Nanoparticles from biological source and polymer nanocomposites

Alain Dufresne

UMR 5518 CNRS / Grenoble Institute of Technology (Grenoble INP), France

2018 IMAGINENANO

IC2 nano International Composites Conference

March 14-15, 2018 ● Bilbao (Spain)

NEW CONFERENCE

Biobased (Green) Materials

Increasing demand for products made from renewable and sustainable non-petroleum based resources (**green materials**)

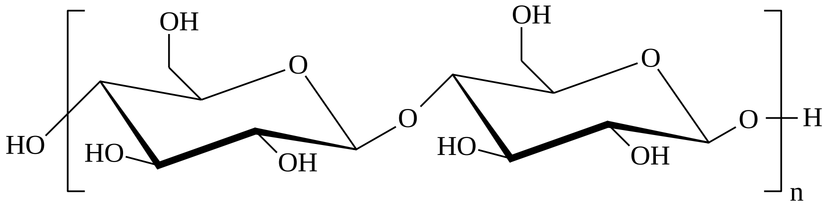


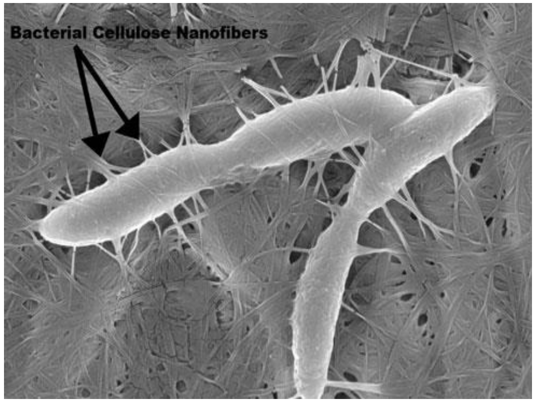

Limitation: economically viable materials → **Polysaccharides?**

LGP2

Cellulose

Structural material in plants, animals, bacteria





Natural (Lignocellulosic) Fibers

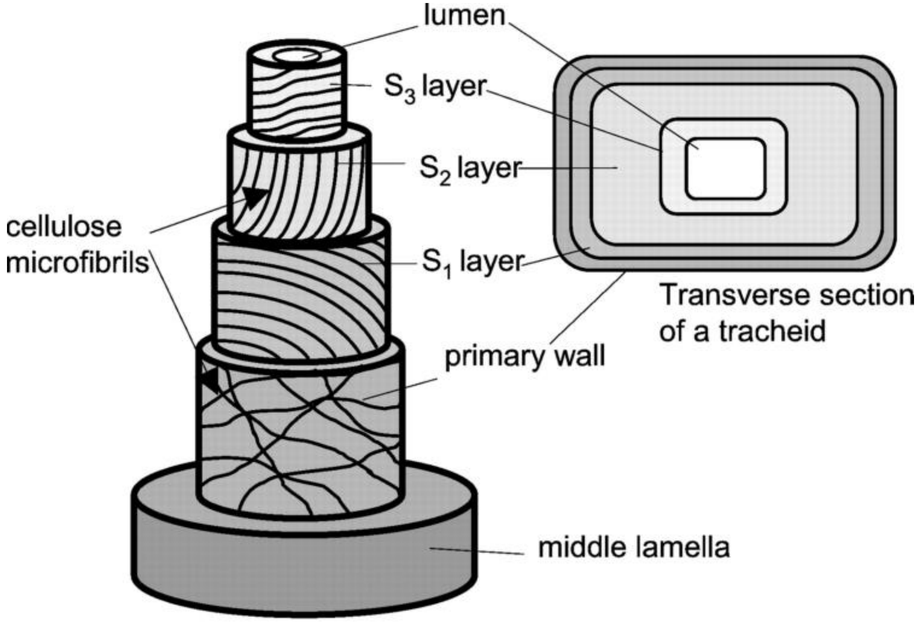
Reinforcing element in composites

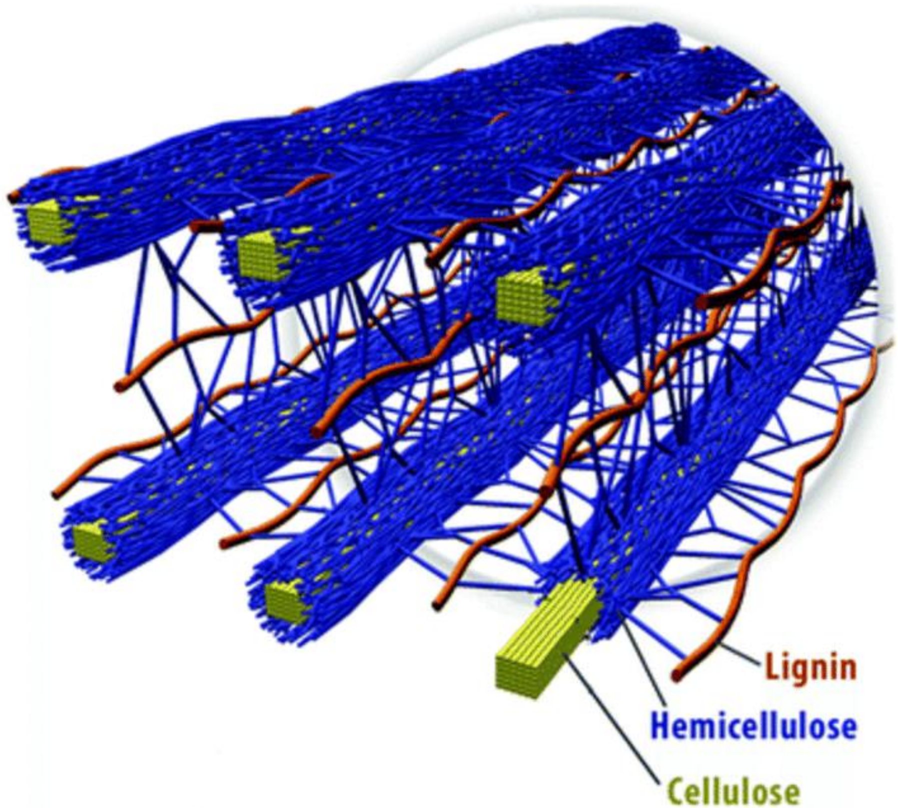
Low density, low cost, high specific strength and modulus, renewability, biodegradability, availability in a variety of forms throughout the World, flexibility, non abrasive nature to processing equipment, non-toxicity, easiness to handle, high ability for surface modification, possibility to generate energy, without residue after burning at the end of their life-cycle, economic development opportunity for non-food farm products in rural areas

Hydrophilic character : poor adhesion and dispersion in non-polar matrix, high moisture absorption, **limited thermal stability** : low permissible temperatures of processing and use

Natural (Lignocellulosic) Fibers

Structure of the cell wall





Cellulose = structural material that confers its mechanical properties to higher plant cells

Natural (Lignocellulosic) Fibers

Big variation of properties inherent to the natural products
(climatic conditions, maturity, type of soil,...)

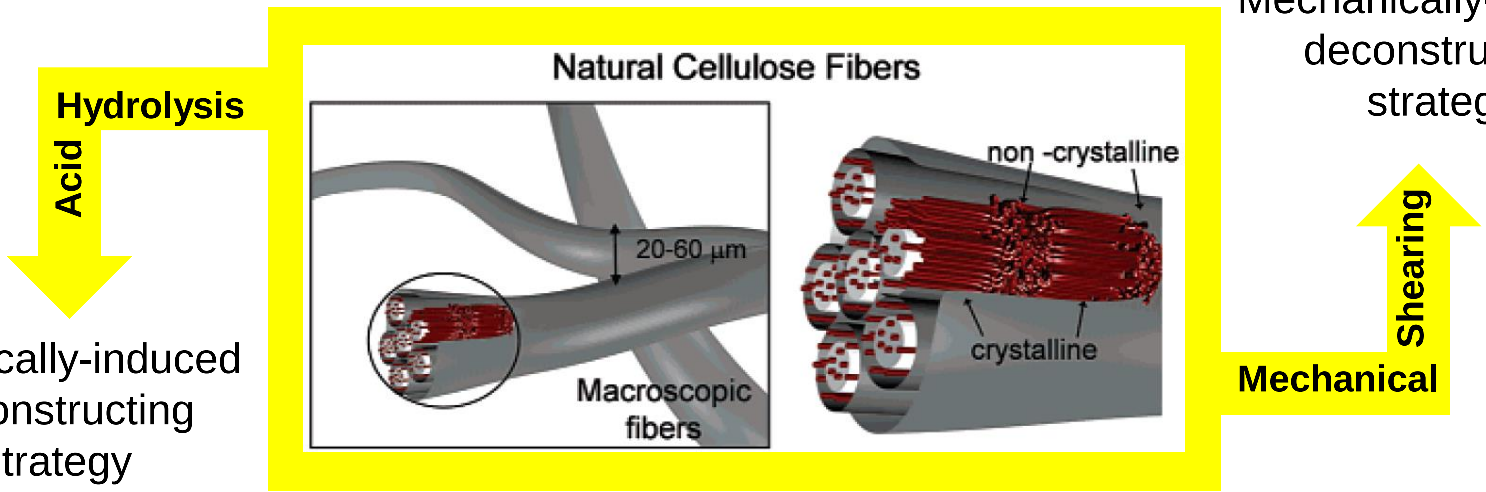
→ enormous scatter of mechanical plant fiber properties

Basic idea to achieve further improved fiber and composite is to eliminate the macroscopic flaws by disintegrating the natural grown fibers, and separating the almost defect free highly crystalline fibrils

LGP2

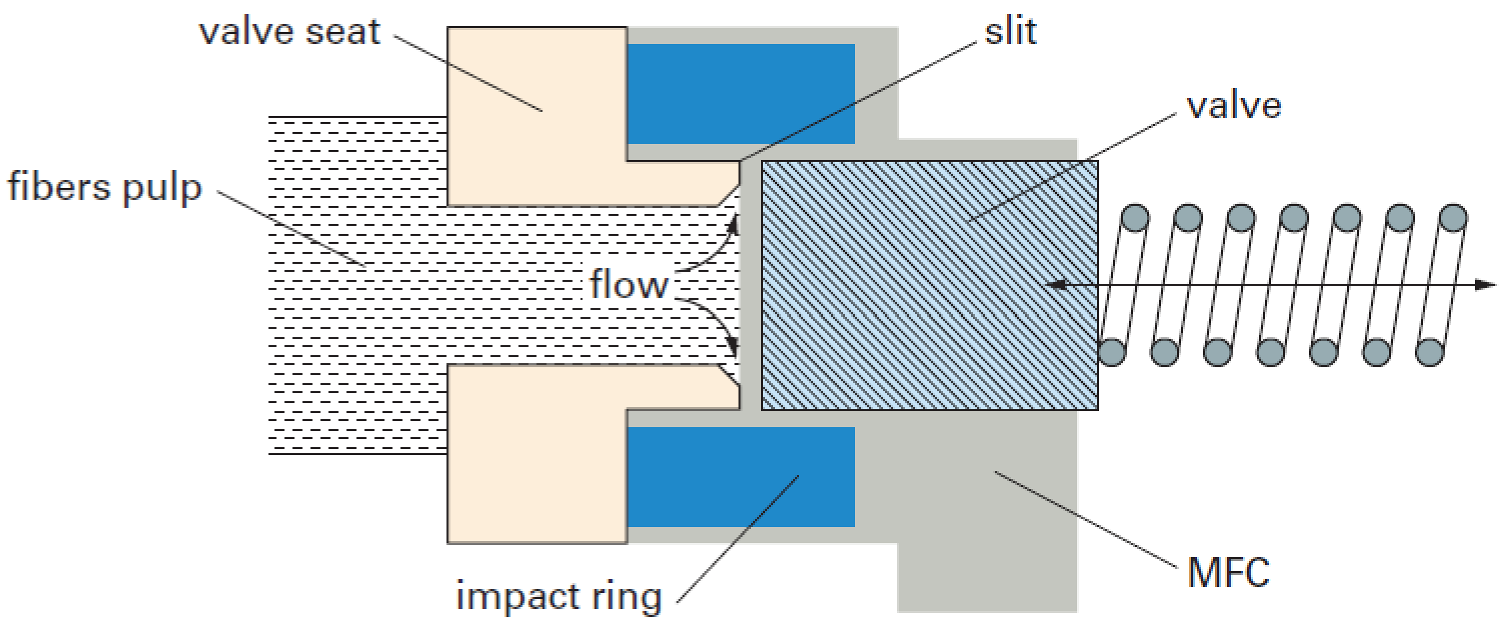
Top-Down Deconstructing Strategy

Mechanically-induced
deconstructing
strategy



Chemically-induced
deconstructing
strategy

Mechanically-induced Deconstructing Strategy



Scheme of the homogenizer

Pretreatments

High energy demand

30,000 kWh/ton (Nakagaito and Yano, 2004)

70,000 kWh/ton (Eriksen et al, 2008)

→ necessity of a pretreatment

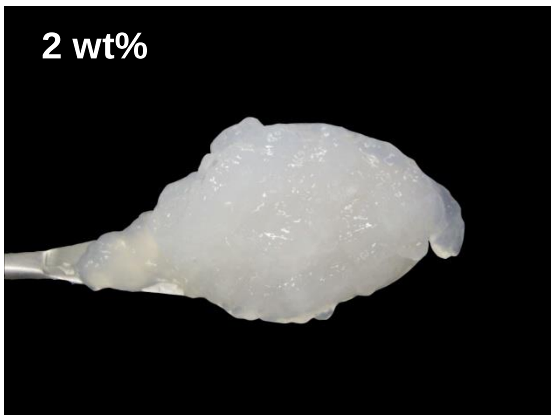
Enzymatic hydrolysis

Carboxymethylation

TEMPO-catalyzed oxidation pretreatment

Cryocrushing

Mechanically-induced Deconstructing Strategy

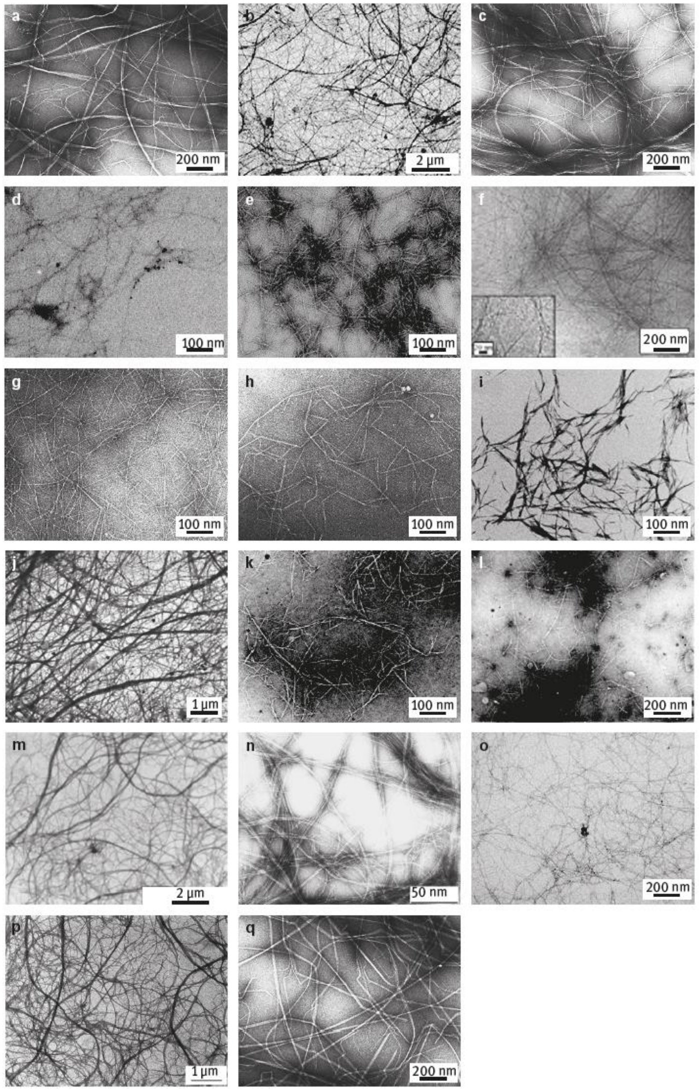


Lavoine et al., *Carbohydr. Polym*. **2012**, 90, 735-764

Malainine et al., *Compos. Sci. Technol.* **2005**, 65, 1520-1526

Width = 3-100 nm
Length > 1 µm ?

