Valorization of Biorefinery Streams by the Development of Advanced Materials from Lignin and Nano/micro-celluloses

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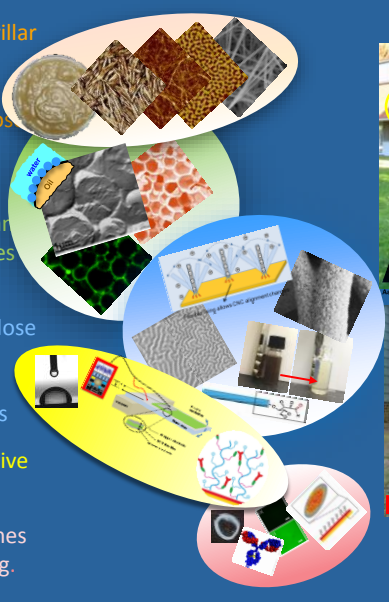
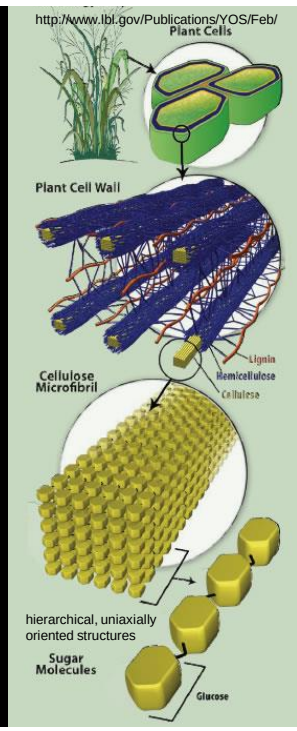
Focus areas

1. Nano/microfibrillar ligno-cellulose, nanocrystals & bacterial cellulos
2. Multiphase systems: dispersions, foar gels, membranes and aerogels.
3. Lignonanocellulose thin films & nanopaper & hybrid materials
4. Stimuli-responsive systems.
5. Proteins, enzymes and (bio)sensing.



Four promising components in the Circular Economy:
Fibre, Lignin, Sugars and Nanocellulose

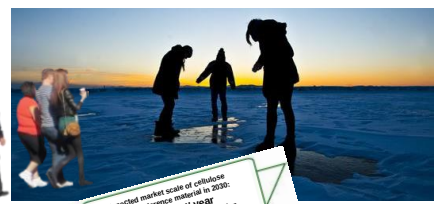


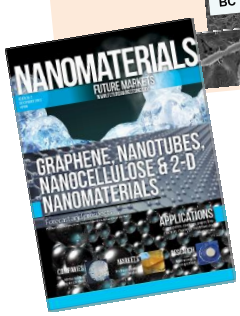
Cellulose
- CNC and coatings
- Nanopaper, films
- Emulsions
- Filaments
- ~~Bioactive Materials~~
- Foams and Aerogels

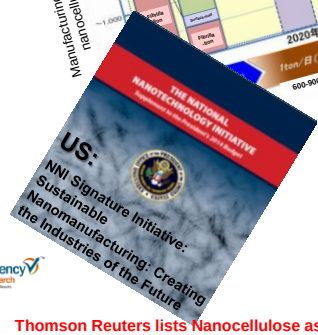
Hemicelluloses
- ~~Barrier effects~~
- ~~Bioconversion~~

Lignin
- Microparticles
- Emulsions
- Micro/nanofibers
- Foams and Aerogels
- ~~Antioxidation~~
- Carbon fibers/electrodes

