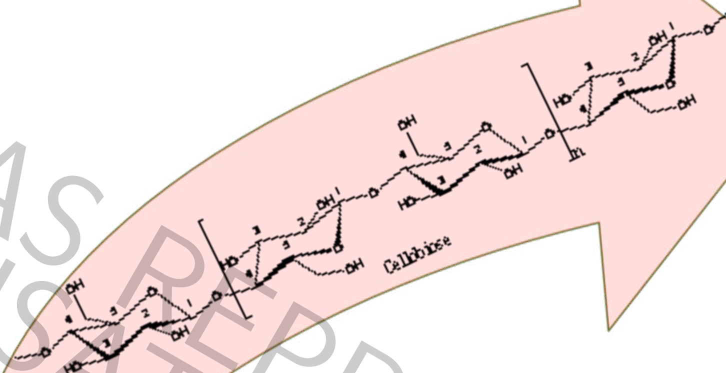
Nanocelluloses: between hype and reality

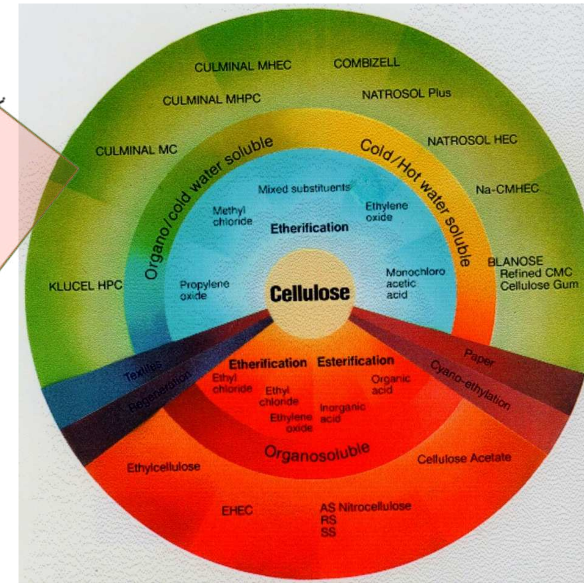
Youssef Habibi
Department of Advanced Materials and Structures
Public Research Center Henri Tudor
Luxembourg

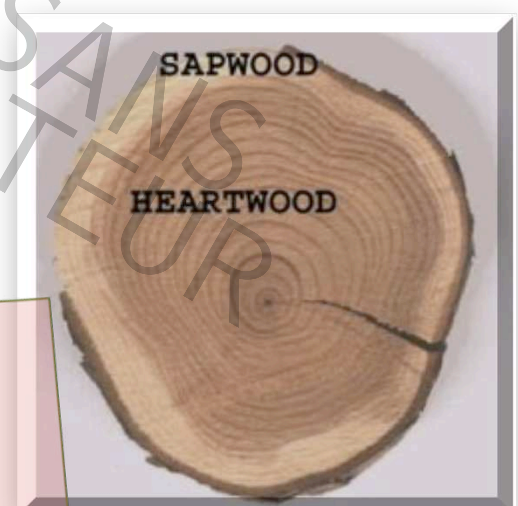
Outline

- Introduction to Nanocellulose
- Type of Nanocellulose
- Applications
- Chemical Modifications
- Outlooks and futures