Mechanically-induced Deconstructing Strategy



TEMs showing cellulose fibers after high-pressure mechanical treatment

(a) bacterial cellulose (Saito et al., 2006)
(b) banana peel (Pelissari et al., 2014)
(c) banana rachis (Zuluaga et al., 2009)
(d) beavertail cactus (*Opuntia basilaris*) (Kakroodi et al., 2015)
(e) bleached eucalyptus kraft pulp (Qing et al., 2013)
(f) bleached sulfite softwood cellulose pulp (Pääkkö et al., 2007)
(g) bleached sulfite wood pulp (Saito et al., 2006)
(h) cotton (Saito et al., 2006)
(i) garlic skin (Zhao et al., 2014)
(j) *Opuntia ficus-indica* (Malainine et al., 2003)
(k) *Posidonia oceanica* balls (Bettaieb et al., 2015)
(l) *Posidonia oceanica* leaves (Bettaieb et al., 2015)
(m) potato pulp (Dufresne et al., 2000)
(n) prickly pear skin (Habibi et al., 2009)
(o) spinifex grass (*Triodia pungens*) (Amiralian et al., 2015)
(p) sugar beet pulp (Dufresne et al., 1997)
(q) tunicin (Saito et al., 2006)

Dufresne, Nanocellulose: From Nature to High-Performance Tailored Materials, 2nd Ed., de Gruyter, 2017

The Need for International Standards - Terminology

Acronym	Terminology	Reference
MFC	Microfibrillated Cellulose	(Herrick et al., 1983; Turbak et al., 1983)
–	Cellulose Microfibrils	(Dufresne et al., 1997; Dinand et al., 1999)
–	Fibrillated Cellulose	(Azizi Samir et al., 2004)
–	Nanofibrillar Cellulose	(Jin et al., 2004)
–	Fibril Aggregates	(Cheng et al., 2007)
–	Nanoscale Cellulose Fibrils	(Pääkkö et al., 2007)
–	Microfibrillated Cellulose Nanofibers	(Henriksson et al., 2007)
–	Cellulose Fibril Aggregates	(Cheng et al., 2007)
CNF	Cellulose Nanofibers	(Abe et al., 2007; Alemdar and Sain, 2008)
–	Cellulose Nanofibrils	(Henriksson et al., 2008; Ahola et al., 2008a; 2008b)
–	Cellulose Microfibers	(Bhattacharya et al., 2008)
–	Microfibril Aggregates	(Abe et al., 2009)
–	Cellulose Microfibril Aggregates	(Abe and Yano, 2009)
–	Cellulose Fibrils	(Cheng et al., 2009a; 2009b))
NFC	Nanofibrillated Cellulose	(Mörseburg and Chinga-Carrasco, 2009; Chinga-Carrasco and Syverud, 2010)
–	Microfibrillar Cellulose	(Spence et al., 2010)

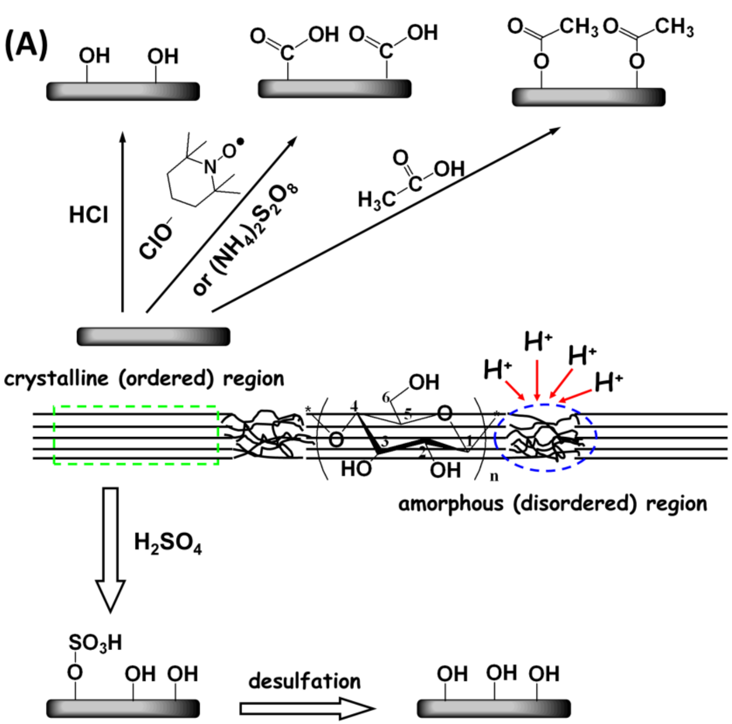
TAPPI, ISO and CSA approved

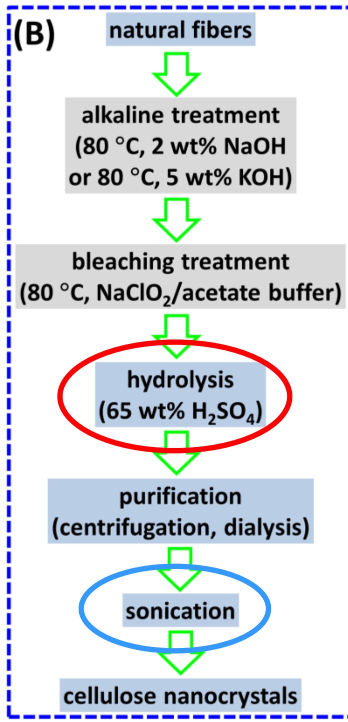
Table 2.1: Different terminologies used in the literature to describe the material resulting from the cellulose fiber fibrillation process.

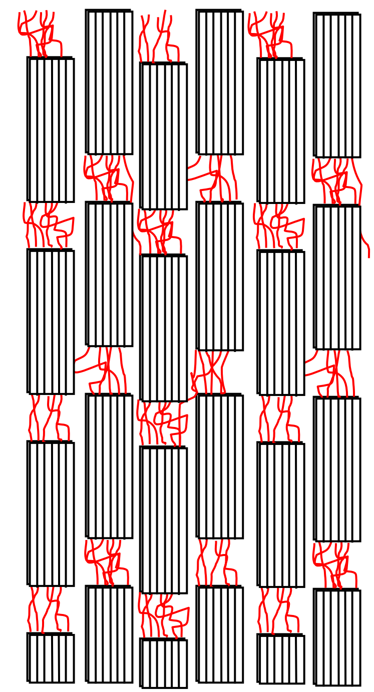
Dufresne, Nanocellulose: From Nature to High-Performance Tailored Materials, 2nd Ed., de Gruyter, 2017

LGP2

Chemically-induced Deconstructing Strategy



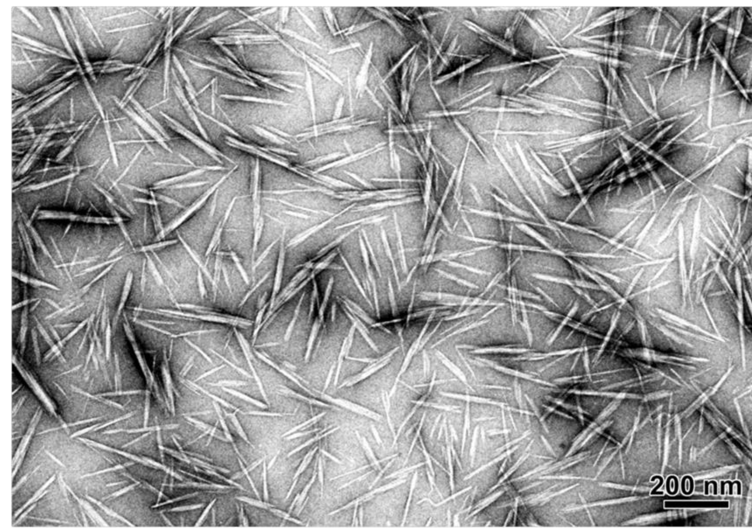




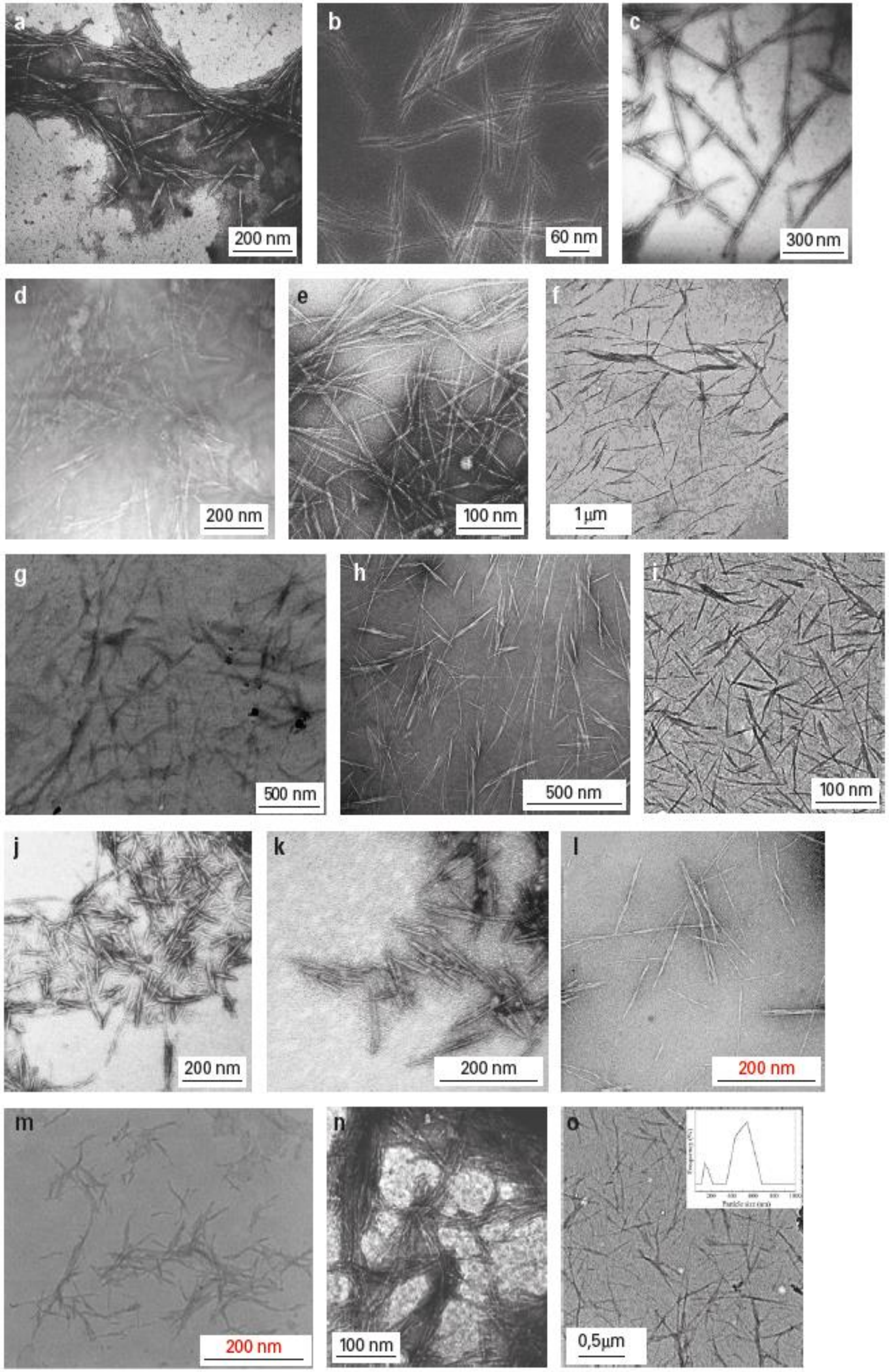
Chemically-induced Deconstructing Strategy