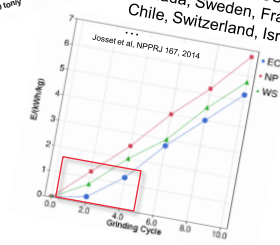
Nanocellulose from wood





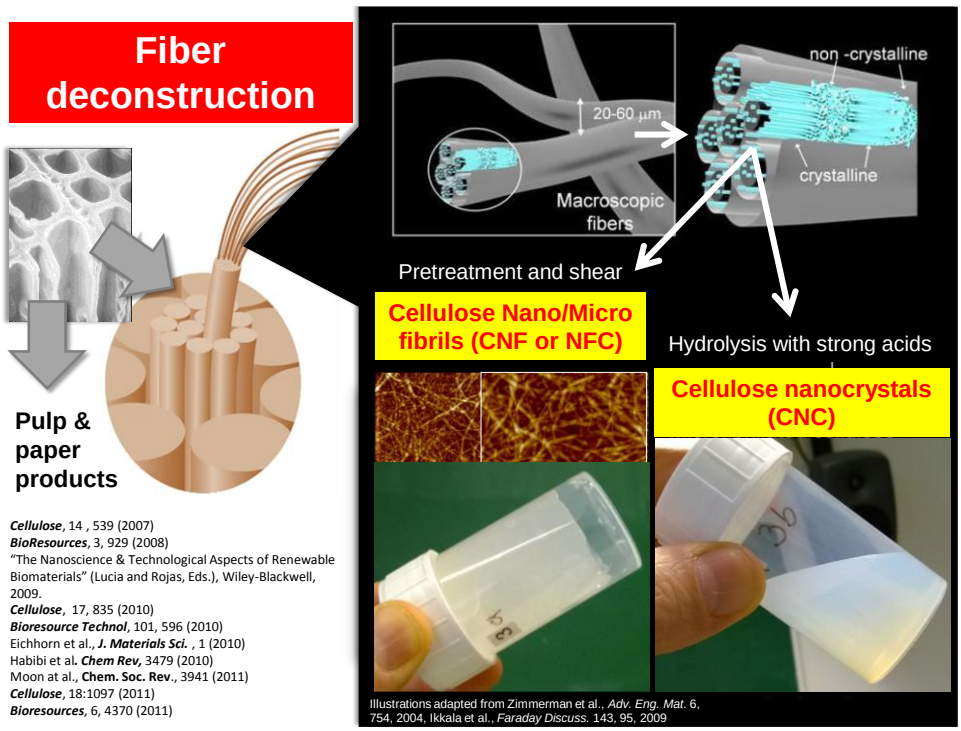


…nd, Sweden, US, Canada, Sweden, France, Chile, Switzerland, Israel …



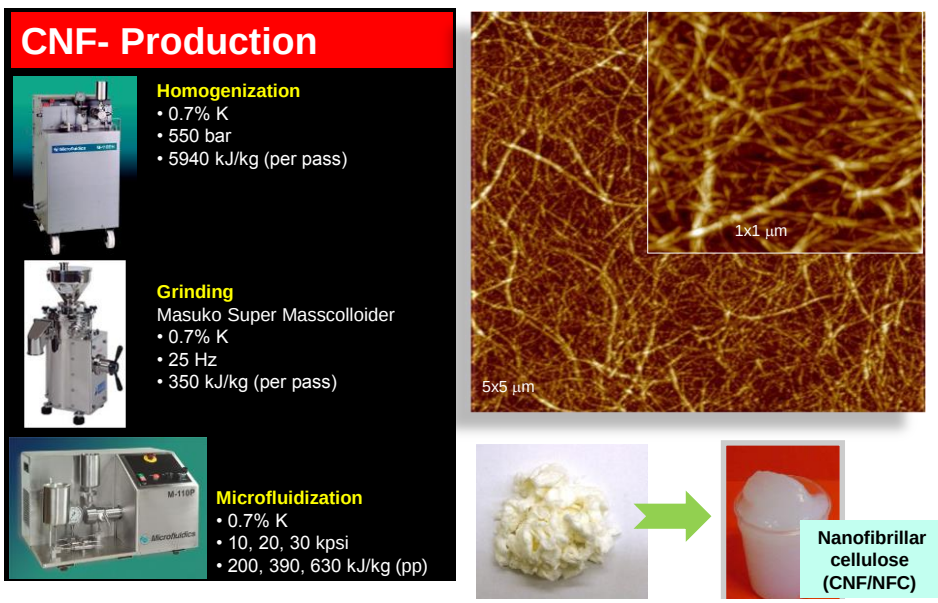
Global nanocellulose market at $55 million in 2014. Anticipated to expand at 34%/y between 2015 and 2023

Thomson Reuters lists Nanocellulose as one of the top 10 innovations by 2025!

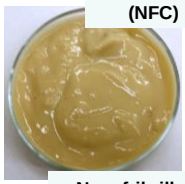


Cellulose, 14 , 539 (2007)
BioResources, 3, 929 (2008)
"The Nanoscience & Technological Aspects of Renewable Biomaterials" (Lucia and Rojas, Eds.), Wiley-Blackwell, 2009.
Cellulose, 17, 835 (2010)
Bioresource Technol, 101, 596 (2010)
Eichhorn et al., ***J. Materials Sci.*** , 1 (2010)
Habibi et al. ***Chem Rev,*** 3479 (2010)
Moon et al., **Chem. Soc. Rev**., 3941 (2011)
Cellulose, 18:1097 (2011)
Bioresources, 6, 4370 (2011)

CNF nanopapers: strong barriers

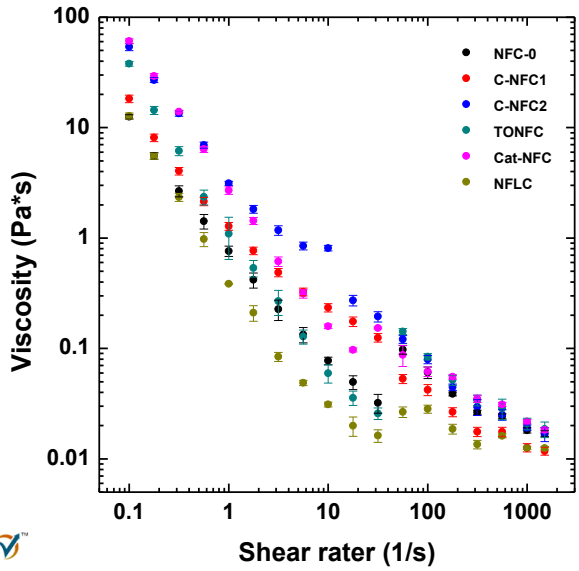


Nanofibrillar cellulose (NFC)



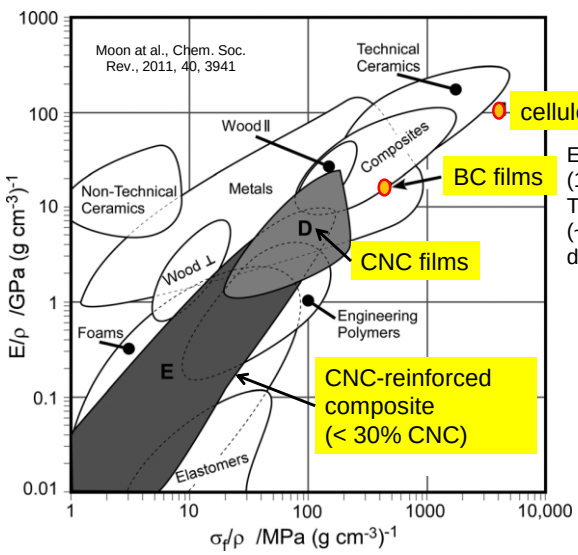
Nanofribrillar lignocellulose (NFLC)