Derivatives from Cellulose Fibers



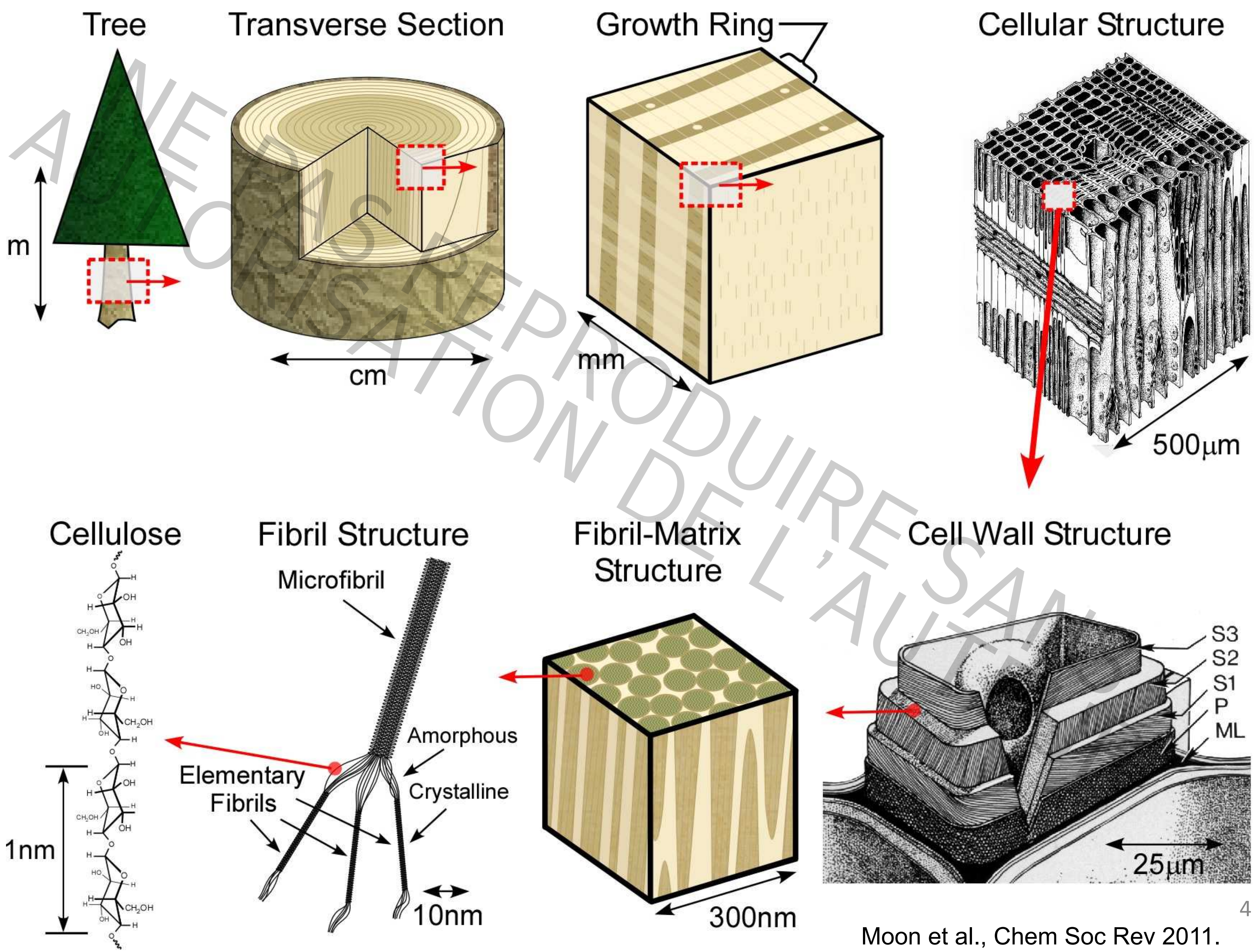




Intermediate substrates

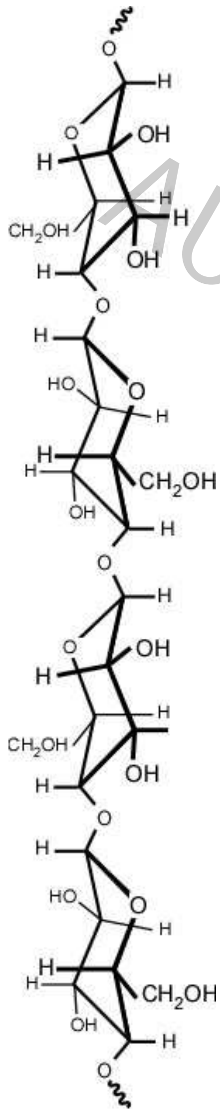
Top-down: deconstruction

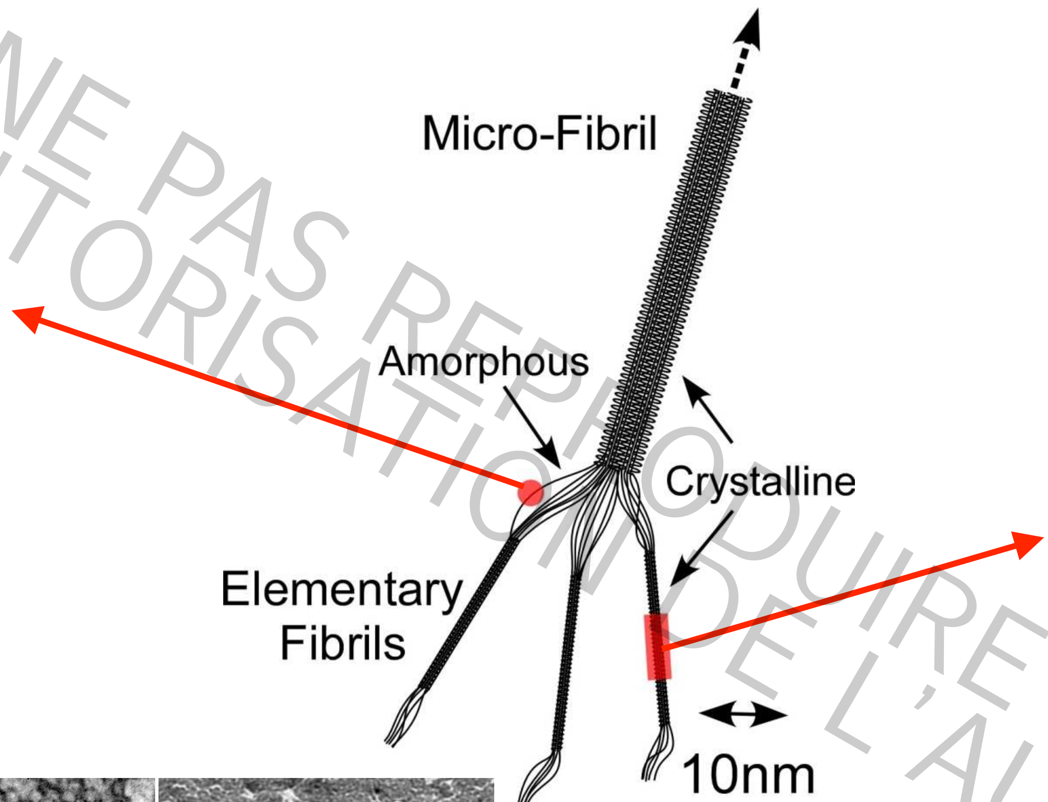
Morphology and organization

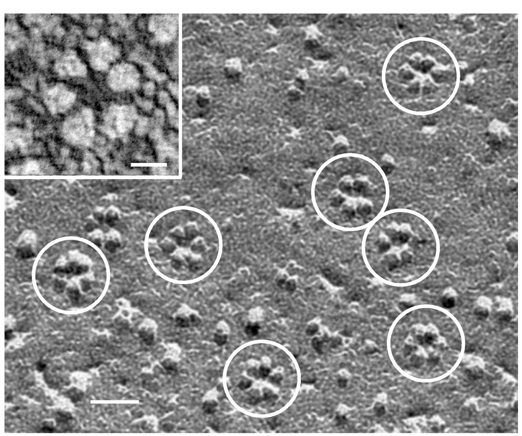


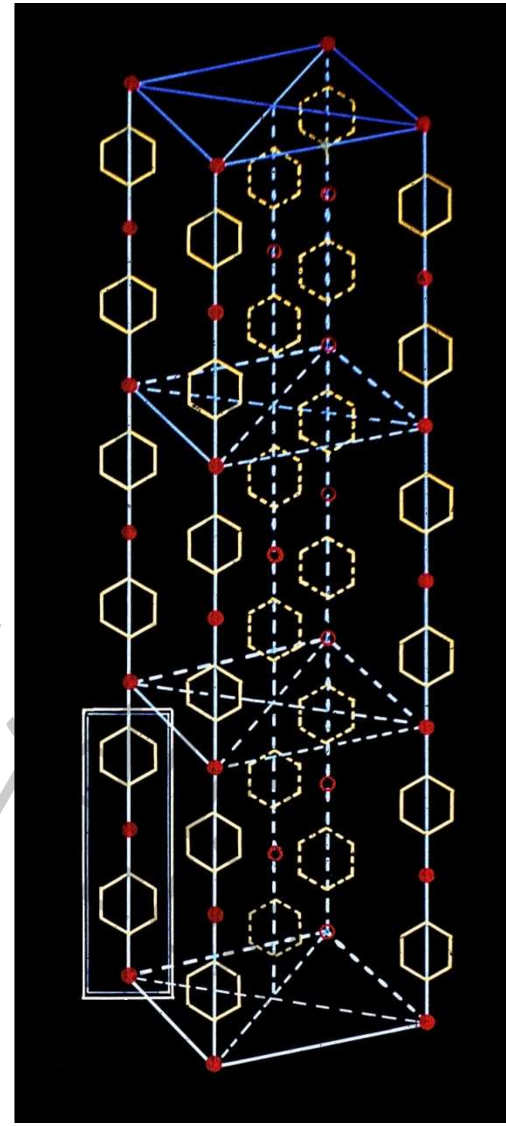
Moon et al., Chem Soc Rev 2011.