Siqueira et al., *Cellulose* **2010**, *17*, 289-298

Width = few nm
Length = few 100 nm



Habibi et al., *J. Mater. Chem.* **2008**, *18*, 5002-5010

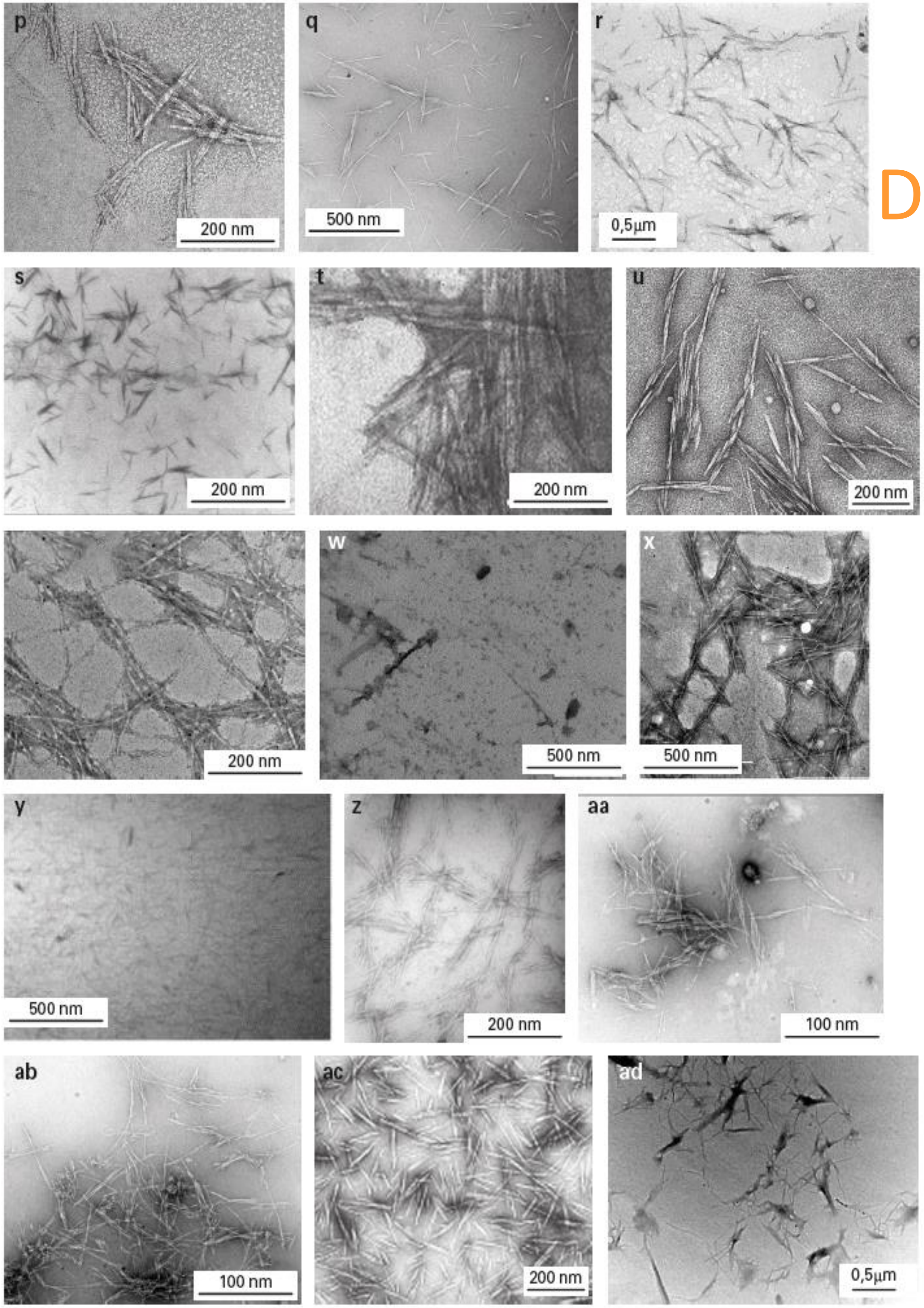


Chemically-induced Deconstructing Strategy

TEMs from a dilute suspension of CNC from:

(a) acacia pulp (Pu et al., 2007)
(b) alfa (Ben Elmabrouk et al., 2009)
(c) bacterial cellulose (Grunert and Winter, 2002)
(d) balsa wood (Morelli et al., 2012)
(e) banana rachis (Zuluaga et al., 2007)
(f) bleached softwood kraft pulp (Araki et al., 1998)
(g) brewer's spent grains (Martínez-Sanz et al., 2015)
(h) Capim dourado (Siqueira et al., 2010)
(i) cotton (Fleming et al., 2000)
(j) curaúa (Corrêa et al., 2010)
(k) eucalyptus wood pulp (de Mesquita et al., 2010)
(l) garlic straw (Kallel et al., 2016)
(m) giant cane (*Arundo donax*) (Barana et al., 2016)
(n) grass of Korea (Pandey et al., 2008)
(o) kelp residue (Feng et al., 2015) (inset: particle size distribution)

Dufresne, Nanocellulose: From Nature to High-Performance Tailored Materials, 2nd Ed., de Gruyter, 2017



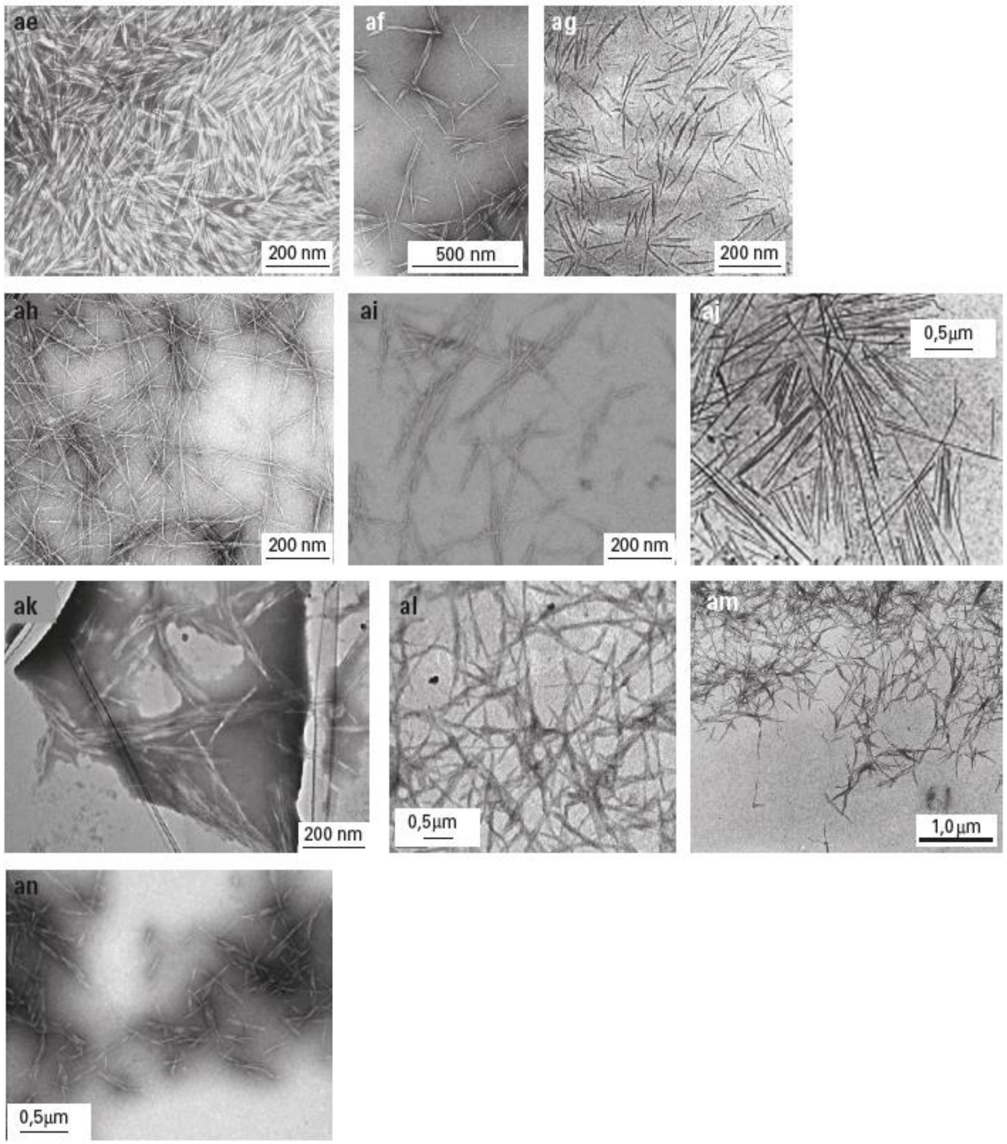
Chemically-induced Deconstructing Strategy

TEMs from a dilute suspension of CNC from:

(p) kenaf (Kargarzadeh et al., 2012)
(q) *Luffa cylindrica* (Siqueira et al., 2010)
(r) maize straw (Rehman et al., 2014)
(s) mango seed (Henrique et al., 2013)
(t) MCC (Bondeson et al., 2006)
(u) mengkuang Leaves (Sheltami et al., 2012)
(v) oil palm trunk (Lamaming et al., 2015)
(w) olive pomace (Martínez-Sanz et al., 2015)
(x) olive stone (Abou-Zeid et al., 2015)
(y) onion skin (Rhim et al., 2015)
(z) *Pennisetum sinese* (Lu et al., 2014)
(aa) *Posidonia oceanica* balls (Bettaieb et al., 2015)
(ab) *Posidonia oceanica* leaves (Bettaieb et al., 2015)
(ac) ramie (Habibi et al., 2008)
(ad) red algae *Gelidium elegans* (Chen et al., 2016)

Dufresne, Nanocellulose: From Nature to High-Performance Tailored Materials, 2nd Ed., de Gruyter, 2017

Chemically-induced Deconstructing Strategy



TEMs from a dilute suspension of CNC from:

(ae) rice straw (Lu and Hsieh, 2012)
(af) sisal (Siqueira et al., 2009)
(ag) sugar beet pulp (Azizi Samir et al., 2004)
(ah) soy hulls (Flauzino Neto et al., 2016)
(ai) tomato peel (Jiang and Hsieh, 2015)
(aj) tunicin (Anglès and Dufresne, 2000)
(ak) waste newspaper (Danial et al., 2015)
(al) waste sackcloth (Cao et al., 2015)
(am) wheat straw (Helbert et al., 1996)
(an) wood fiberboard waste (Couret et al., 2017)

Dufresne, Nanocellulose: From Nature to High-Performance Tailored Materials, 2nd Ed., de Gruyter, 2017

The Need for International Standards - Terminology

Acronym	Terminology	Reference
–	Cellulose Micelles	(Rånby, 1949)
–	Level-off D.P. Cellulose Product	(Battista and Smith, 1961)
Wh	Whiskers	(Helbert et al., 1996; Dufresne, 2008)
–	Cellulose Crystallites	(Dong et al., 1996)
–	Cellulose Microcrystals	(Araki et al., 2001)
CNC	Cellulose Nanocrystals	(Grunert and Winter, 2002; Paralikar et al., 2008; Mangalam et al., 2009)
CNW	Cellulose Nanowhiskers	(Oksman et al., 2006; Petersson et al., 2007; Habibi et al., 2008; Braun et al., 2008; Rojas et al., 2009)
–	Nanocellulose	(Morán et al., 2008)
NCC	Nanocrystalline Cellulose	(Bai et al., 2009)

TAPPI, ISO and CSA approved

Table 3.1: Different terminologies used in the literature to describe the material resulting from the cellulose fiber fibrillation process.

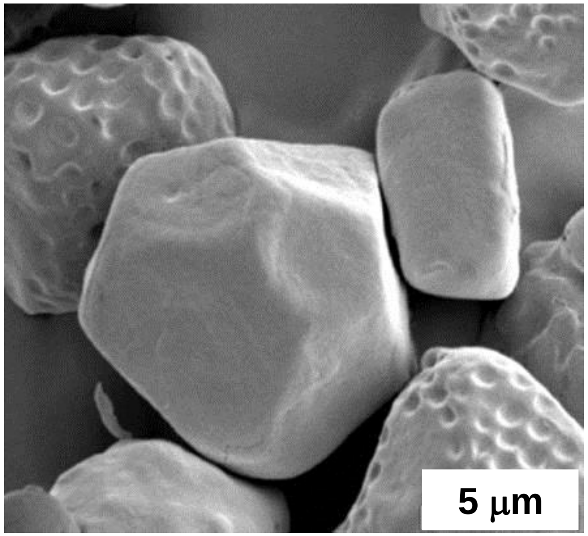
Dufresne, Nanocellulose: From Nature to High-Performance Tailored Materials, 2nd Ed., de Gruyter, 2017

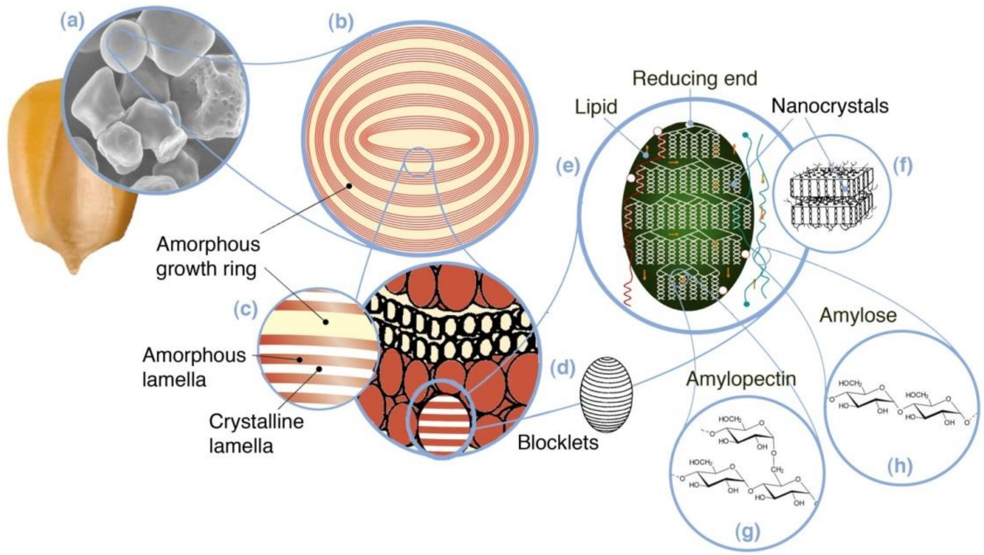
Starch

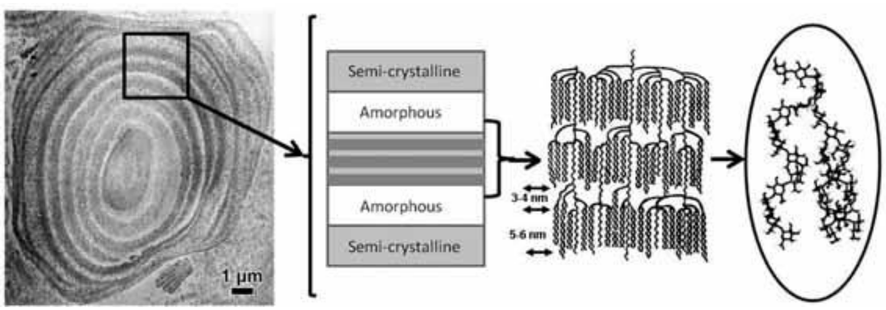
Starch = storage polymer → native starch = discrete and partially crystalline microscopic granules