Nanocellulose: rheological modifier in drilling fluids



Oil and gas is likely to be the fastest growing end-user for nanocellulose in the near future

Transparency Market Research



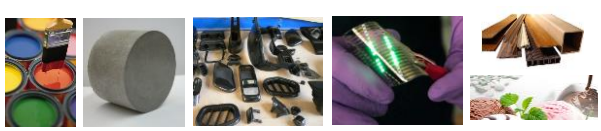
cellulose I

BC films

CNC films

CNC-reinforced composite (< 30% CNC)

Elastic modulus (100-150 GPa)
Tensile strength (~10 GPa) in axial direction

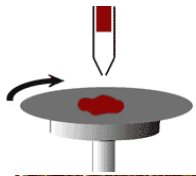


Coatings

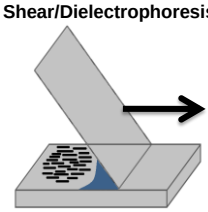
CNC

Film casting

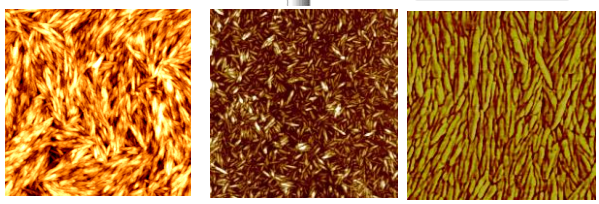
Spin coating



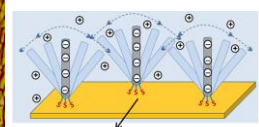
Shear/Dielectrophoresis



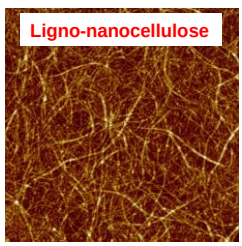
Soft Matter 7 , 1957 (2011)
Biomacromolecules, 11, 2683 (2010)
Biomacromolecules , 11, 674 (2010)
Appl. Mater. Interfaces , 1, 1996 (2009)
Langmuir, 26, 990 (2010)
Thin Solid Films, 517(15), 4348 (2009)
ChemSusChem, http://dx.doi.org/10.1002/cssc.201500819 (2015)

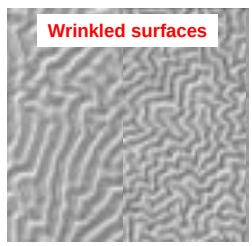


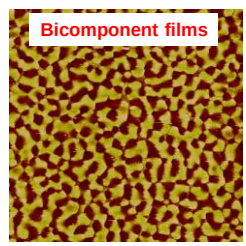
End-on assembly



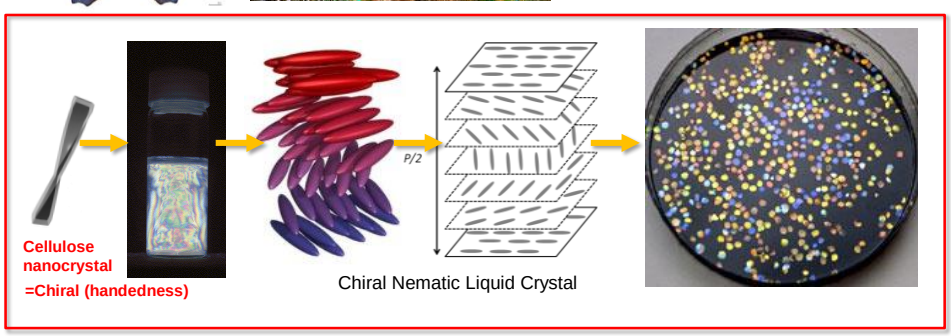
CNF+…



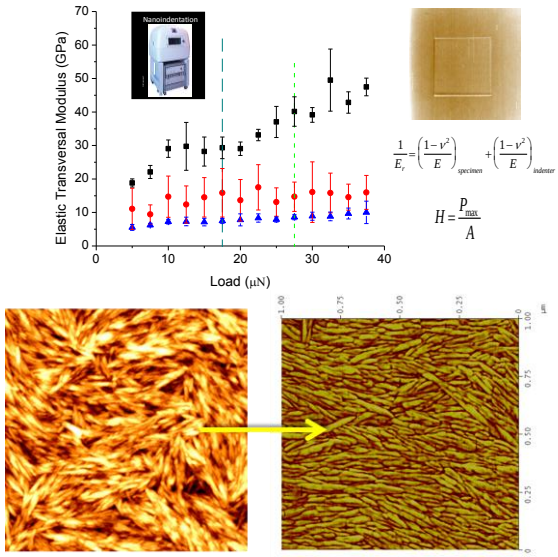




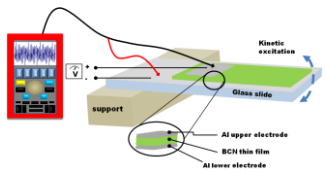
CNC self-assembly: liquid crystals & coatings



Aligned CNC: strong coatings and piezoelectric actuation



Energy harvesting: Converse Piezoelectric Effect



Langmuir, 26, 990 (2010)
ACS Macro Letters, 1, 867 (2012)
JCIS, 363, 206 (2011)
Soft Matter, 7, 1957 (2011)

Ligno-nanocelluloses from residual fibers

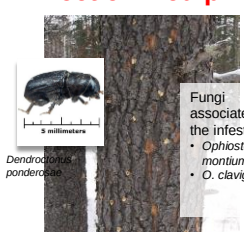
Coconut husk (coir fibers)