Cellulose Microfibrils : organization and morphology





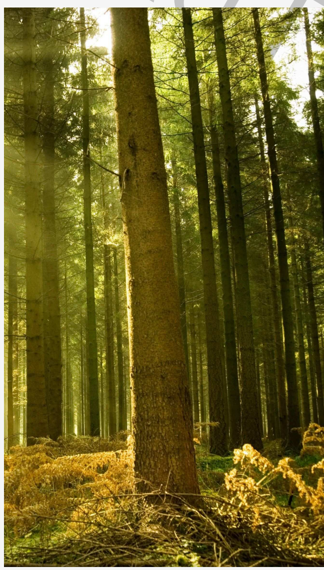




Wide Variety of Sources

Trees

Soft and Hard woods



Cellulose Pulp
MCC

Plants

Hemp

Cotton

Ramie

Sisal

Sugar Beet

Wheat Straw

Alfa, Hemp, Flax, Jute, Banana
Rachi, Potato, etc

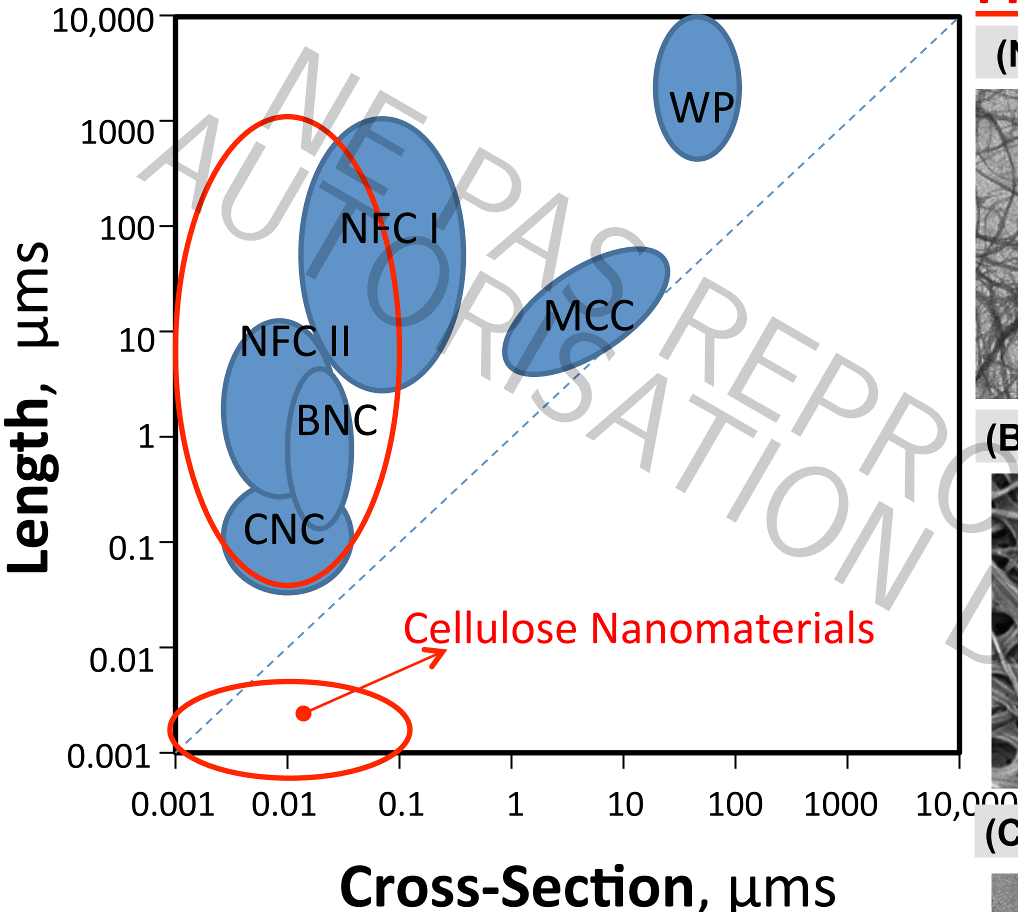
Others

Tunicate

Bacteria

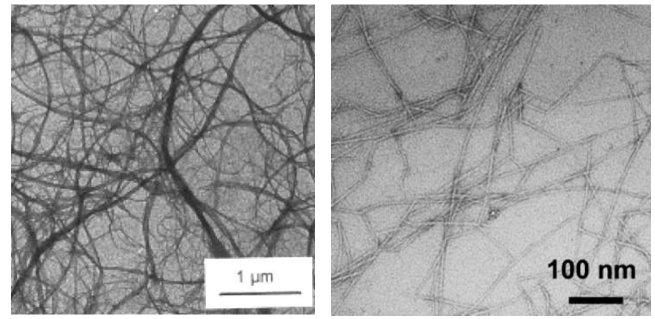
Algae

Types of Nanocellulose

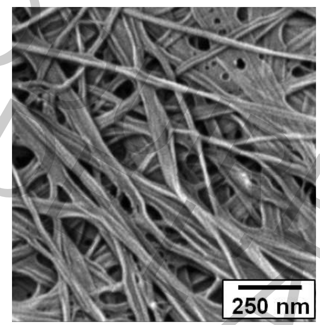


Fibrillar Types:

(NFC) Nanofibrillated Cellulose

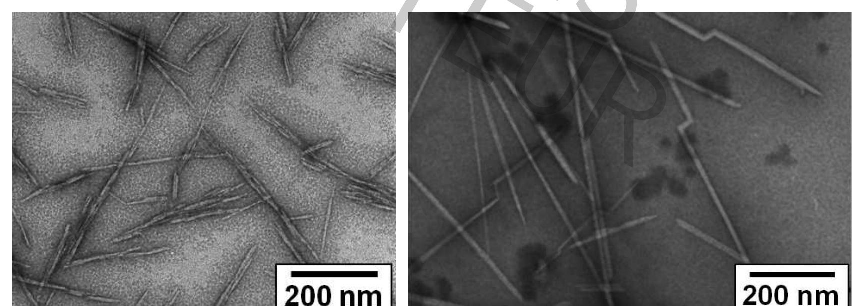


(BNC) Bacterial NanoCellulose



Rod Types:

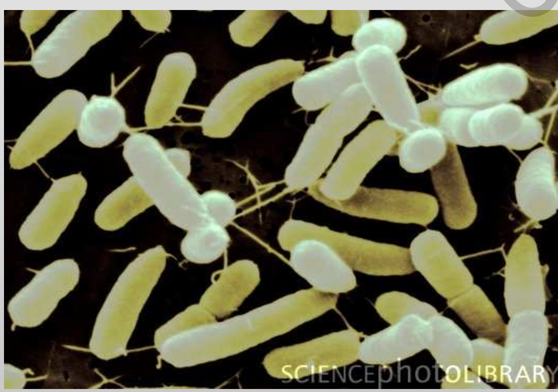
(CNC) Cellulose Nanocrystals



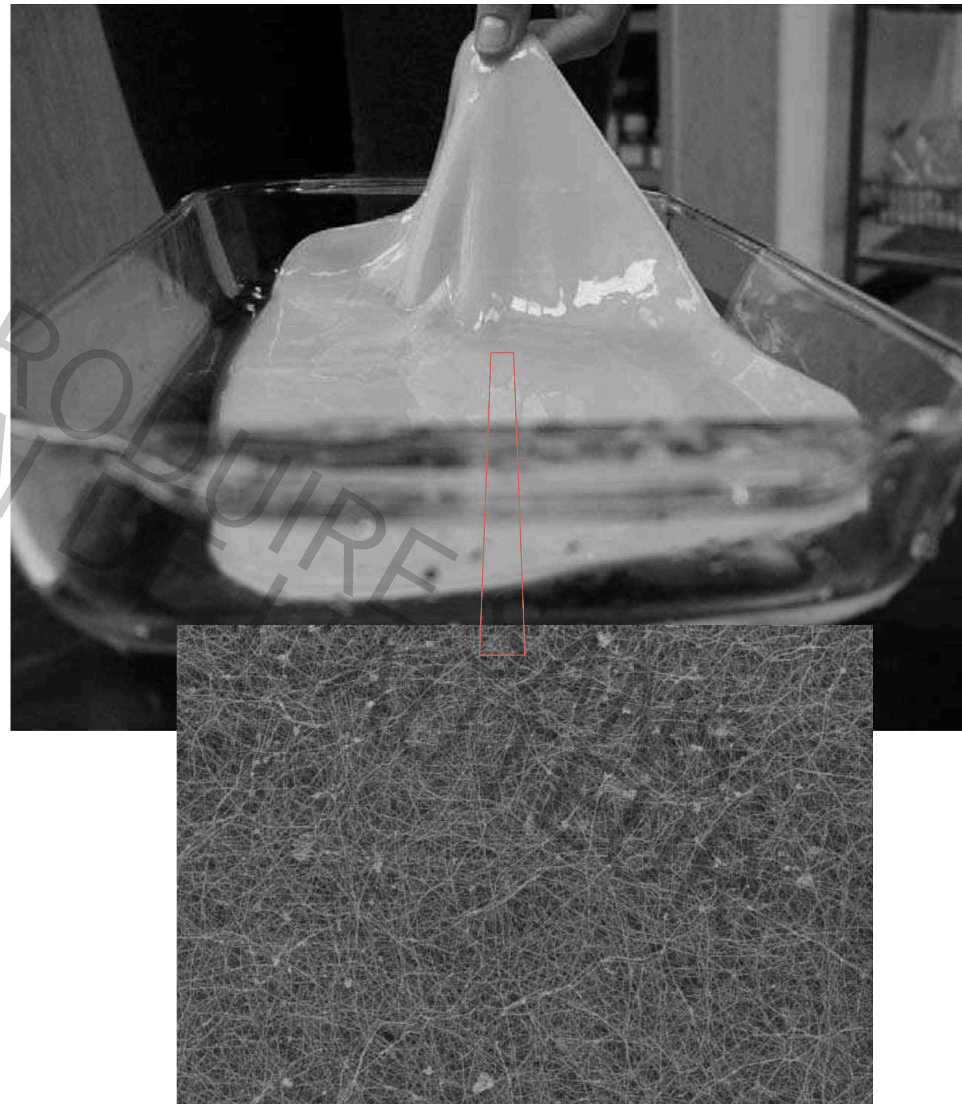
Bacterial Cellulose

Nutriments

+

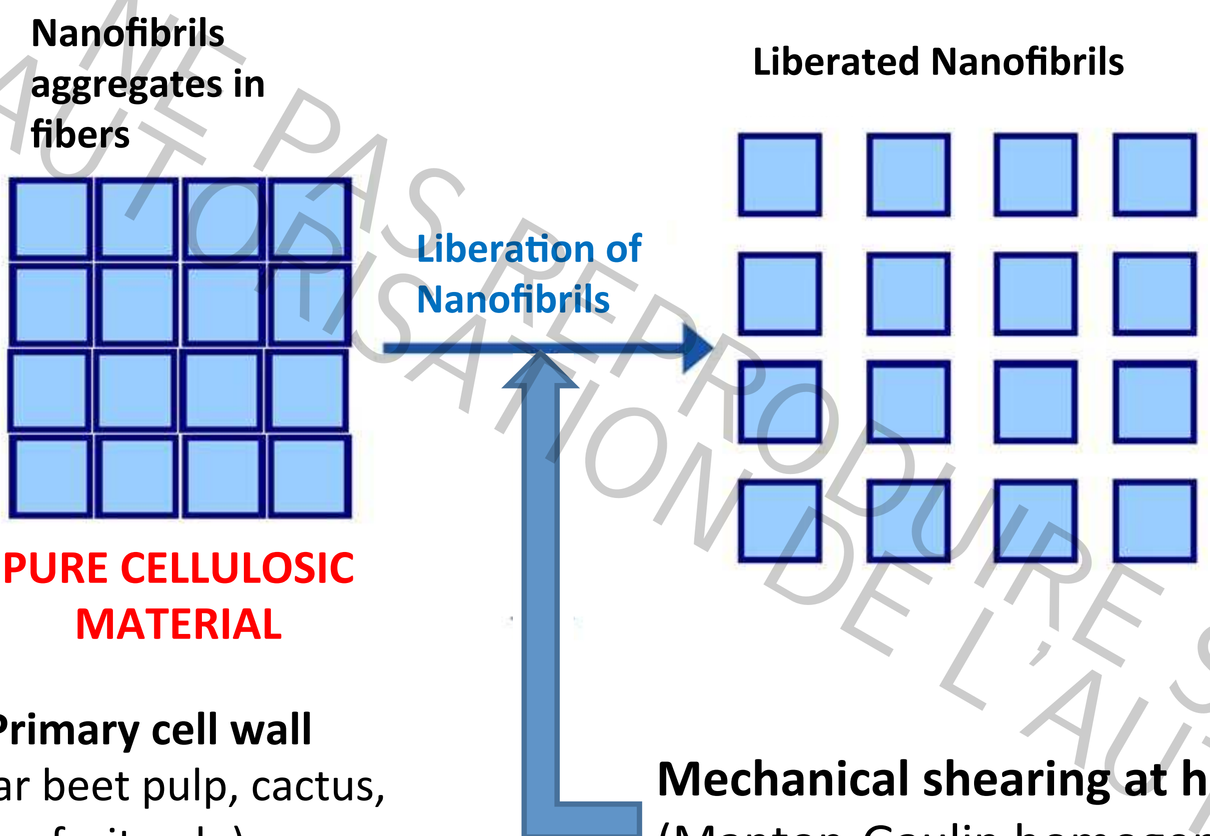


Biomaterials, 2006, 27, p145



Production and Processing

Mechanical Processing= NFC



PURE CELLULOSIC MATERIAL

Primary cell wall (sugar beet pulp, cactus, fruit pulp)

Secondary cell wall (wood, bacterial

Mechanical shearing at high pressure (Manton-Gaulin homogenizer, Microfluidizer, Grinder)

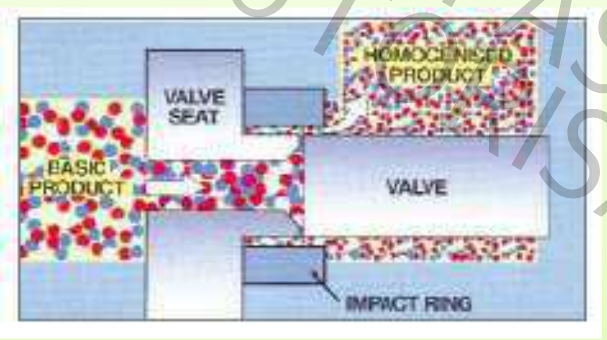
+ Pretreatments (chemical + enzymatic, …)

Production and Processing

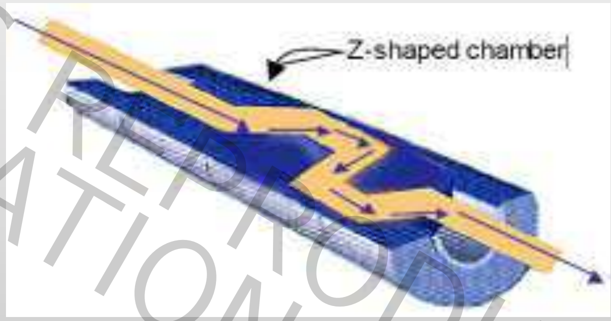
Mechanical Processing= NFC

Nanofibrillated cellulose → Fiber Cell Wall Delamination

Manton-Gaulin Technology



Microfluidizer Technology



Masuka Grinding Technology

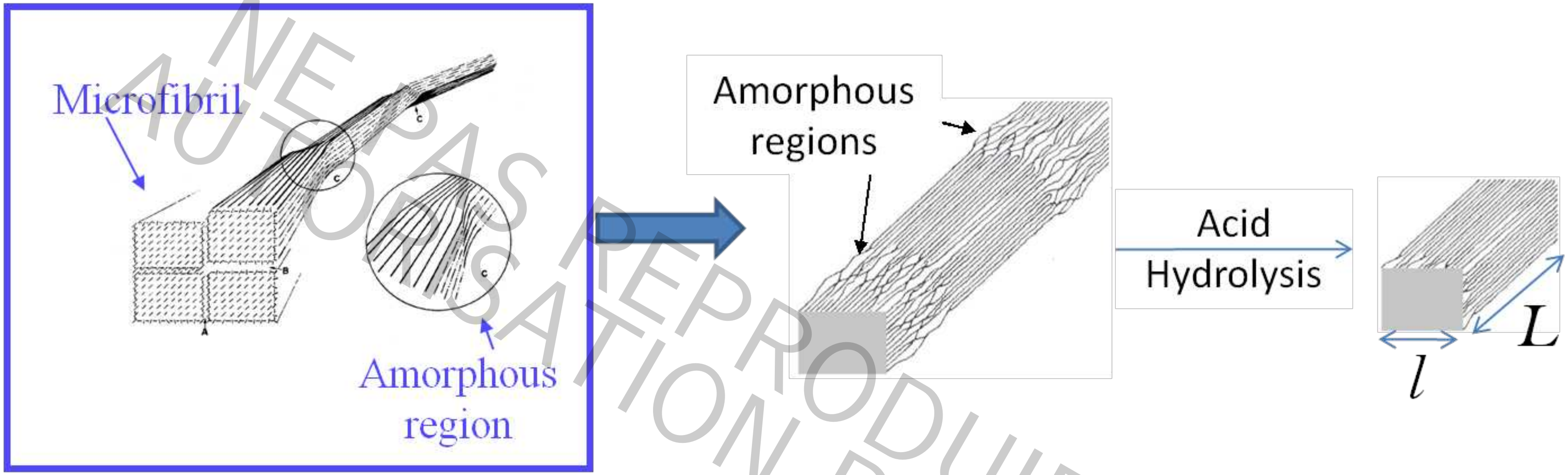
High Energy Consumption
Processing problems

✓Mechanical pretreatments

✓Enzymatic pretreatments

✓Chemical pretreatments (TEMPO-NaOCl-NaBr mediated oxidation)