corn, wheat, rice,
potato, tapioca, peas

Starch







(a) starch granules

(b) amorphous and semi-crystalline growth rings

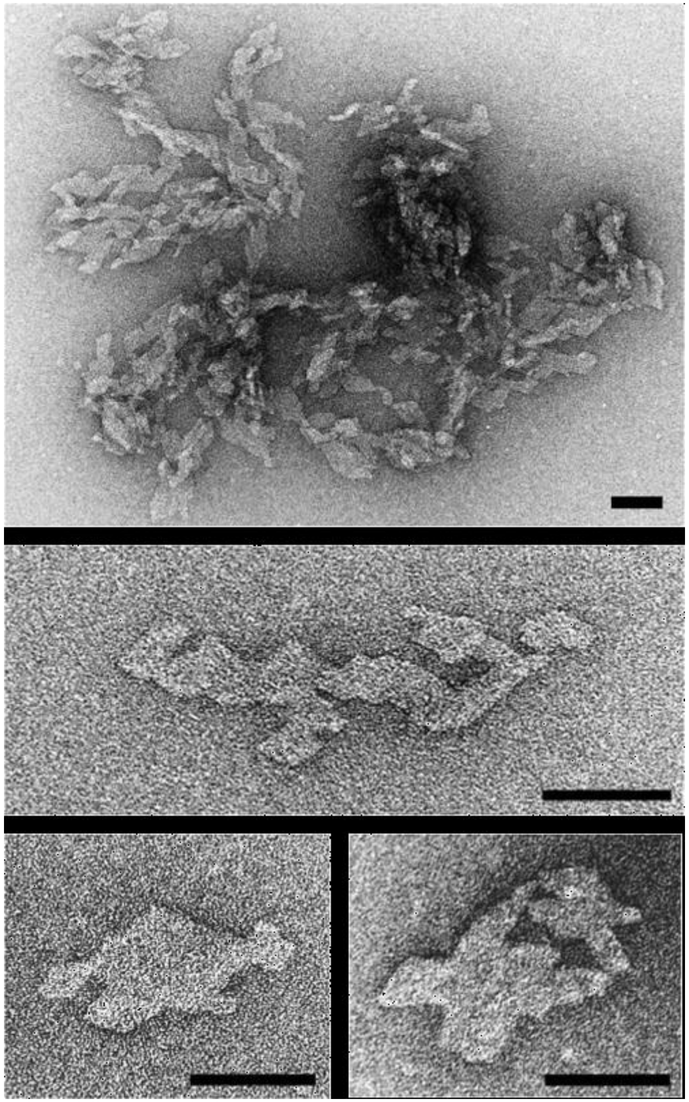
(c) amorphous and crystalline lamellae

(d) blocklets, (f) nanocrystals

(g) amylopectin, (h) amylose

Le Corre et al., *Biomacromolecules* **2010**, 11, 1139-1153

Starch Nanocrystals

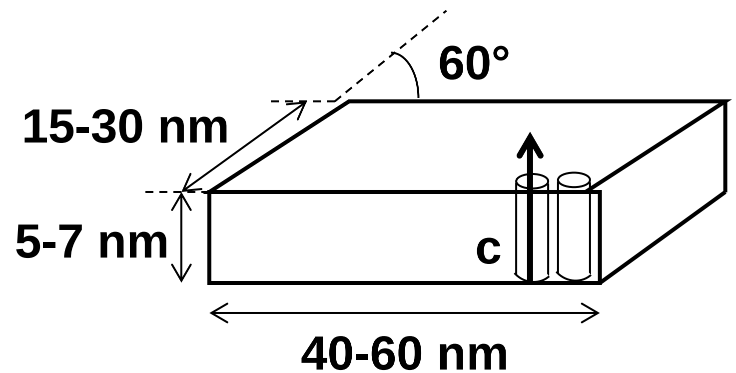


TEM of negatively stained SNC obtained after 3.16 M H_2SO_4 hydrolysis of waxy maize starch granules during 5 days, at 40 °C, 100 rpm and with a starch concentration of 14.69 wt %

(a) *Aggregates of nanocrystals*

(b–d) organizations of nanoplatelets

Scale bar: 50 nm.

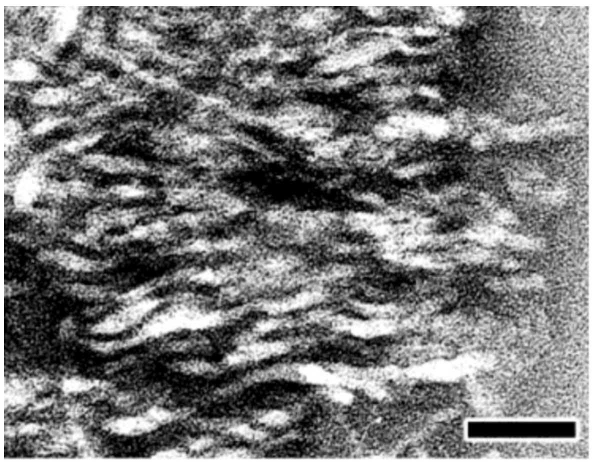


Putaux et al., *Biomacromolecules* **2003**, 4, 1198-1202

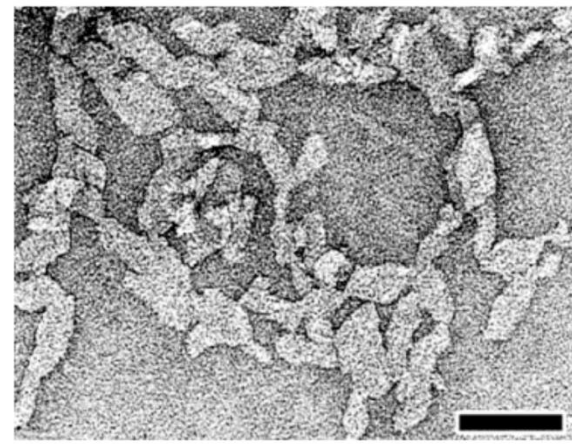
Angellier et al., *Biomacromolecules* **2004**, 5, 1545-1551

Starch Nanocrystals

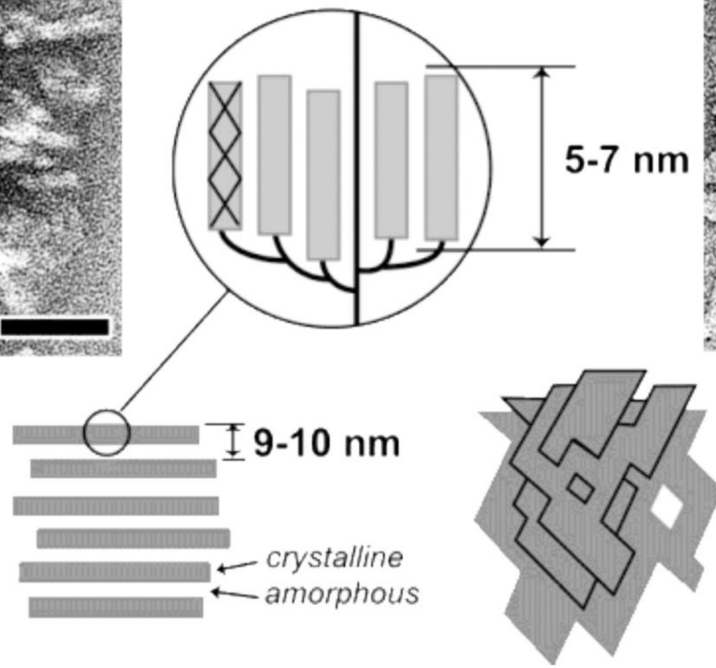
2 weeks hydrolysis (2.2 N HCl at 36°C)



6 weeks hydrolysis (2.2 N HCl at 36°C)



Longitudinal view



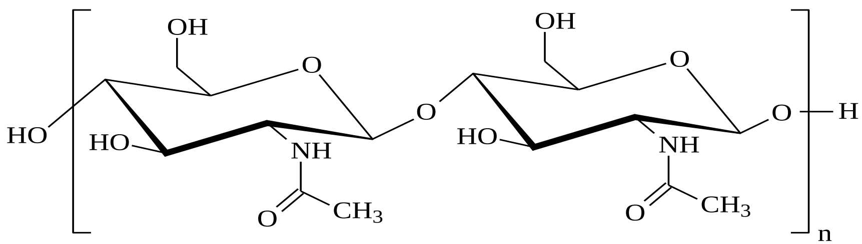
Planar view

https://www.youtube.com/watch?v=hdx2A5gq9js

Putaux et al., *Biomacromolecules* **2003**, 4, 1198-1202

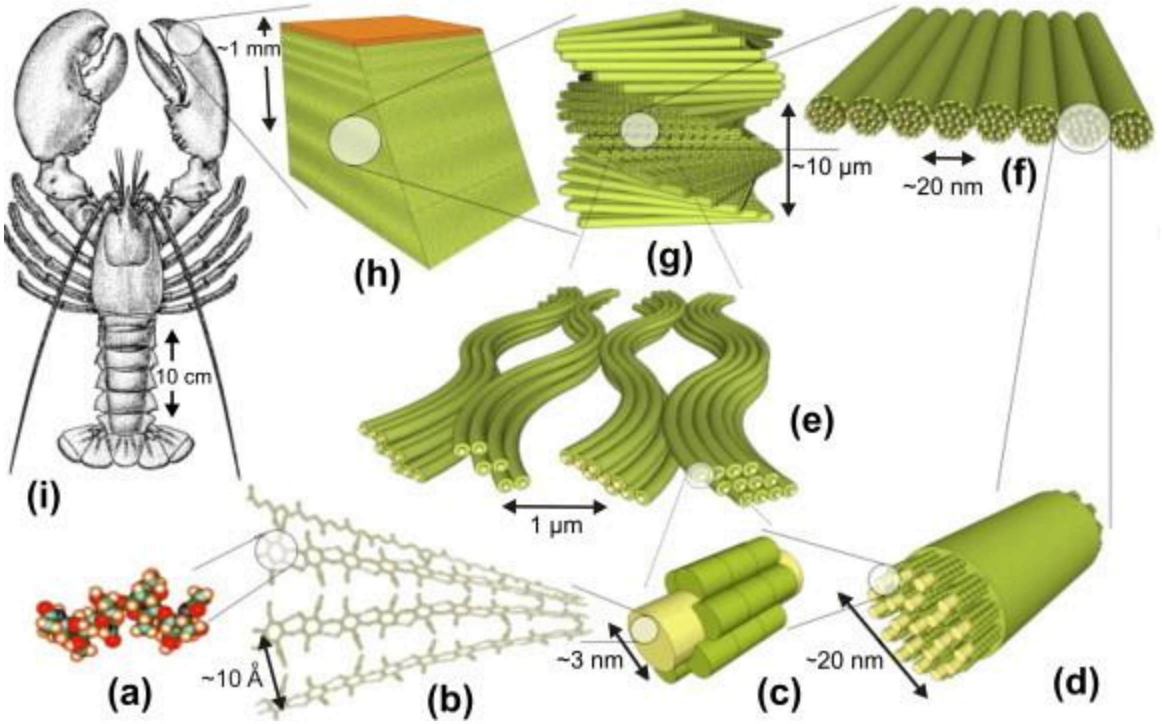
Chitin

Main component of the cell walls of fungi, the exoskeletons of arthropods (crabs, lobsters, shrimps) and insects, the radulas of mollusks, and the beaks of cephalopods (squid, octopuses)



Chitin

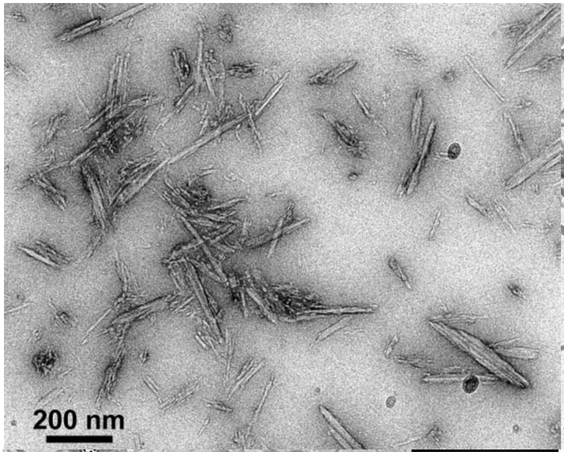
Exoskeleton of lobster (*Homarus americanus*)



Nikolov et al., *J. Mech. Behav. Biomed.* **2011**, 4, 129-145

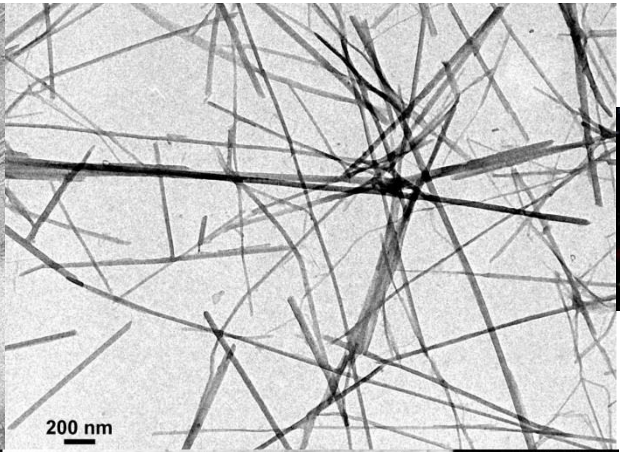
Chitin Nanocrystals

Squid pen



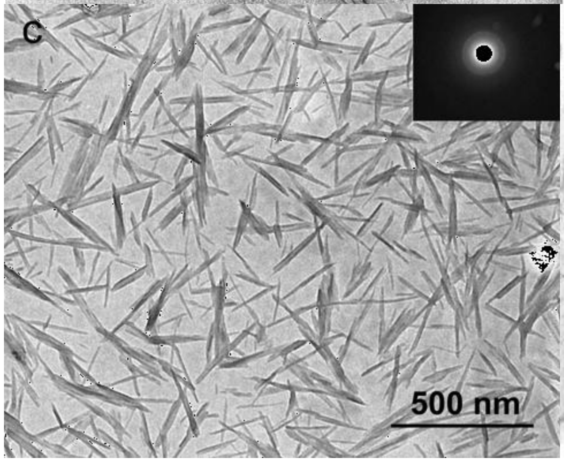
Paillet and Dufresne, *Macromolecules* **2001**, 34, 6527-6530

Riftia tubes



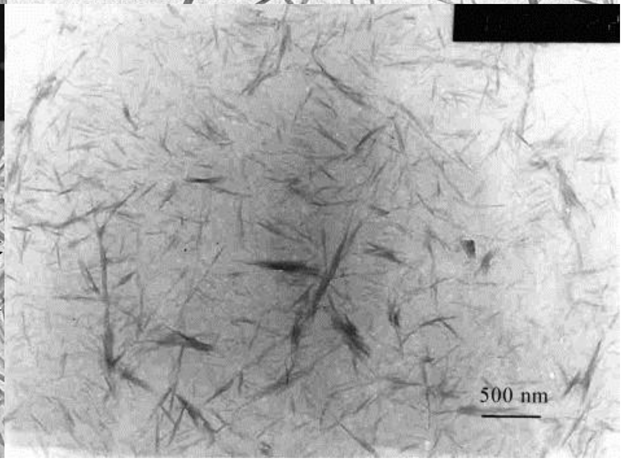
Morin and Dufresne, *Macromolecules* **2001**, 35, 2190-2199