Cacao pod husk

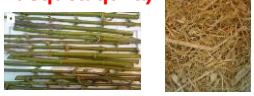
Bioresource Technology, 125, 249 (2012)
Cellulose, 19, 2179 (2012)
Journal Forest Science, 60, 3, 502 (2014)
Green Chemistry, 17, 1853 (2015)

Technical fibers (TMP, kraft, SEW fibers)

Beetle-killed pine



Quila (Chusquea quila)

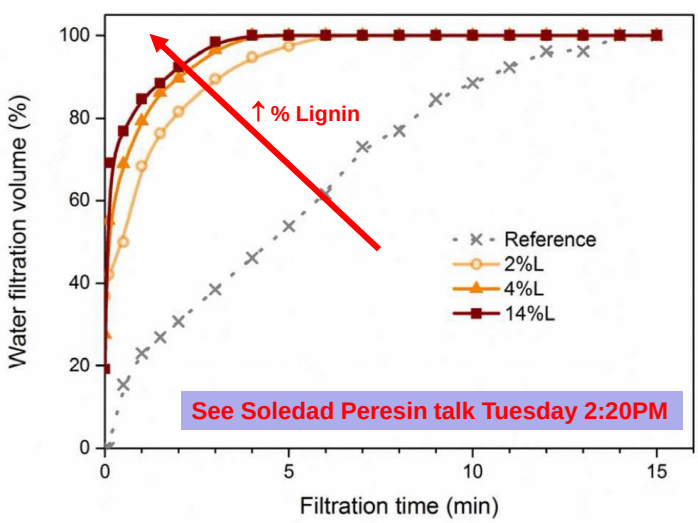


Soybean hulls

Palm empty fruit bunches

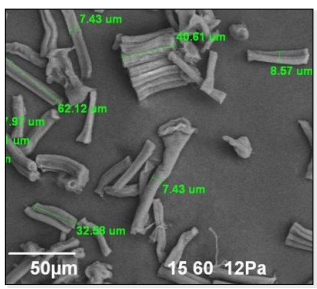
Ligno-nanocellulose

Film manufacture: improved dewatering with residual lignin



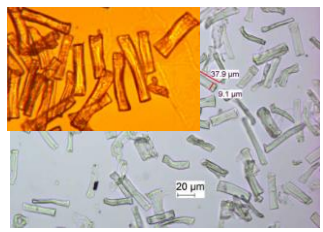
BITE125, 249 (2012)
Cellulose, 19, 2179 (2012)
Bioresources, 6, 4370 (2011)
Cellulose, 18,1097 (2011)
Cellulose, 17, 835 (2010)
BITE 101, 5961 (2010)
Green Chemistry, 17, 1853 (2015)
Biomacromolecules, 16,1062 (2015)

Soybean hull microparticles: shapes matter



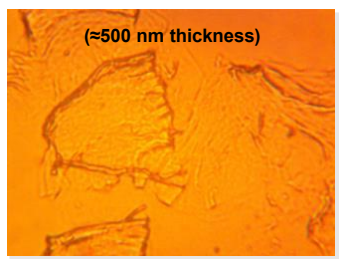
Pulping process releases individual and clusters of cellulose microfibrils

Cellulose 22, 3919 (2015)



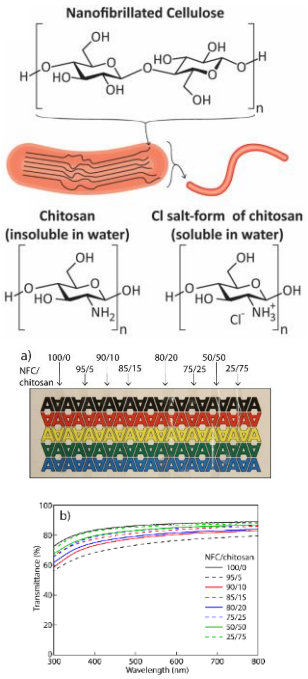
Processing allows the complete separation of individual cellulose microfibrils

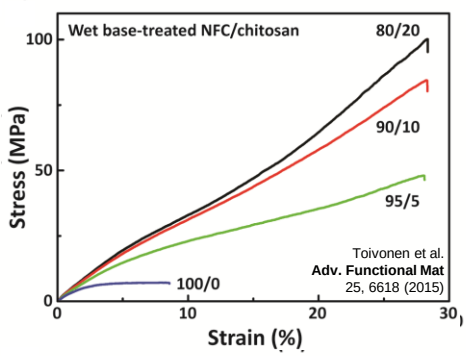
Cellulose microfibrils (CMF)



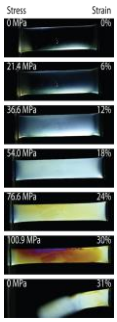
Cellulose microparticles (CMP)

CNF+Chitosan



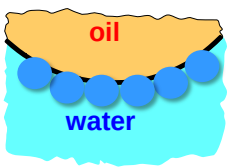


Toivonen et al.
Adv. Functional Mat
25, 6618 (2015)

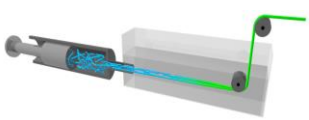


CNF, CNC, Lignin and starch

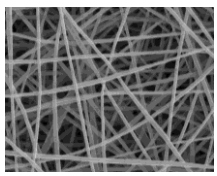
emulsions



Filaments (hydrogel spinning)