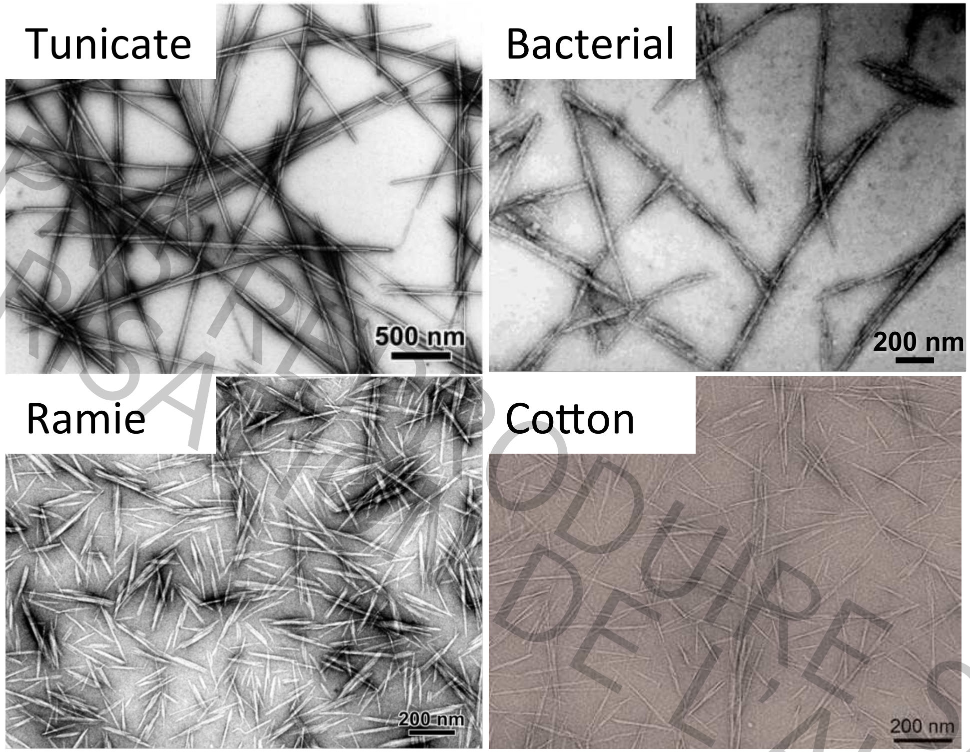
Chemical Processing= CNC

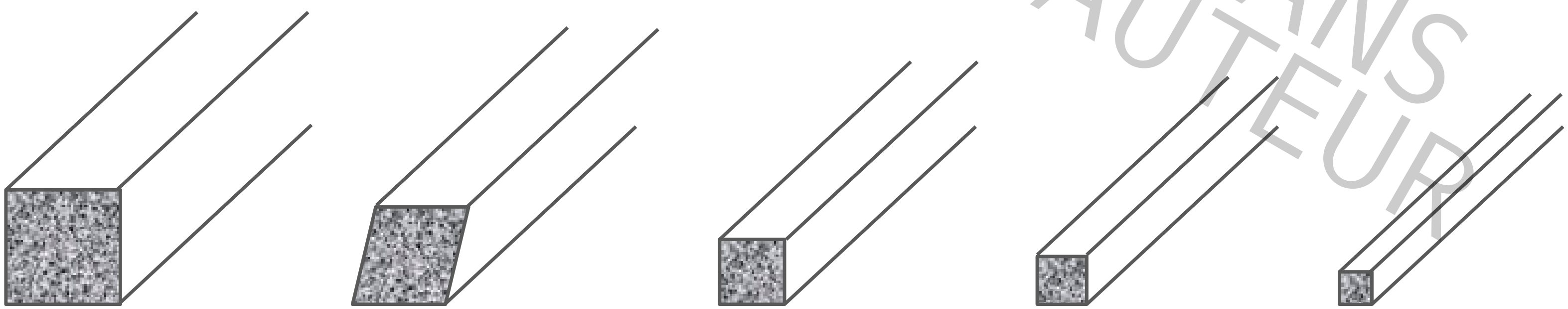


Typical Conditions:

Acid	H_2SO_4	HCl
Concentration	65% (wt)	2.5 – 4 M
Temperature	RT – 70˚C	Reflux
Time	30 min -overnight	1 to 4hours

Chemical Processing= CNC





15-25 nm
Valonia

10-15 nm
Tunicate

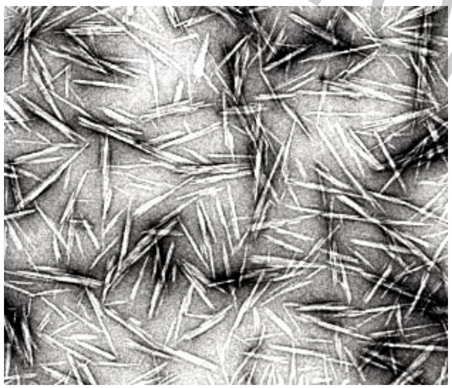
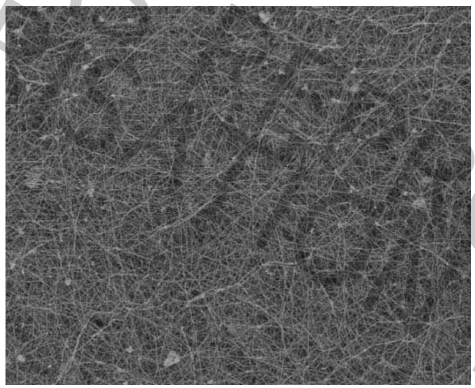
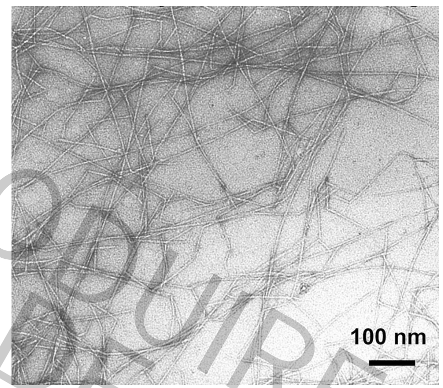
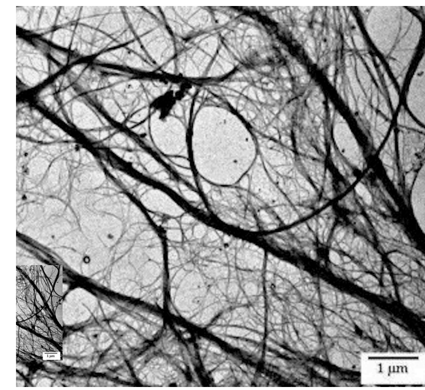
8-9 nm
Bacterial

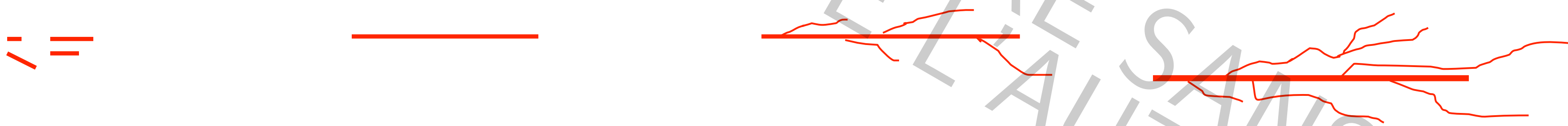
5-6 nm
Cotton & Ramie

3-5 nm
Wood

Morphological Features

↑ **branching**

CNC	**BC**	**NFC II**	**NFC I**
			



•**Diameter:** 3-20 nm	•30-50, 6-10nm	•4-40 nm	•40-100 nm
•**Length:** 50-500 nm	•> 1µm	•> 1um, ?	•> 1um, ?
•**Branching:** low	•low	•medium	•high

Nomenclature

Rod Types:

- CNC
- NCC
- CNW
- NCXLS

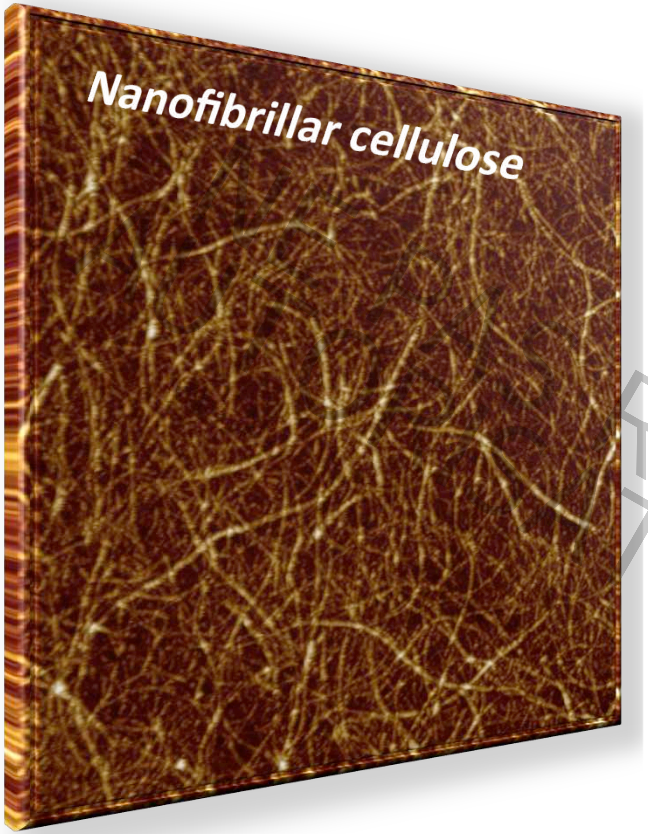
Fibrillar Types:

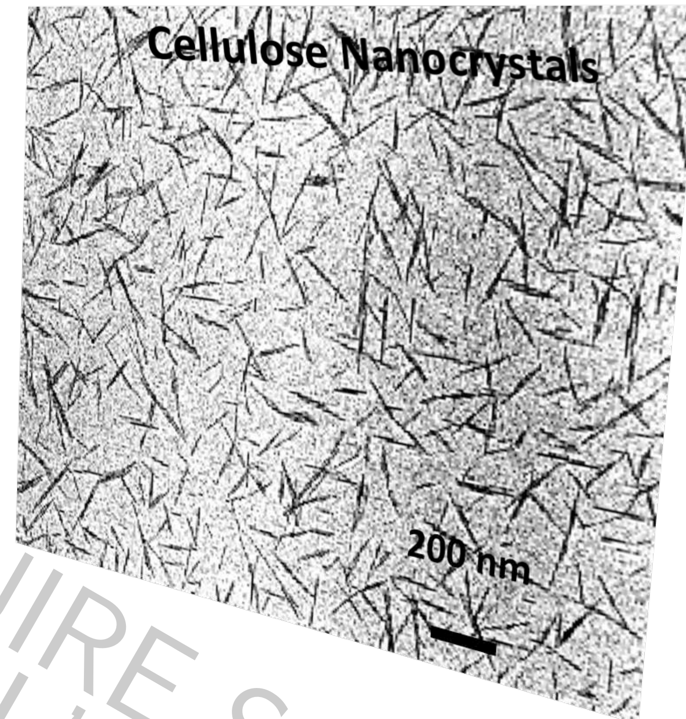
- CNF
- MFC
- NFC
- BC (Bacteria cellulose)
- AC (algae cellulose)

Some "relief"?

•TAPPI Standard Development:

Cellulose Nanomaterial Nomenclature

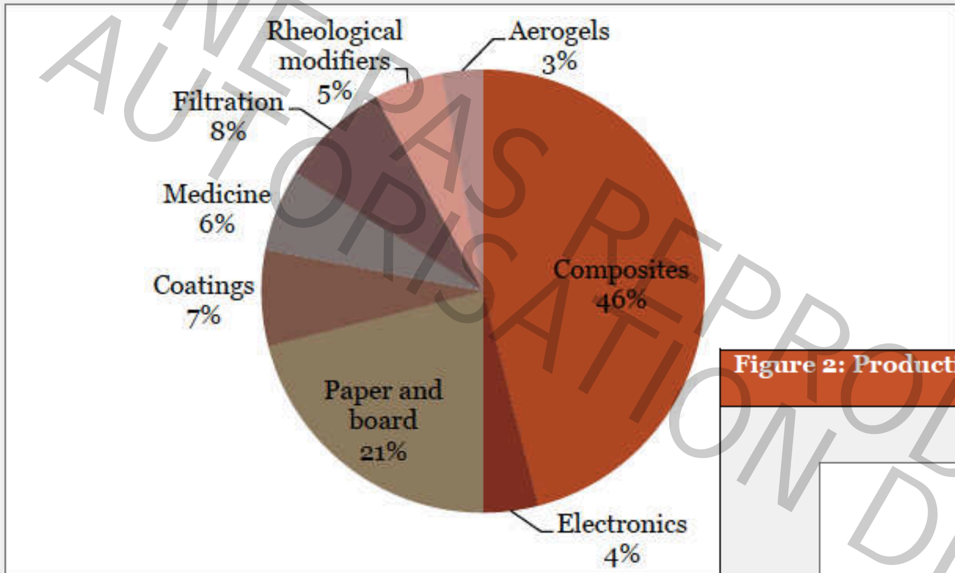




Nanocellulose is a unique material : *hydrophilicity*, *biocompatibility*, *stereoregularity*, *biodegradability*, *chemical stability*, *reactive hydroxyl groups* and the ability to form *superstructures*.