Crab shell



Gopalan Nair and Dufresne, *Biomacromolecules* **2003**, 4, 657-665

Shrimp shell



Sriupayo et al., *Polymer* **2005**, 46, 5637-5644

Applications of Cellulose Nanomaterials

Coatings

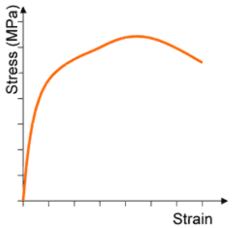
Adhesives

Energy

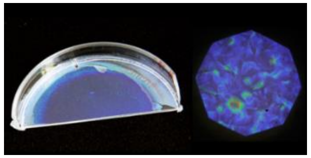
Inks/printing

Pulp & paper

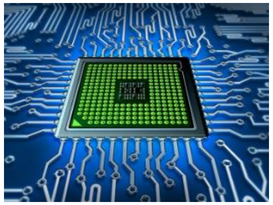
Composites



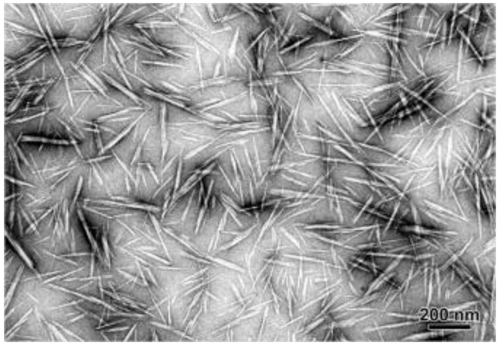
Films



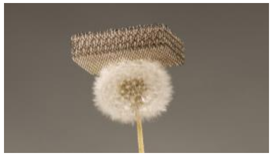
Electronics



Biomedical



Filtration



Detergents

Cosmetics

Food industry

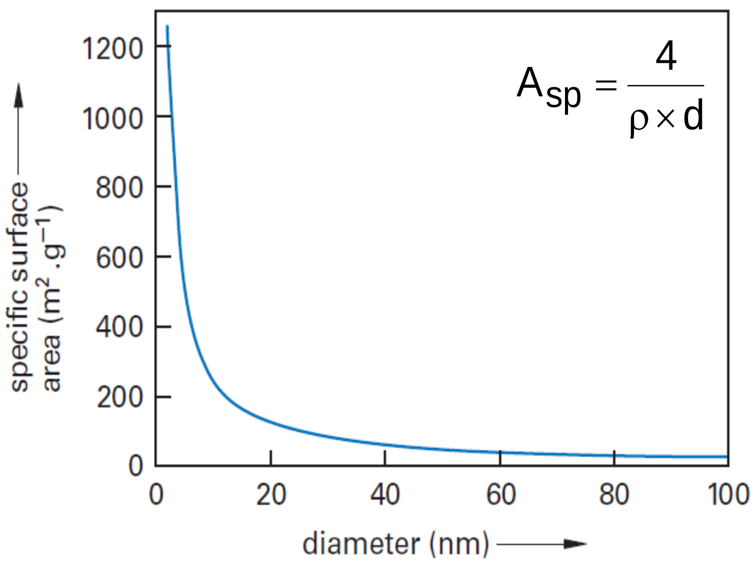
Packaging

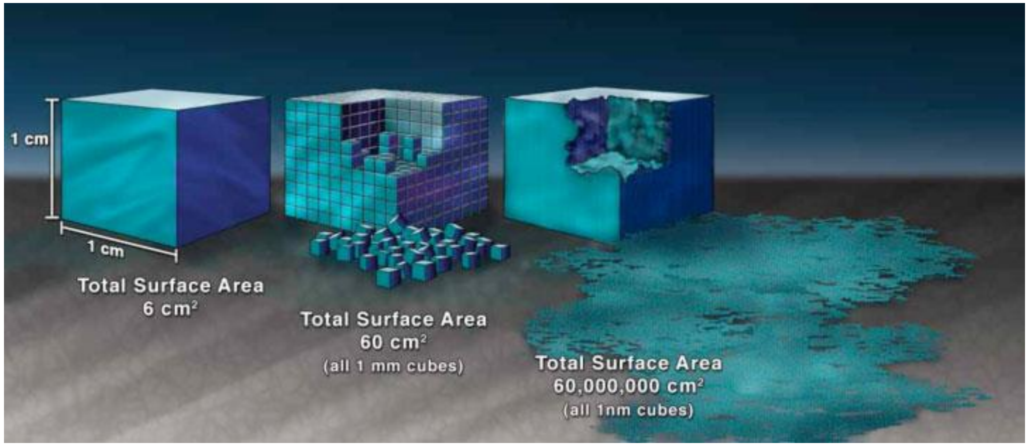
Construction

Textiles

Nanoparticles vs. Microparticles

❶ Increase of the specific area (~ 100 $m^2.g^{-1}$ vs. ~ 1 $m^2.g^{-1}$)

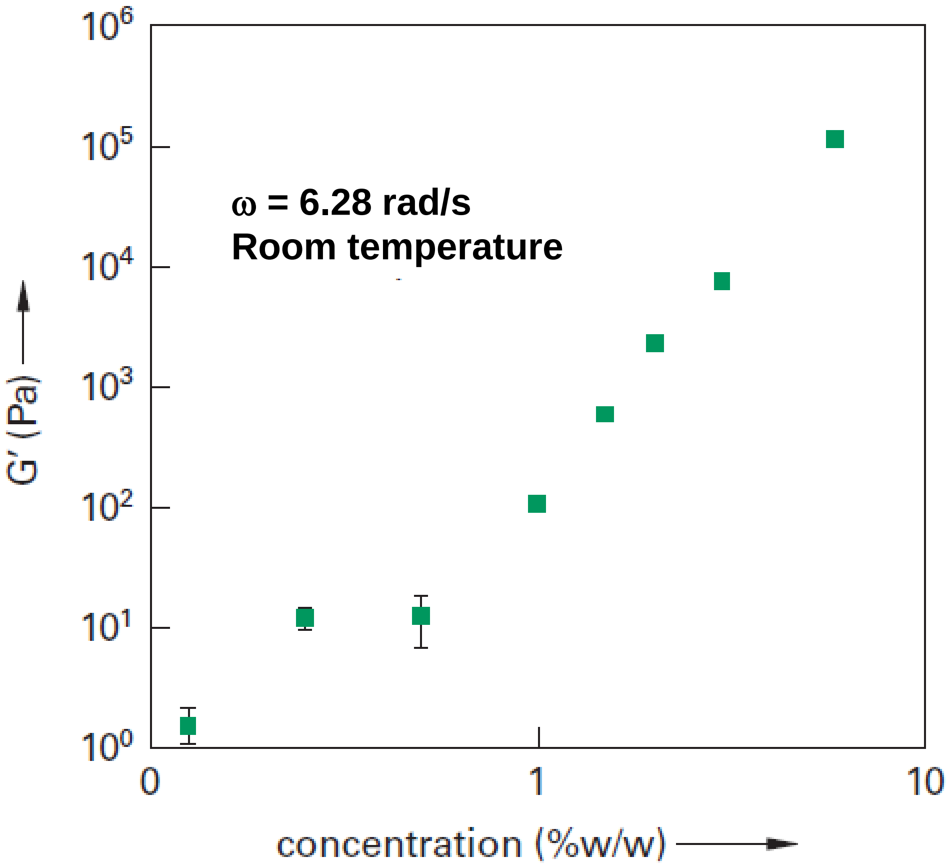




More surface is better surface !

High Specific Surface Area

Lavoine et al., *Carbohydr. Polym*. **2012**, *90*, 735-764

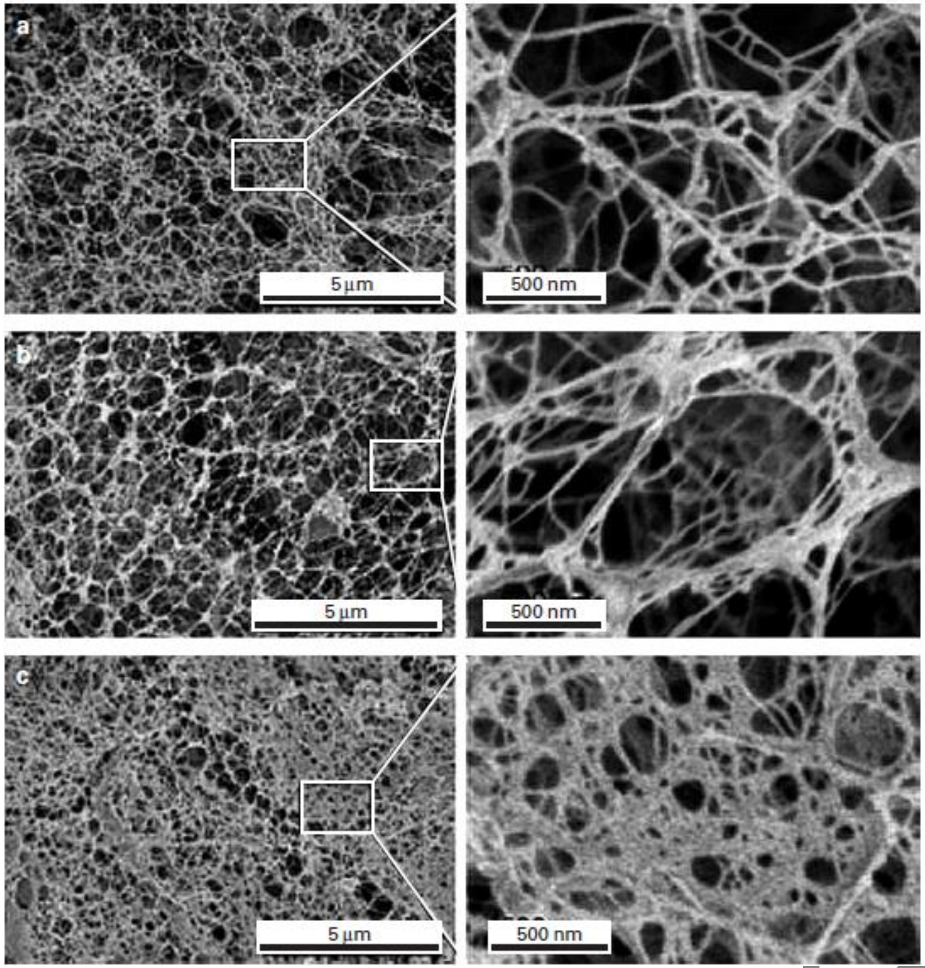


Applications

Food, cosmetic, pharmaceutical industries

Pääkkö et al., *Biomacromolecules* **2007**, 8, 1934-1941

High Specific Surface Area



Sehaqui et al., *Soft Matter* **2010**, 6, 1824-1832

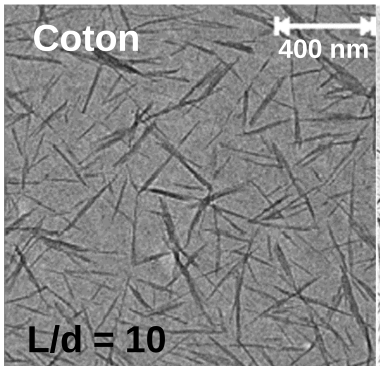
Production of foams and aerogels

Density
(a) 7 $kg.m^{-3}$
(b) 32 $kg.m^{-3}$
(c) 79 $kg.m^{-3}$

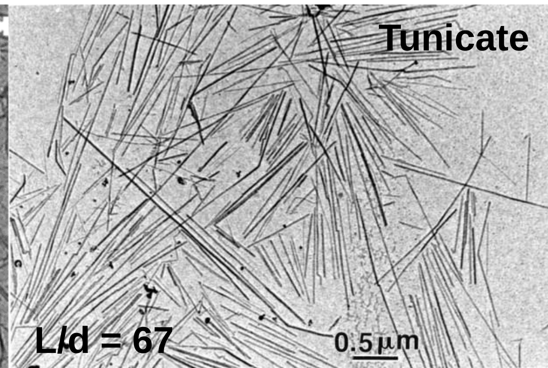
Applications
Porous templates, filtration

Nanoparticles vs. Microparticles

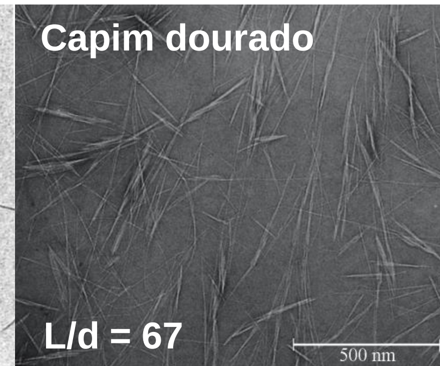
❷ High aspect ratio (10-100 for CNC, much higher for CNF)



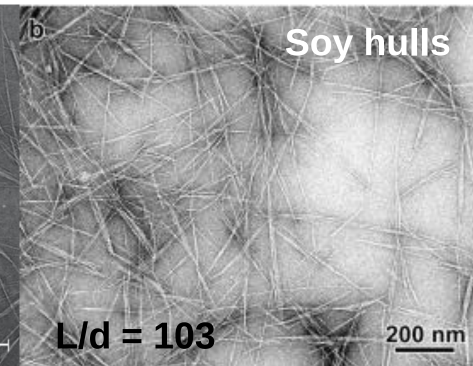
Fleming et al., *J. Am. Chem. Soc.* **2010**, 122, 5224-5225