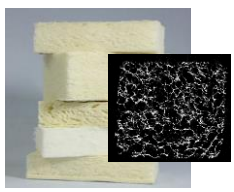


Fiber networks



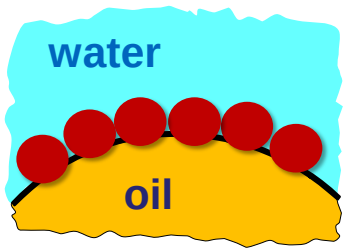
Bioactive surfaces

Aerogels and foams

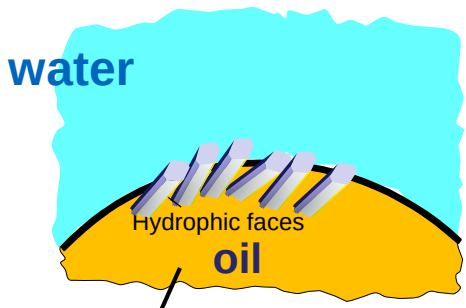


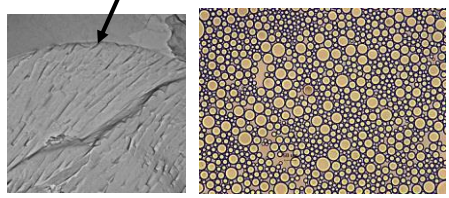
(Pickering) emulsions

Case of micro/nanoparticles



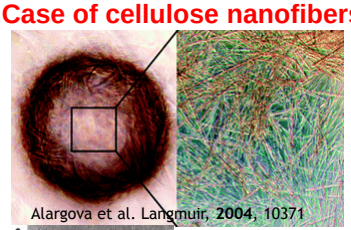
Case of cellulose nanocrystals

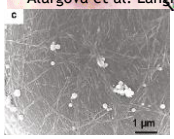




Soft Matter 2046 (2015)
Biomacromolecules, 12, 2788 (2011)
J Colloid & Interface Sci, 369, 202 (2012)

Case of cellulose nanofibers

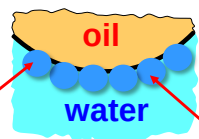


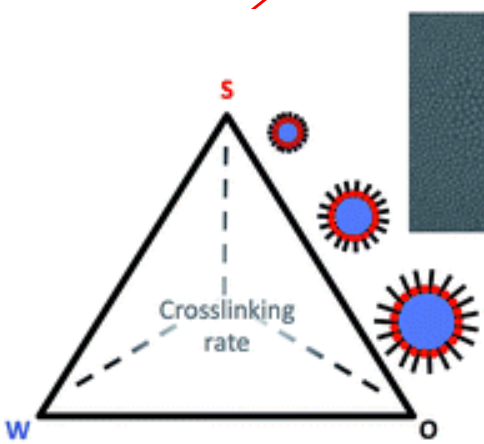


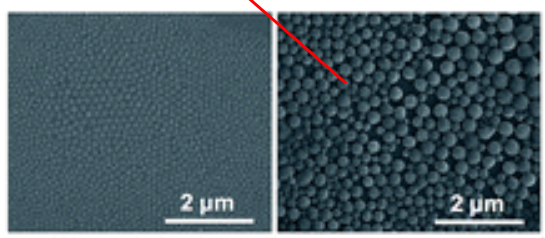
Kalashnikova et al.:
Langmuir 2011, 7471
Biomacromolecules 2011, 267.
Soft Matter 2013, 9,952

Lignin:

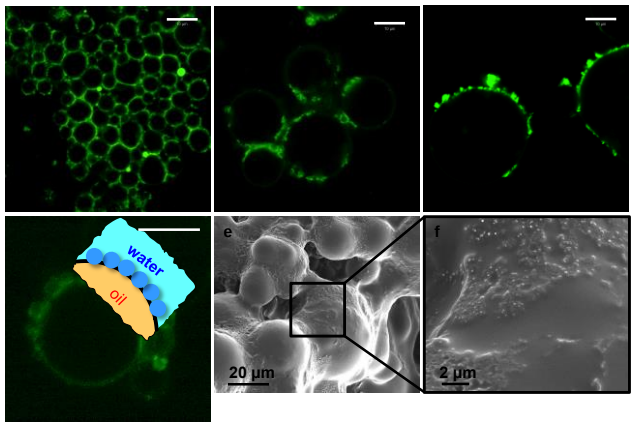
Hydrophilic particles







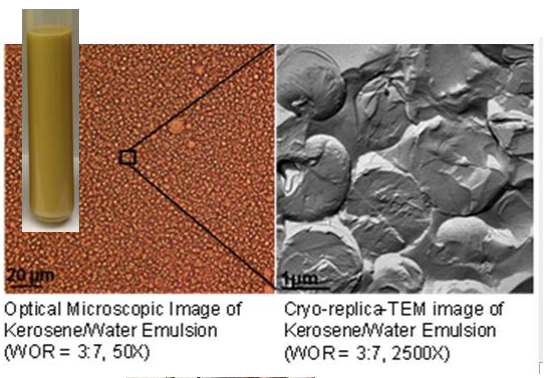
Soft Matter 2046 (2015)



Lignin supracolloids synthesized from (W/O) microemulsions: use in the interfacial stabilization of Pickering systems and organic carriers for silver metal

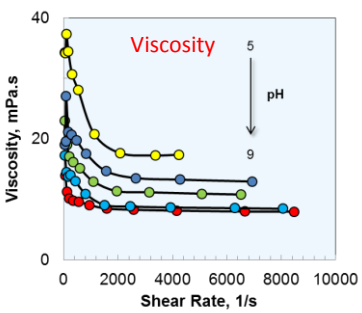
Nypelö, Carrillo et al, *Soft Matter* 2046 (2015)

