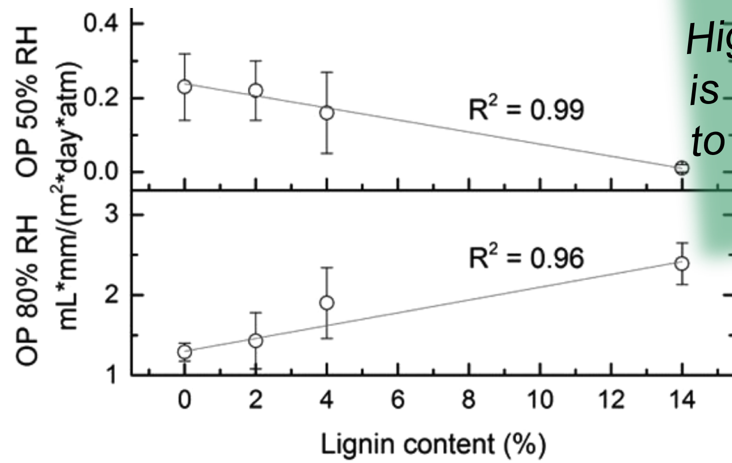
Relative water absorption capacity (RWAC)

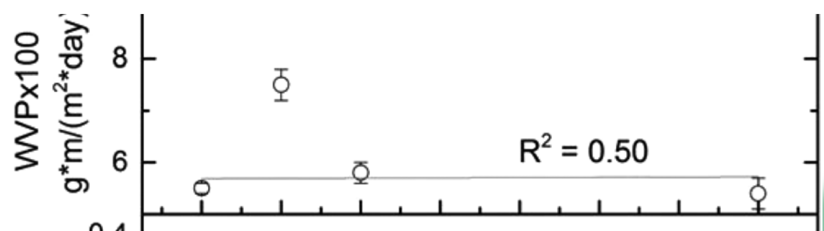


- Oxygen permeability



Higher RH decrease in OP is not significant compared to 15-fold decrease at 50% RH

- Water vapor transmission rate (23 °C, 50% RH "wet cup")



RWAC decreases with lignin

- Less porous structure
- Lower surface energy

WVTR is not affected by lignin ("...depends most significantly on ρ..." Kelley L. Spence)

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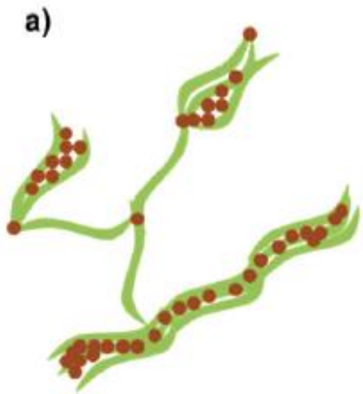
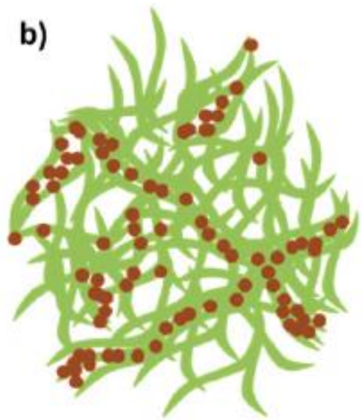
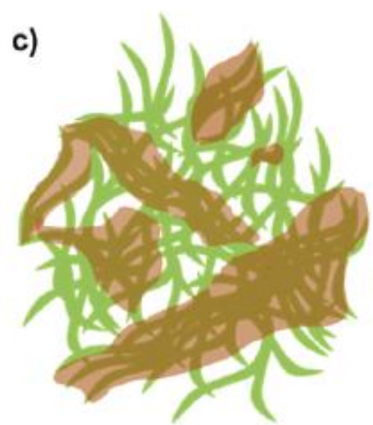
Hypothesis



Fibrillation: Detaching of lignin nanoparticles (NPs) from- and adherence to- CNF in suspension



Filtering: lignin starts filling some voids between the fibers



Pressing (100 °C@220 bar): lignin softening and completely filling voids

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Summary

- *Reduces filtration time*
- *Reduces roughness*
- *Competitive mechanical properties*
- *Reduces size and number of micropores*
- *Reduces surface energy (base component)*
- *Increases hysteresis (WCA) and chemical heterogeneity*
- *Increases WCA and hydrophobicity*
- *Reduces water absorption capacity*
- *Impairs O_2 transmission at low RH*

Lots of work to do!

- CNFs have a great potential as strength additives, in multilayer films&membranes and as rheology modifiers
- Application driven approach: Combine the right raw material with the most suitable production technology
- Think out the box: different is good! Original pulp composition might be beneficial
- Team work is needed!

CAN CELLULOSE REALLY REPLACE PLASTICS IN AN ECONOMICALLY FEASIBLE MANNER?

Muchas gracias!!!

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Under the theme: "***Building bridges in research and innovation for sustainable bioeconomy***", the IX Ibero-American Conference on Pulp and Paper Research, CIADICYP 2016 will be held in FINLAND, on September 25-28, 2016.

The call for papers will open soon.

September 25-28 2016

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IX CONGRESO IBERO-AMERICANO DE INVESTIGACIÓN EN CELULOSA Y PAPEL - CIADICYP 2016

Bajo el lema: "***Construyendo puentes en investigación e innovación para la bioeconomía sostenible***", el IX Congreso Ibero-Americano de Investigación en Celulosa y Papel, CIADICYP 2016 se realizará en FINLANDIA, del 25 a 28 septiembre 2016.

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