Anglès and Dufresne, *Macromolecules* **2000**, 33, 8344-8353



Siqueira et al., *Cellulose* **2010**, 17, 289-298



Flauzino Neto et al., *Carbohydr. Polym.* **2016**, 153, 143-152

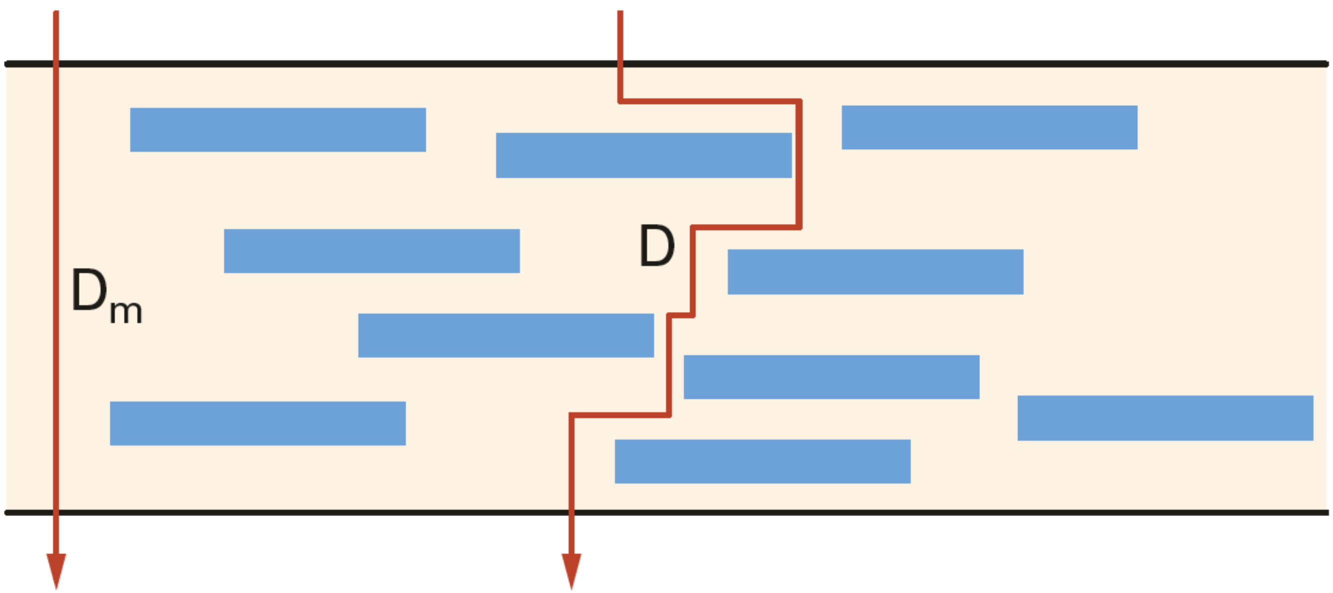
LGP2

Nanoparticles vs. Microparticles

❸ The average inter-particles distance decreases as their size decreases
→ particle-particle interactions

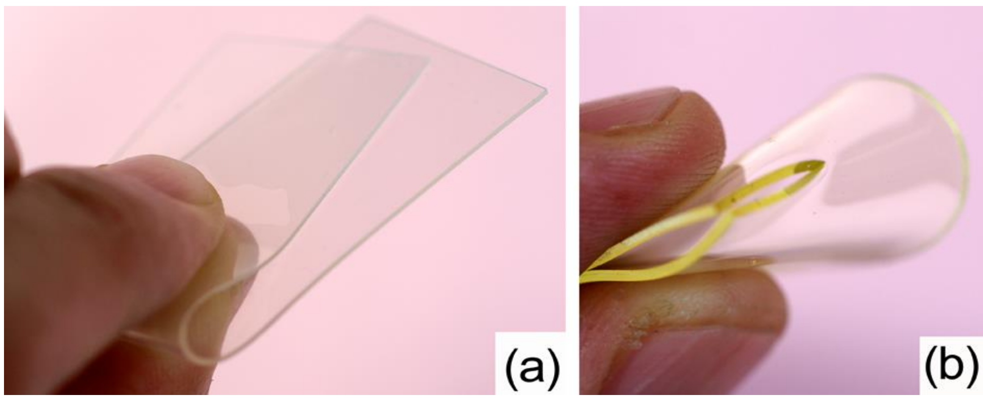
❹ Nanoparticles are weight efficient: improved properties for low filler content without detrimental effect on impact resistance and plastic deformation

❺ Reduction of gas diffusion (barrier effect)



Nanoparticles vs. Microparticles

❻ Small particles are "invisible": transparent coatings/films are attainable



Foldable transparent acrylic resin sheet with 5 wt% BC nanofibers

More fragile neat acrylic resin sheet

Nogi and Yano, *Adv. Mater.*, **2008**, 20, 1849-1852

Flexibility and transparency of acrylic resin film with 60 wt% BC nanofibers

Yano et al., *Adv. Mater.*, **2005**, 17, 153-155

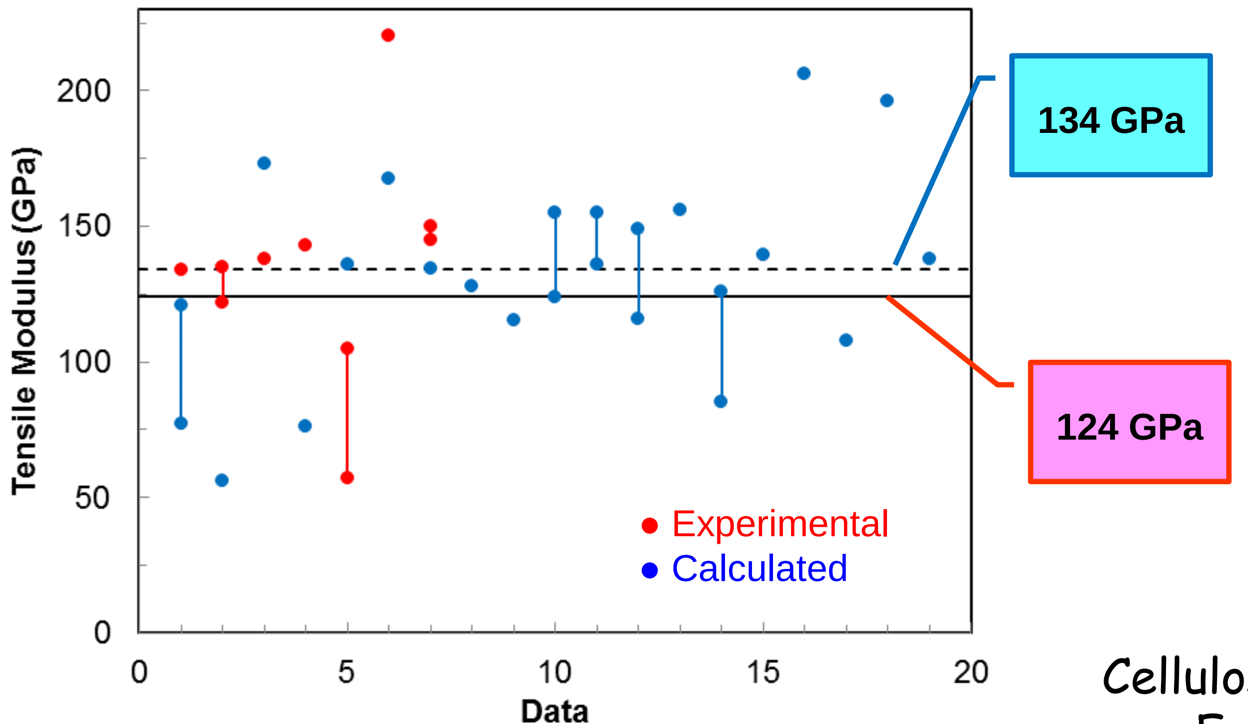
Applications

Electronics (flexible circuits)

Energy (solar panels)

Nanoparticles vs. Microparticles

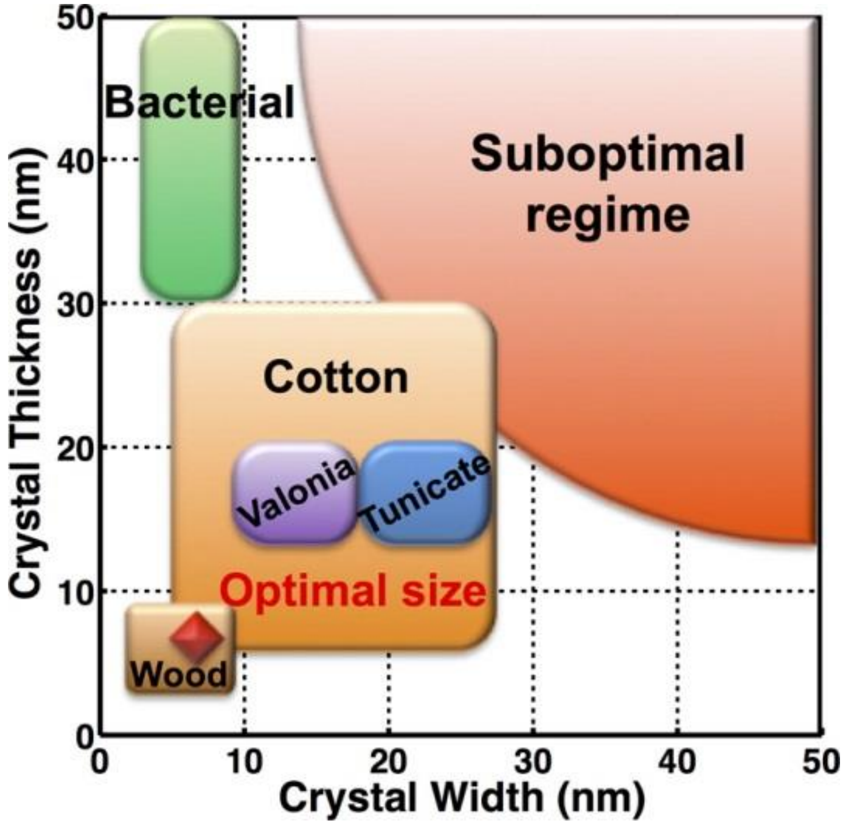
❼ Because cellulose nanomaterials contain only a small number of defects, their axial Young's modulus is close to the one derived from theoretical chemistry



Cellulose nanofibrils
E ~ 100 GPa

Dufresne, *Curr. Opin. Colloid Interface Sci.* **2017**, 29, 1-8

Nanoparticles vs. Microparticles



Atomistic simulations on the fracture energy of Iβ cellulose nanocrystals

Ideal dimensions optimizing fracture energy are:

4.8-5.6 nm in thickness (6-7 chain layers)

6.2-7.3 nm in width (6-7 chain layers)

Sinko et al., *ACS Macro Lett.* **2014**, 3, 64-69

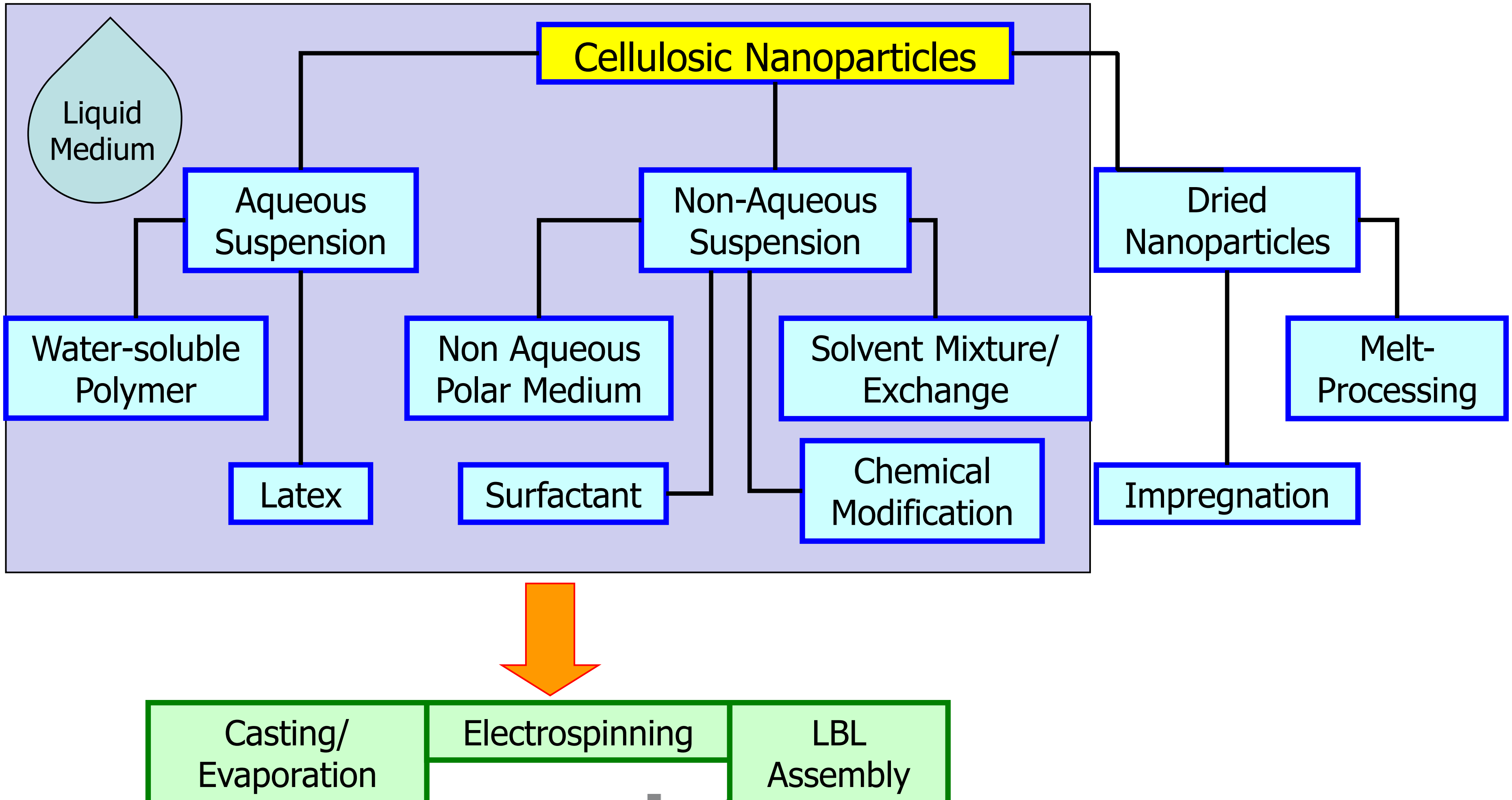
Nanoparticles vs. Microparticles

❽ **Lightweight material**: Cellulose nanomaterial modulus potentially stronger than steel and similar to Kevlar

Material	Modulus (Gpa)	Density ($g.cm^{-3}$)	Specific Modulus ($J.g^{-1}$)
Glass	70	2.6	27
Kevlar	60-125	1.45	41-86
Steel	200-220	8	25
MFC	100	1.5-1.6	65
CNC	130	1.5-1.6	85