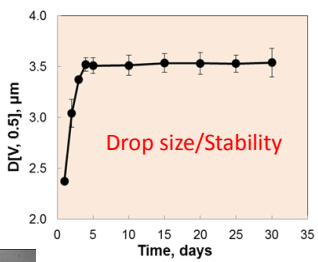
Fuel emulsions



Optical Microscopic Image of Kerosene/Water Emulsion (WOR = 3:7, 50X)

Cryo-replica-TEM image of Kerosene/Water Emulsion (WOR = 3:7, 2500X)

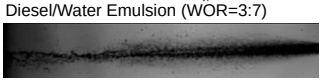




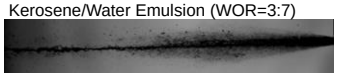
Bitumen
Biodiesel

Diesel

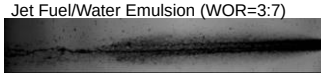
Diesel/Water Emulsion (WOR=3:7)



Kerosene/Water Emulsion (WOR=3:7)



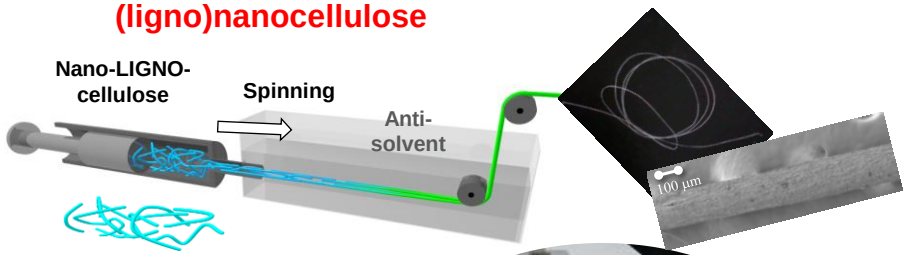
Jet Fuel/Water Emulsion (WOR=3:7)



Reduce viscosity
Improve combustion efficiency
Reduce NOX, SOx

Cellulose I filaments: technical textiles & composites

Wet (hydrogel) spinning of (ligno)nanocellulose



Lignin

Design Driven Value Chains in the World of Cellulose DWoC

See Johanna Buchert talk Monday 1:40

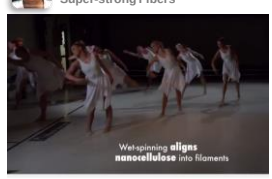
Hydrogel and Wet spinning

Design Driven Value Chains in the World of Cellulose, DWoC

J. Mater. Chem. A, 2014, 2, 10776

Tero Kämäräinen
Supra-colloids

Meri Lundahl
Super-strong Fibers



Dance your PhD 2015 Chemistry: Wet-spinning of Nanocellulose

https://www.youtube.com/watch?v=qqZV55yqCiA

Aalto University
School of Chemical Technology

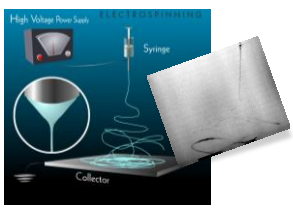
Micro-Fiber networks & nonwovens

Appl. Mater. Interfaces, 1, 1996 (2009)
Biomacromolecules, 11: 674 (2010)
Biomacromolecules 11: 2471 (2010)

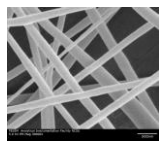
J. Polym. & Environ., 20, 1075 (2012)
Biomacromolecules, 13: 918 (2012)

J. Appl. Polym Sci., 131, 11 (2014)
ACS Appl. Mat. & Interfaces, 4(12): 6849 (2012)

Reactive & Functional Polym, 85, 221 (2014)
ACS Applied Mat. & Interfaces, 5, 11768 (2013)



Lignin fibers



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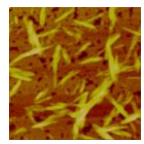

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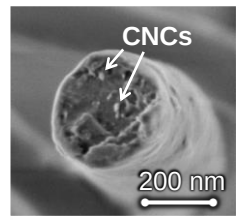
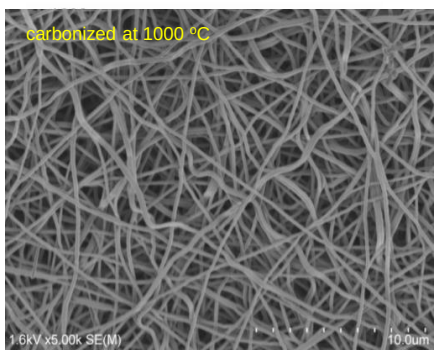
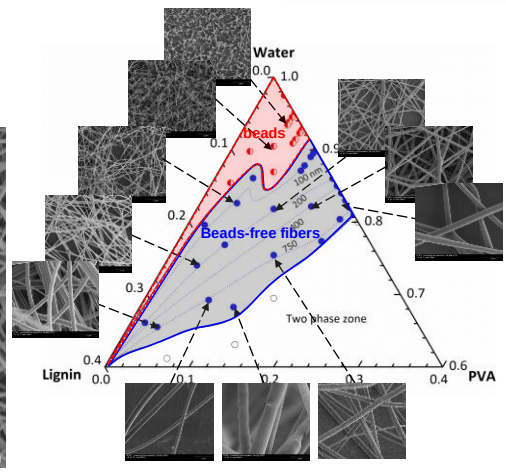
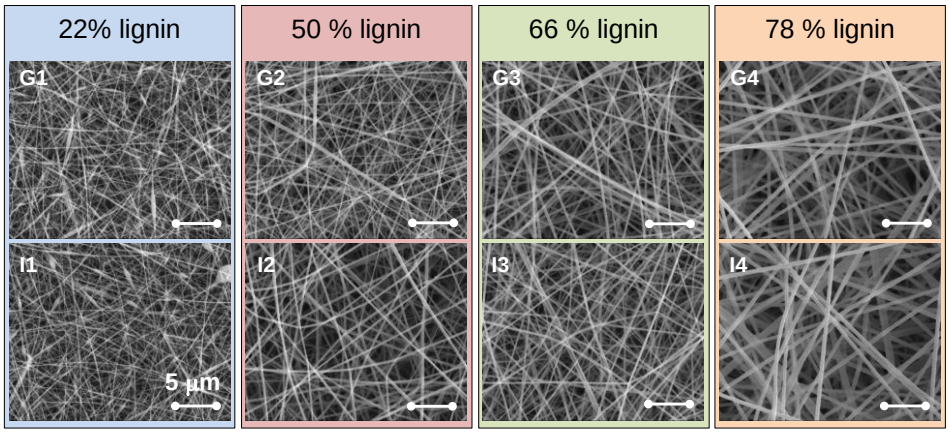