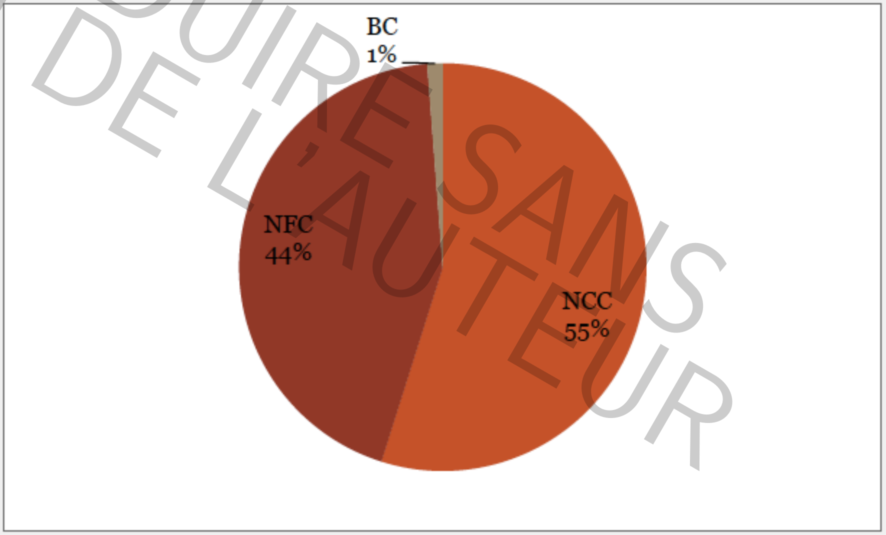
Interests and Application Domains

Figure 3: Demand for nanocellulose by market, 2011



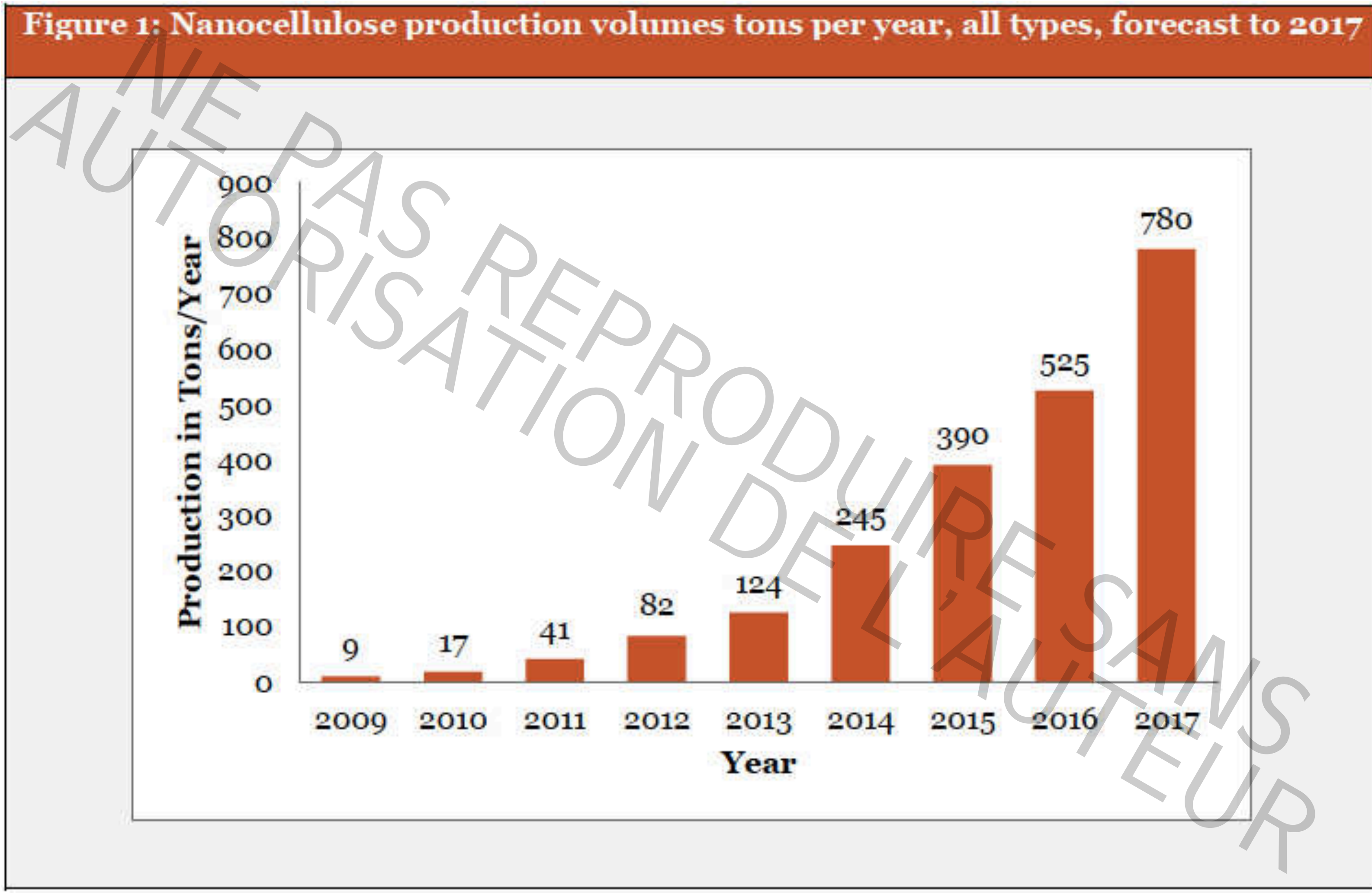
Source: Future Markets, Inc.

Figure 2: Production of nanocellulose by type, 2011

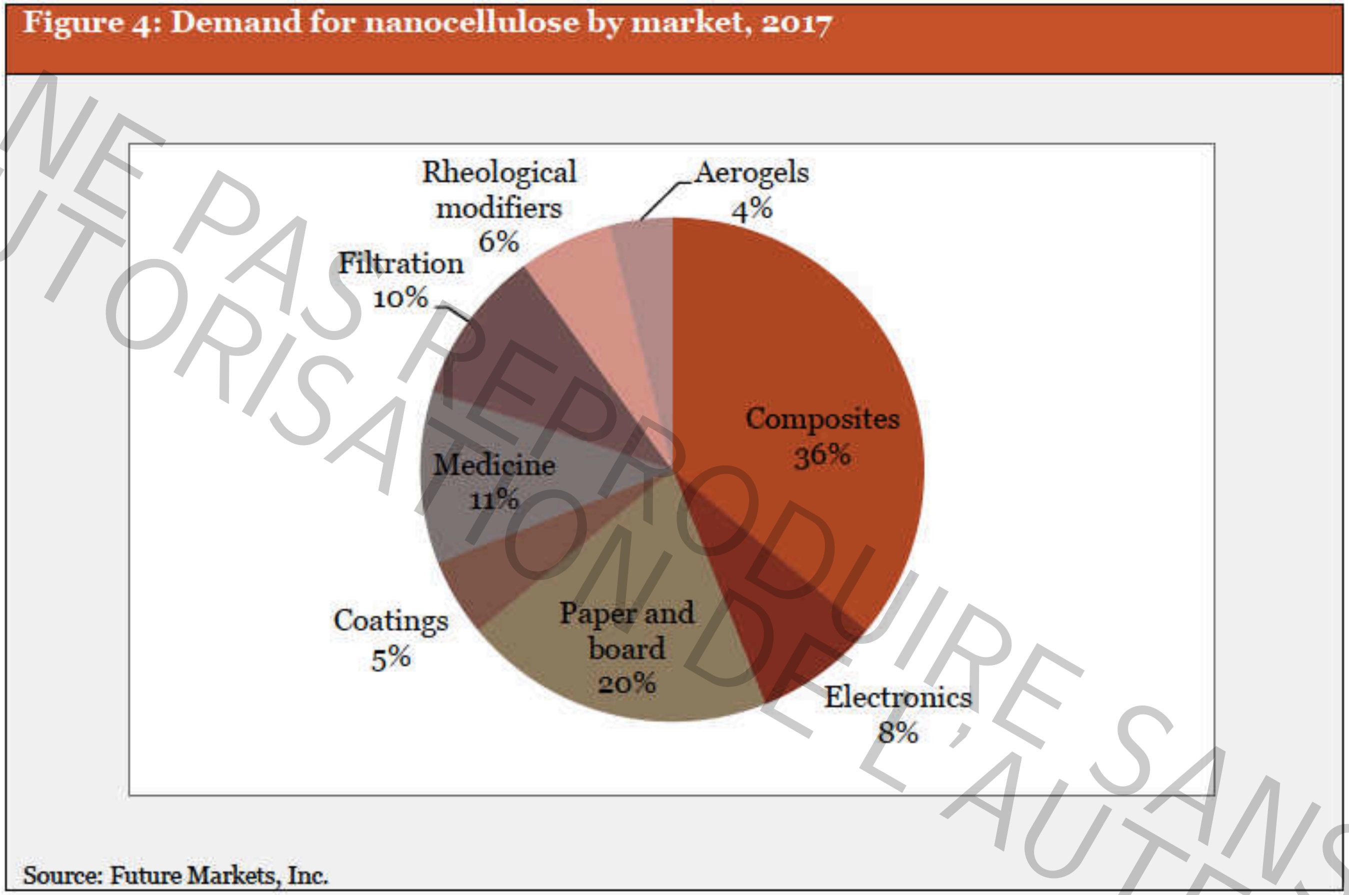


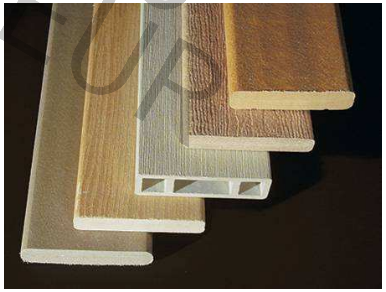
Source: Future Markets, Inc.