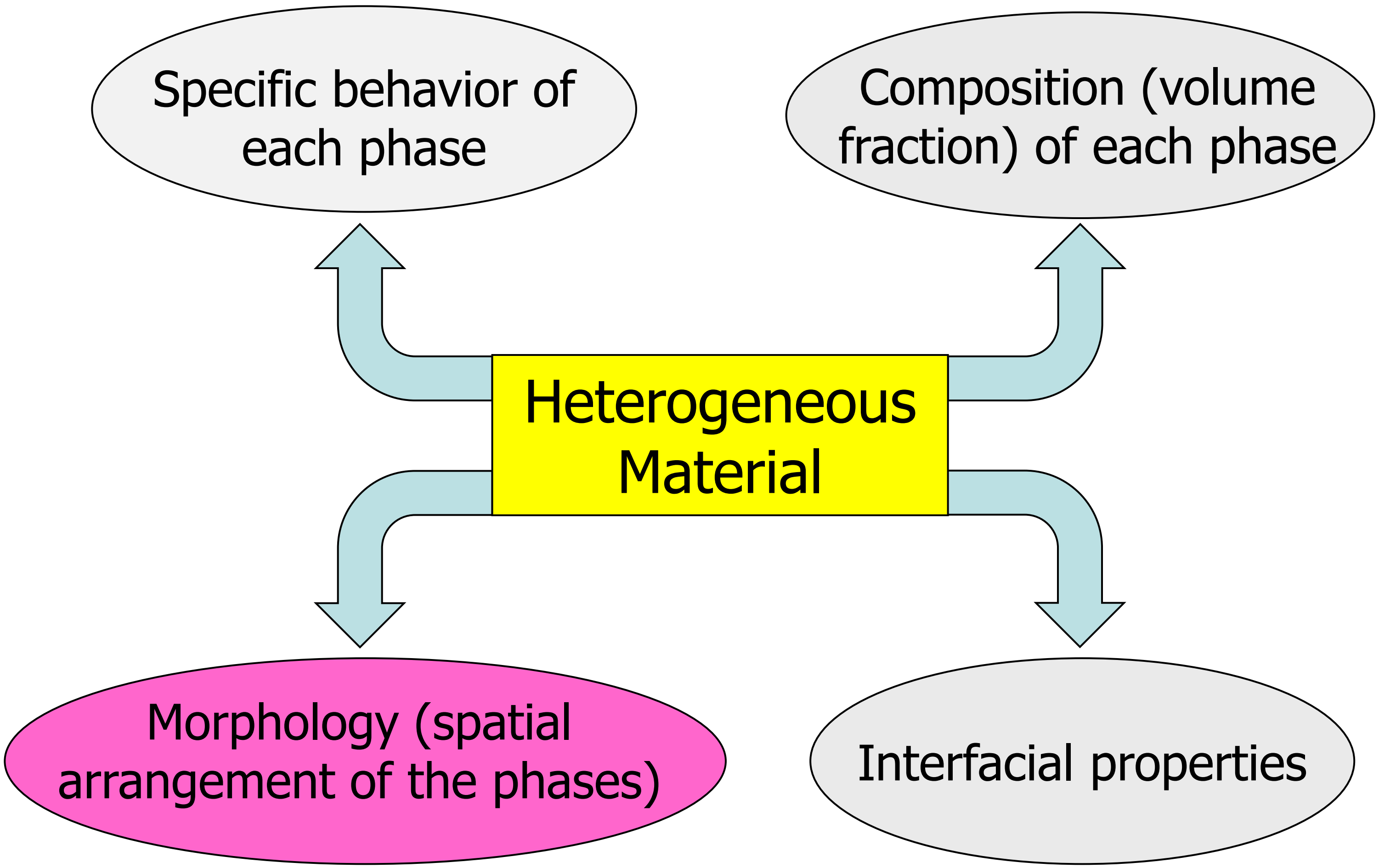
Dufresne, *Mater. Today* **2013**, 16, 220-227

Processing of Nanocomposites



Dufresne, *Mater. Today* **2013**, 16, 220-227

Cellulose Based Nanocomposites

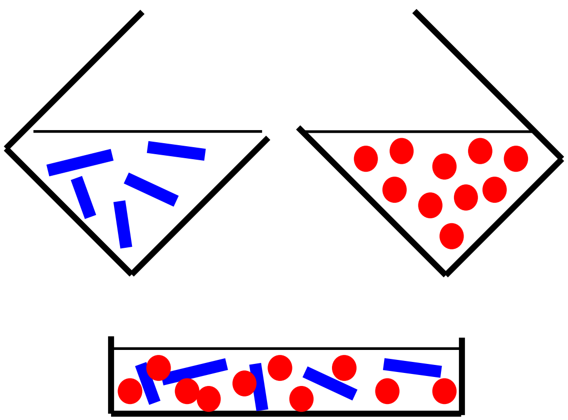


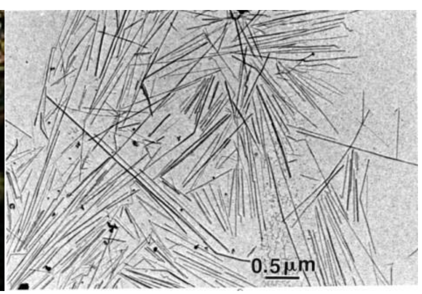
Cellulose Nanocomposites – Pioneering Work

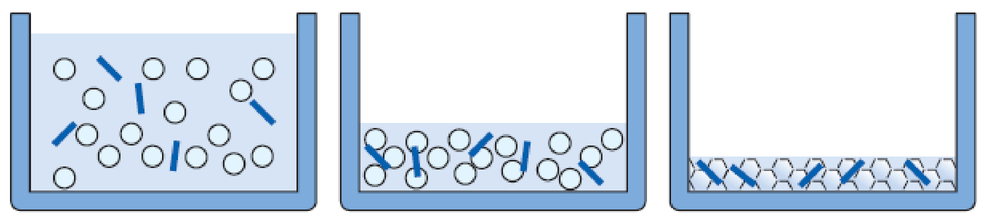
Preferred processing medium = water because of high stability of aqueous cellulose nanomaterial dispersions

Matrix = water-soluble polymer or latex (poly(S-co-BuA))

water evaporation (T>Tg) → particle coalescence → nanocomposite film

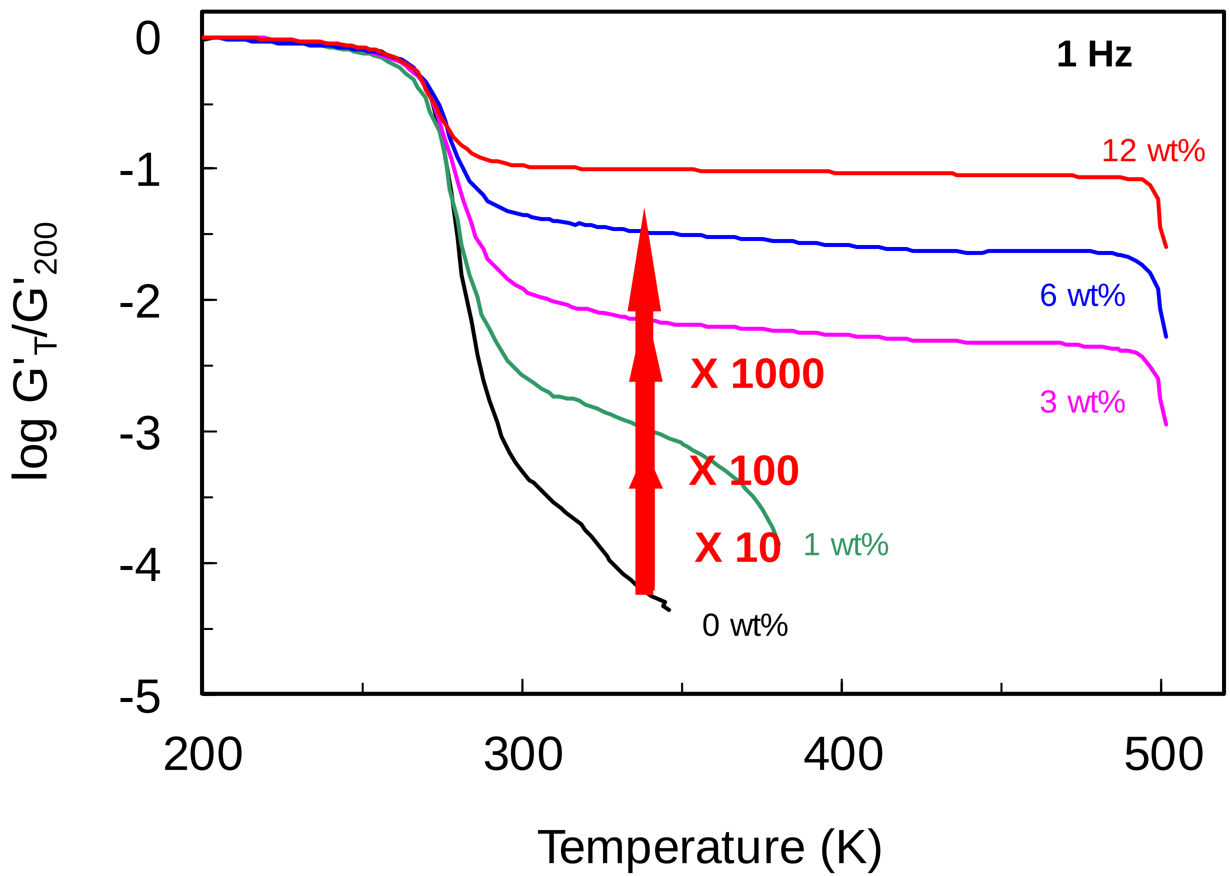






Favier et al., *Polym. Adv. Technol.*, **1995**, 6, 351-355

Cellulose Nanocomposites – Pioneering Work



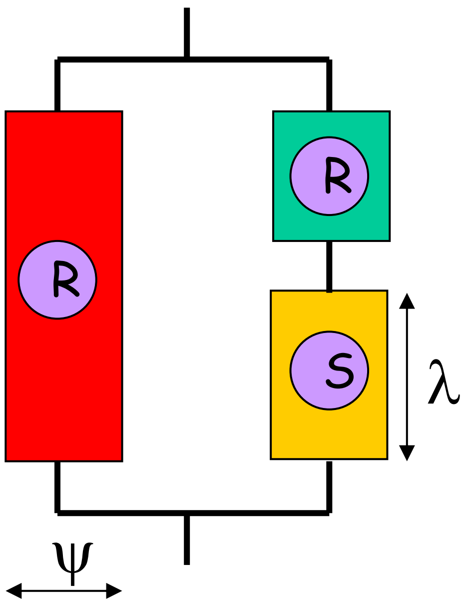
High reinforcing effect at T > Tg

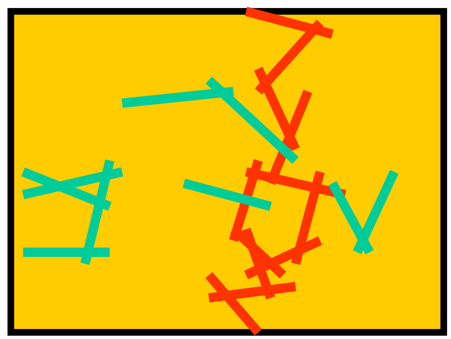
Thermal stabilization up to 500 K (ϕ_R > 1wt%) (degradation cellulose)

Favier et al., *Polym. Adv. Technol.*, **1995**, 6, 351-355

Cellulose Nanocomposites – Pioneering Work

Percolation Approach: Takayanagi Model





$$G = \frac{(1-2\psi+\psi\phi_R)G_S G_R + (1-\phi_R)\psi G_R^2}{(1-\phi_R)G_R + (v_R-\psi)G_S}$$

if $G_R >> G_S \Rightarrow G = \psi G_R$

$\psi = 0$ for $\phi_R < \phi_{Rc}$

$\psi = \phi_R \left(\frac{\phi_R - \phi_{Rc}}{1-\phi_{Rc}} \right)^b$ for $\phi_R \geq \phi_{Rc}$

percolating whiskers network :
E_R = 15 GPa → G_R = 5 GPa

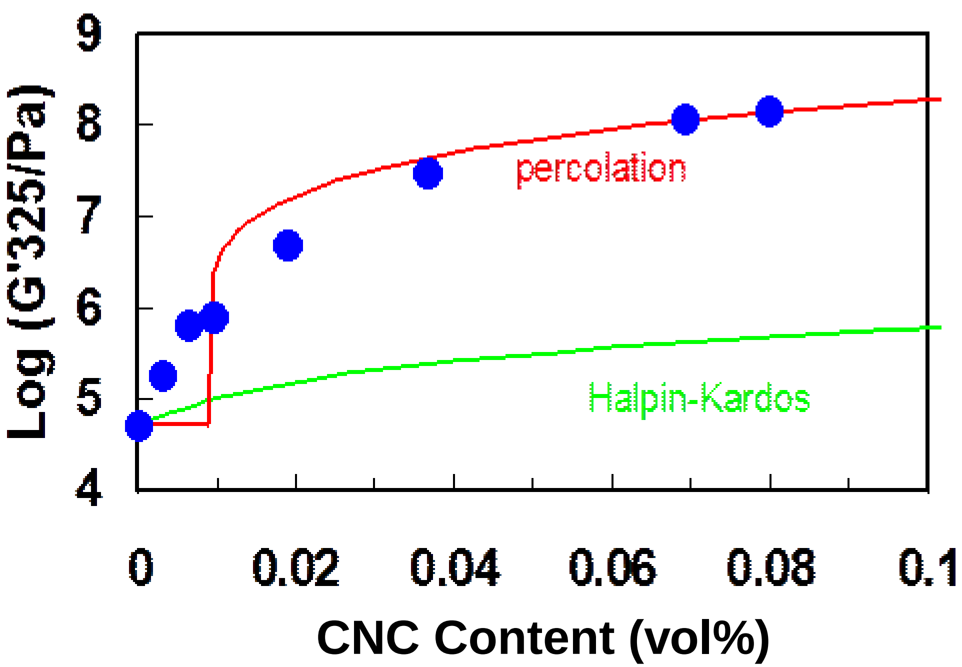
L/d = 67 → ϕ_{Rc} = 1%
b = 0.4 (3D system)

ψ = volume fraction of the percolating rigid phase
ϕ_R = volume fraction of filler
ϕ_{Rc} = critical volume fraction at the percolation threshold
b = critical exponent
G_R = modulus of the percolating CNC network

Favier et al., *Polym. Adv. Technol.*, **1995**, 6, 351-355

LGP2

Cellulose Nanocomposites – Pioneering Work



Favier et al., *Polym. Adv. Technol.*, **1995**, 6, 351-355

Good agreement between experimental and predicted data

Strong interactions between CNCs (H-bonding forces) → formation of a rigid cellulose CNC network for $\phi_R > \phi_{RC}$

Mechanical percolation effect

- High reinforcing effect
- Thermal stabilization of the composite modulus

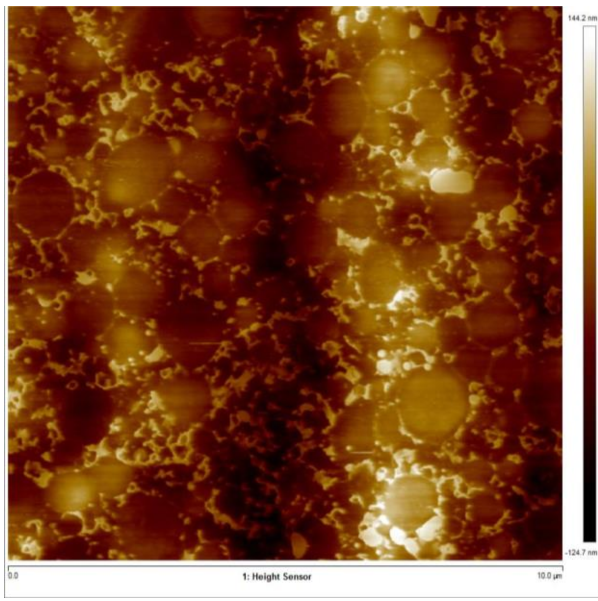
(water evaporation = slow process)