Ago, et al., *Biomacromolecules*,13: 918 (2012)

Lignin-Soy protein Nanofibers



Fiber diameter (nm)

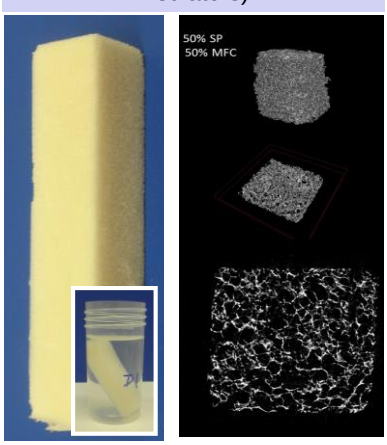
Sample	Glycinin	Isolate
1	125±27	113±26
2	191±31	246±38
3	280±38	222±29
4	392±50	438±49

Reactive & Functional Polymers , **85, 221(2014)**

Aerogels and foams

Aerogels:

low density solid foam materials that contain ~98% air (very light, extremely strong, and excellent insulators)



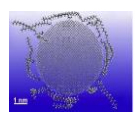
Arboleda et al., **Cellulose** 20, 2417 (2013)
Toivonen et al. **Biomacromolecules**, 16:1062 (2015)

High specific surface area + low density:

Thermal/sound insulation

Packaging

Nonwoven

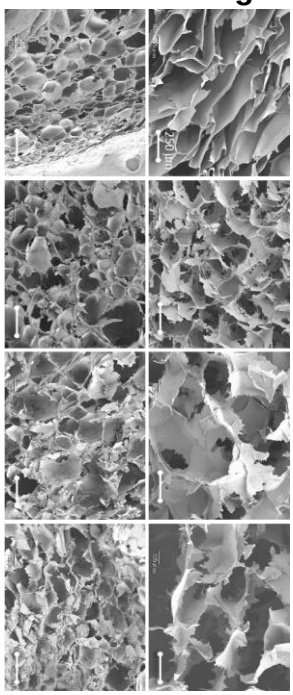


Surface chemistry and catalysis

Absorption

Filters

Starch-CNF aerogels

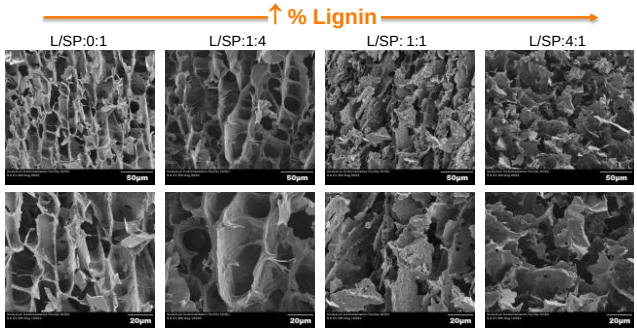


Completely biodegradable and physical/mechanical properties comparable to products from synthetic polymers.

Single-use EPS

New York City has banned single-use expanded polystyrene (EPS) foam items and packaging, starting July 1 2015.

Soy Protein-lignin aerogels



Foam Forming

<1982: US 4488932 A
>2000: VTT

Fibers are mixed with foam instead of water

- Prevent fiber flocculation
- Reduce water consumption

Pilot Scale Foam Forming – Suora (VTT)

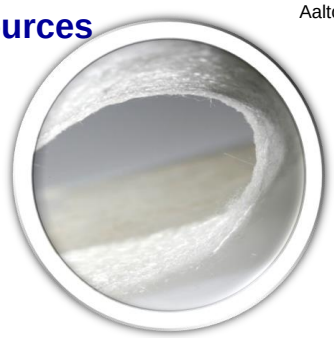
Eerkki. Hellén and Harri Kiiskinen. *VTT Business Review Webinars. 2014*

Potential Applications

Packaging
Tissues
Insulation
Hygienic products
Composites…

Foam-formed paper is being produced from different surfactant types, fiber sources and refining levels

Forest Meets Chemistry
Aalto VTT Bioeconomy



		TMP (644(H)/466(M) / 166(L) CSF)	Pine Kraft (17.7(L)/22.4(M)/ 38.5(H) SR)
SURFACTANTS	Anionic	✓	✓
	Cationic	✓	✓
	Nonionic	✓	✓
	Amphoteric	✓	✓

→ Foam forming
→ Water forming

Properties tested

- Density
- Formation
- Strength (*)
- Elongation at break (*)
- Light scattering
- Scott bond (*)
- Permeability
- Water retention

((*)both, in machine and cross-direction)