Percolation Threshold

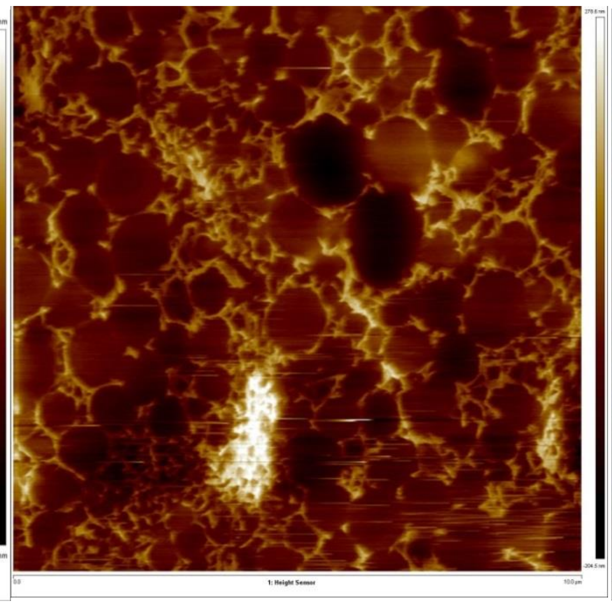
	CNC			
Source	L (nm)	D (nm)	L/D	Φ_R (vol%)
Cotton	170	15	10	7
Flax	300	20	15	4.6
Sisal	250	4	60	1.1
Luffa	183	5	37	1.8
Sugar beet Pulp	210	5	42	1.3
Palm tree rachis	260	6	43	1.3
Palm tree foliol	180	6	30	2.3
Wheat straw	220	5	45	1.6
Hard wood	200	4	50	1.4
Soft wood	200	4	50	1.4

$$\Phi_R = \frac{0.7}{L/D}$$

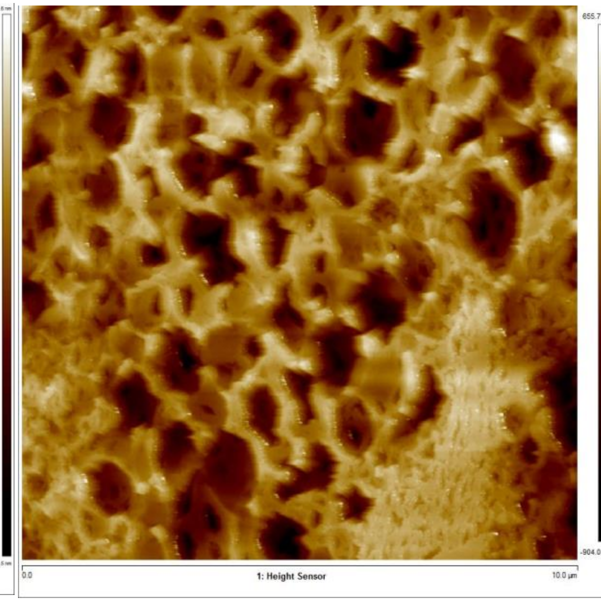
Percolation Network



NR



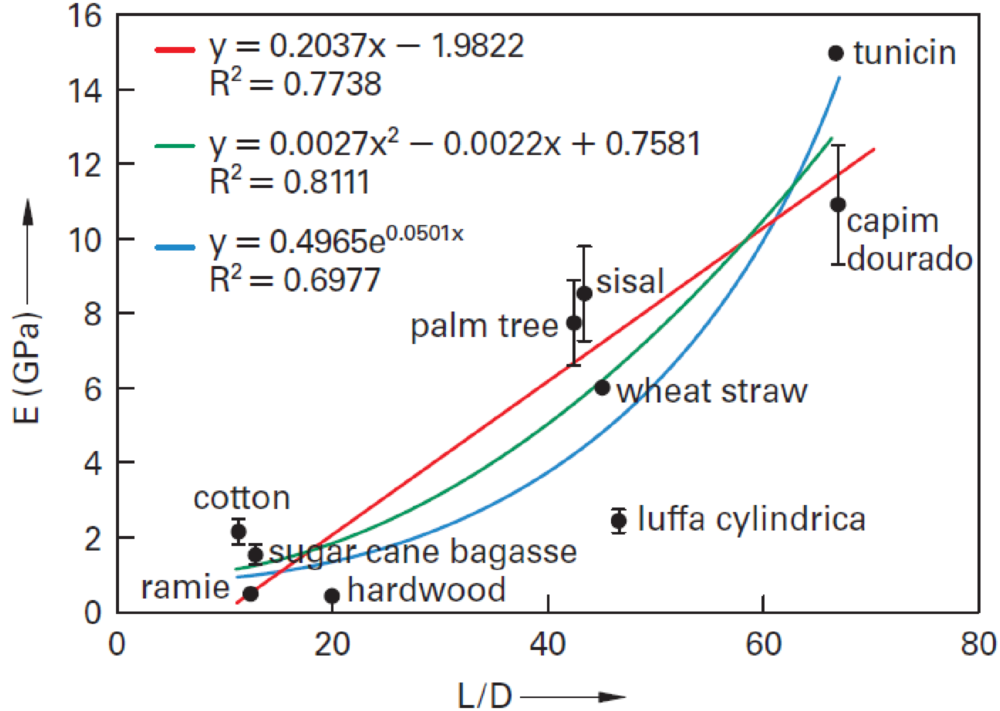
NR + 8.2 wt% CNC



NR + 16.4 wt% CNC

Stiffness of the Percolating Network

$$G = \psi \, G_R$$

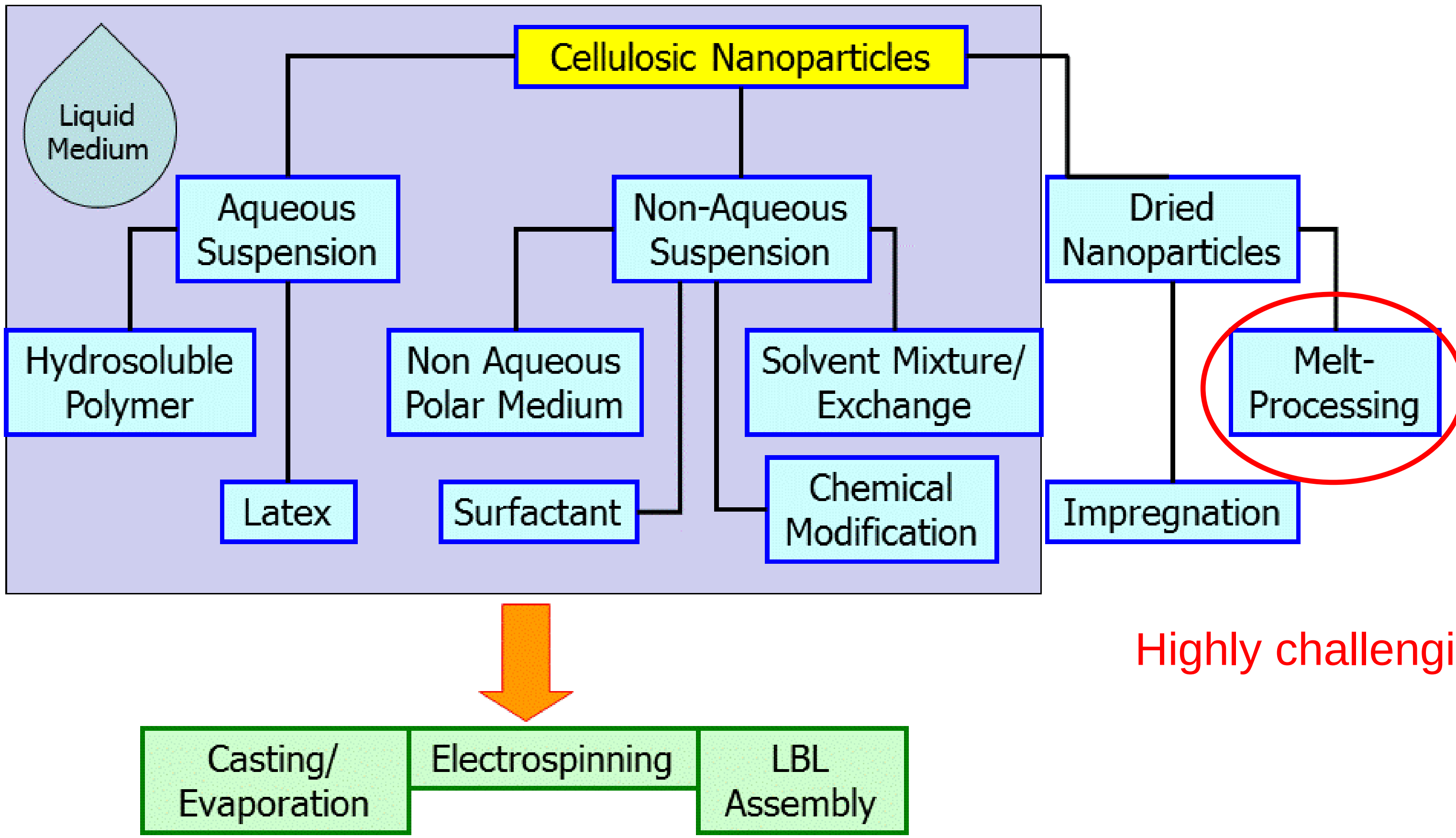


High L/d CNC → low percolation threshold

High stiffness of the percolating CNC network

Bras et al., *Carbohydr. Polym.* **2011**, 84, 211-215

Processing of Nanocomposites



Highly challenging !

Dufresne, *Mat. Today*, **2013**, 16, 220-227

Processing of Nanocomposites

Solvent/wet approach (casting/evaporation)

Preservation of the dispersion state in the liquid medium

Limitation of the number of polymer matrices

Non-industrial and non-economic

Polymer melt approach (extrusion, injection molding)

Green process

Industrially and economically viable

Hydrophilicity → aggregation of cellulosic nanoparticles upon drying

Difficulties for uniform dispersion within the polymer melt

Low thermal stability

Structural integrity of the nanoparticle

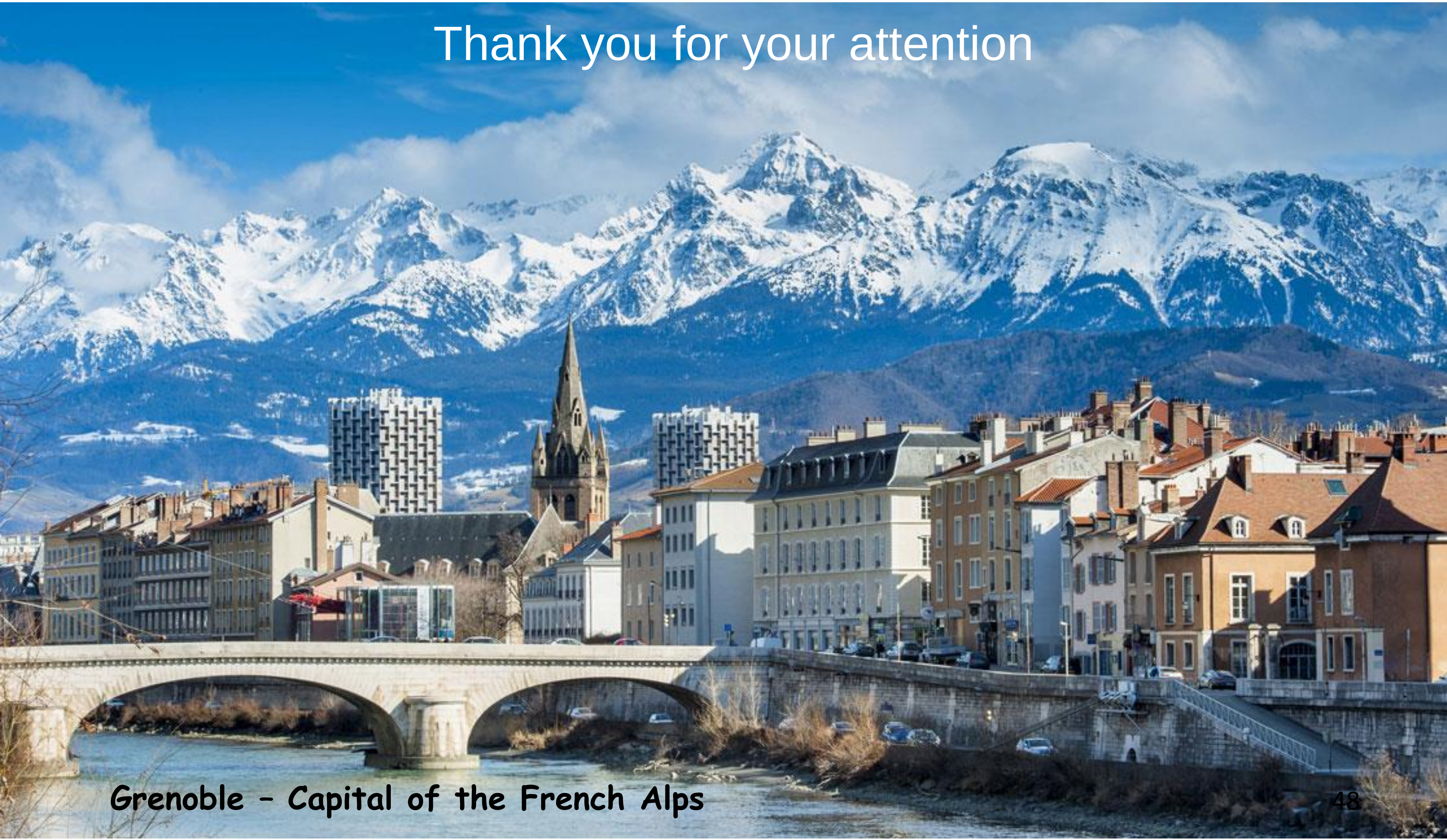
Orientation of the nanoparticle

Conclusion

- Growing interest in both the non-food usage of renewable resources and nanosized particles
- Polysaccharide : low cost material, abundant, renewable
- Preparation of nanoparticles with different aspect ratios
- Nanosized particles : mechanical properties (strength, modulus, dimensional stability), decreased permeability to gases and water, thermal stability, heat distorsion temperature
- Many possible applications: optical, mechanical, barrier, rheological properties
- **Challenges:**
  - Sustainability of supply
  - Melt processing of cellulose based nanocomposites
  - Improvement of nanocomposite properties in moist atmosphere

LGP2

Thank you for your attention



Grenoble – Capital of the French Alps