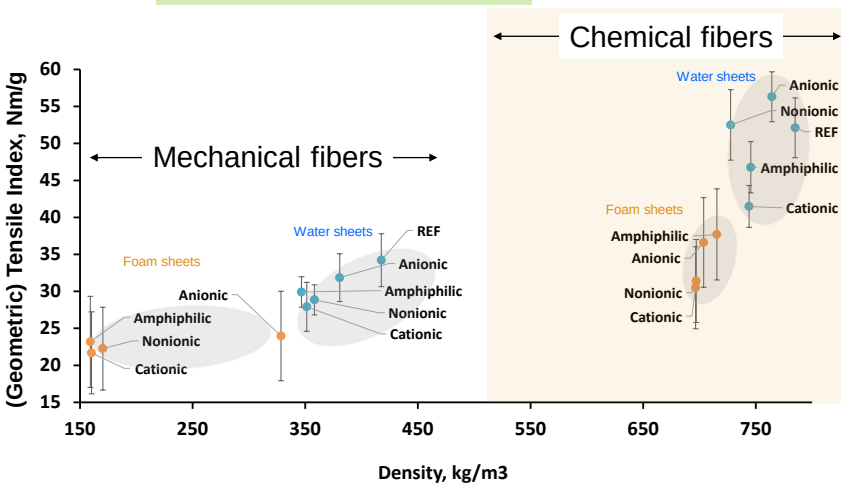
Strength of Foam-formed Paper

(as an example)

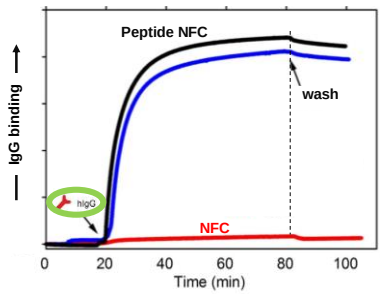
Aalto University

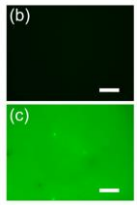
Forest Meets Chemistry
Aalto VTT Bioeconomy

Foam forming improves:
✓Formation (uniformity)
✓Bulk (low density structures)
✓Dryness after wet pressing

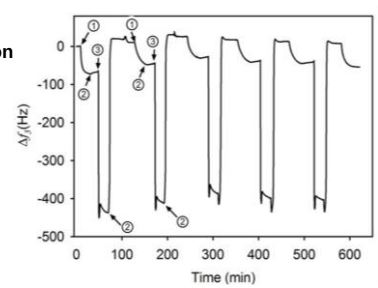


Biomolecule binding, detection, biofiltration

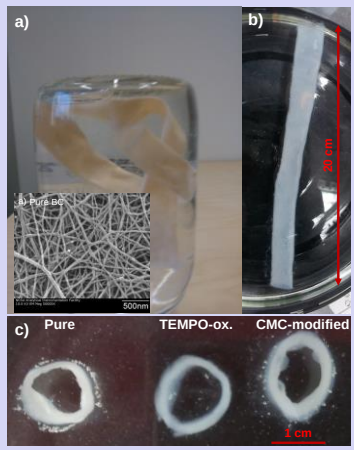




Regeneration

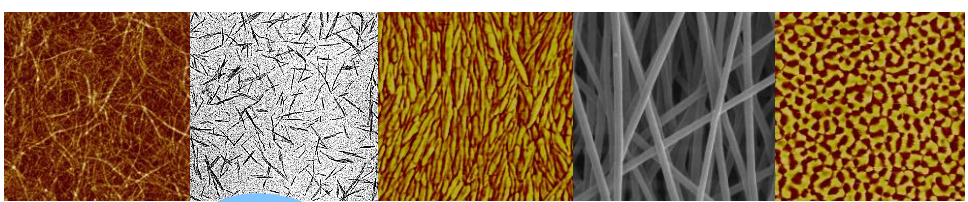


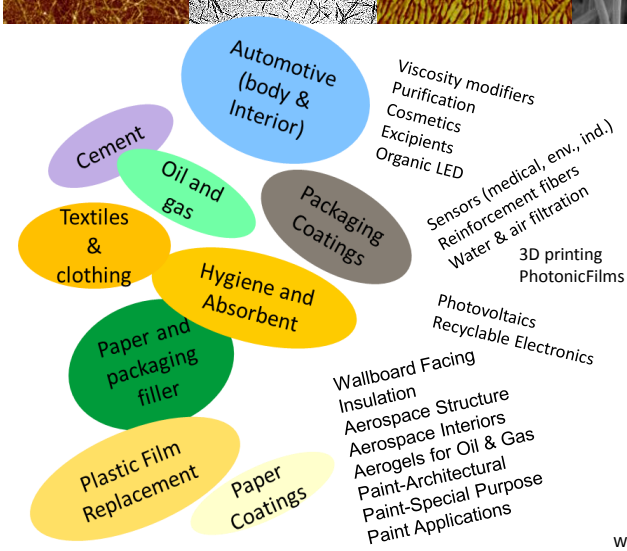
Engineered tubes in biofiltration via bioactive molecule functionalization



See Ilari Filpponen talk Tuesday 2:00PM

RSC Advances, 4, 51440 (2014)
Anal. Chem, 85, 1106 (2013)
Biointerphases, 7, 61 (2012)
Biomacromolecules, 12, 4311 (2011)
Biomacromolecules, 13, 2802 (2012)
Carbohydrate Polymers, 100, 107 (2014)
Carbohydrate Polymers, 100, 166 (2014)
Carbohydrate Polymers 126, 32 (2015)





More in:
www4.ncsu.edu/~ojrojas/publications.htm