Interests and Application Domains



Interests and Application Domains





Nanomaterials / Nanocomposites

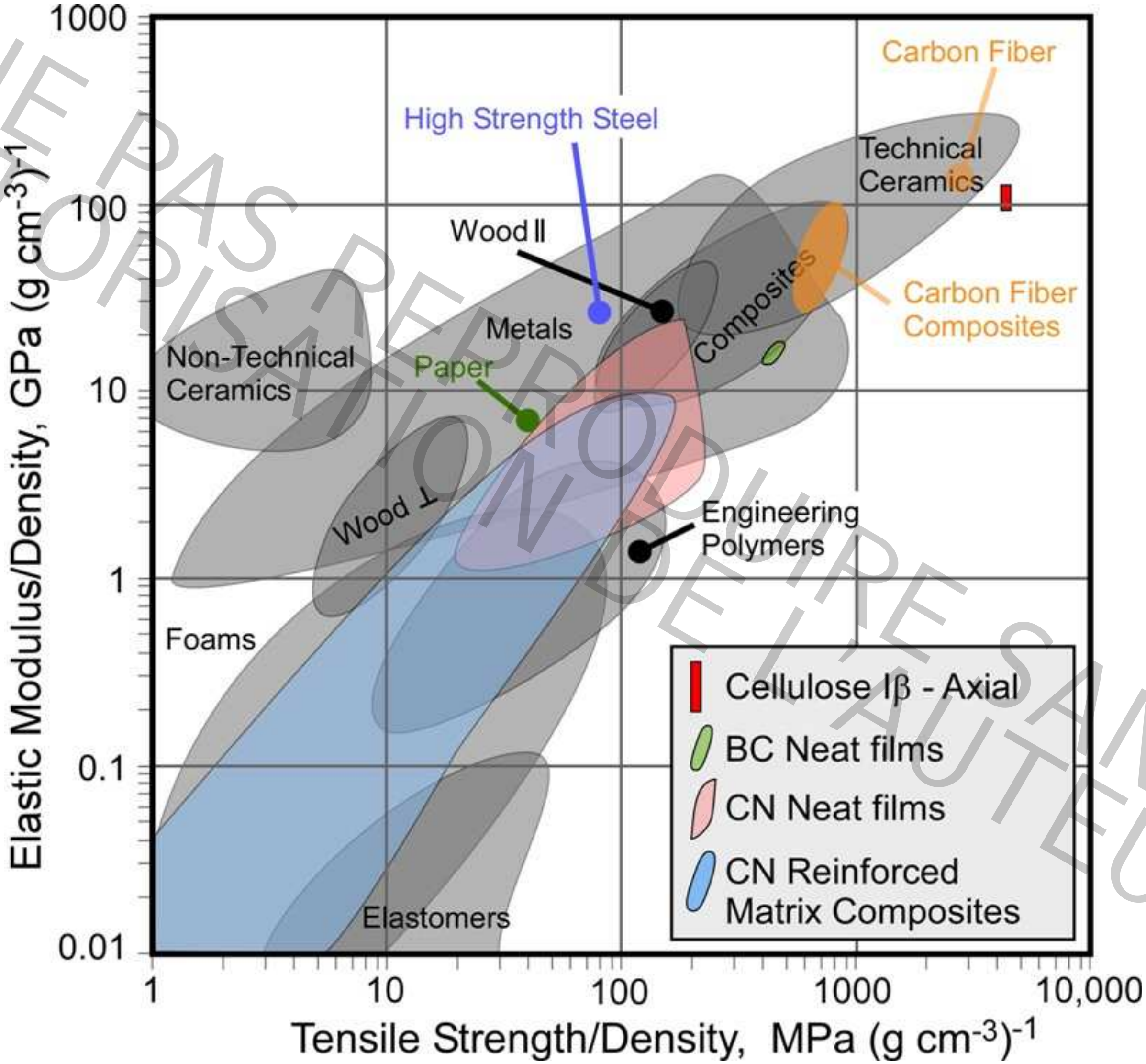

Nogi et al., Adv. Mater, 2009

Okahisa et al., Compos Sci Technol, 2009, 69:1958.


Nimeskern et al. *J. Mech. Behav. Biomed. Mater.* **2013**

- Several Composite Types
- Unique Optical Properties
- Mechanical Properties
- Biocompatibility
- Low Density
- Multifunctional
- “Green”

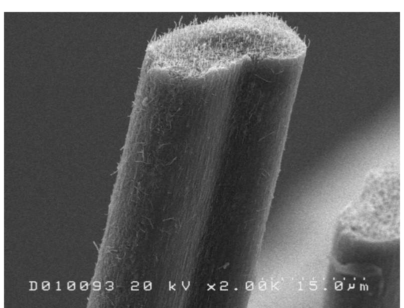
High Elasticity & Strength:

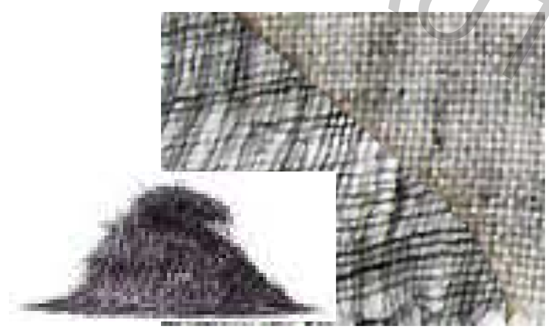


Moon et al., Chem Soc Rev 2011

Nanocomposites

Material	*Tensile strength (GPa)*	*Modulus (GPa)*	**Density**
Cellulose Nanocrystal	7.5	145	1.566
Glass fiber	4.8	86	2.500
Steel wire	4.1	207	7.85
Graphite whisker	21	410	1.800
Carbon nanotubes	11-63	270-970	1.330
Aramide	3.2	65	1.400
Kevlar	3.0	120	1.450



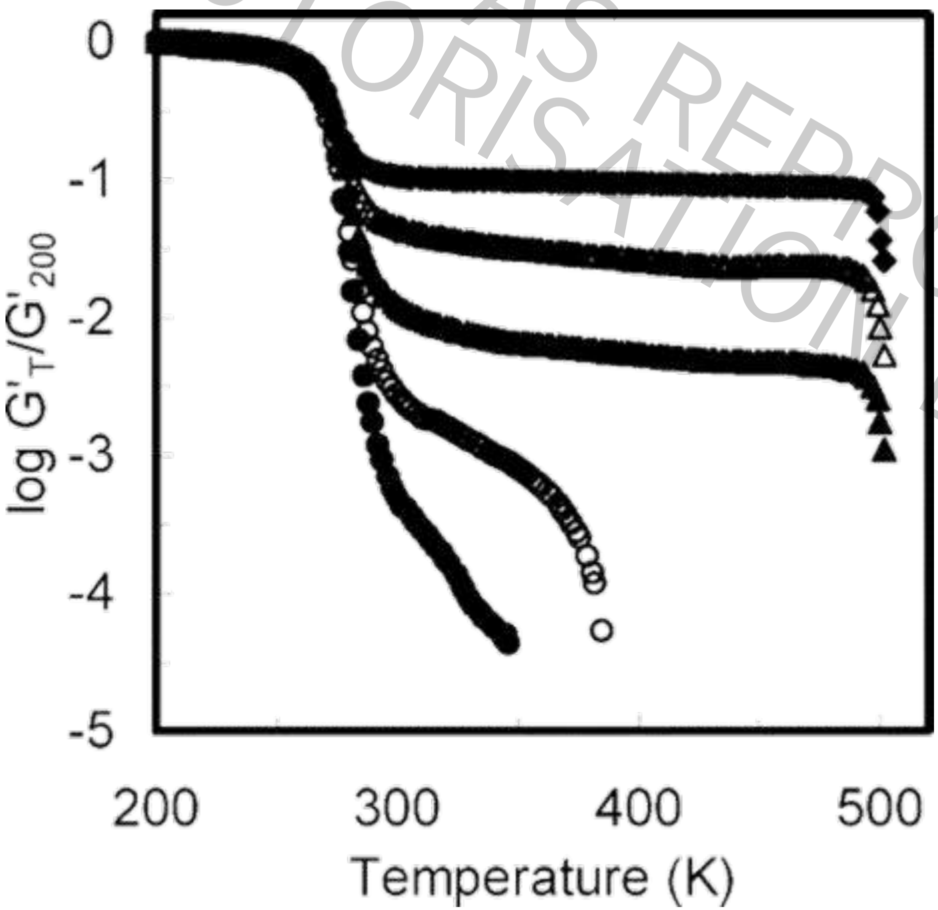


Nanocomposites

Nanocellulose
HYDROPHILIC

⟷

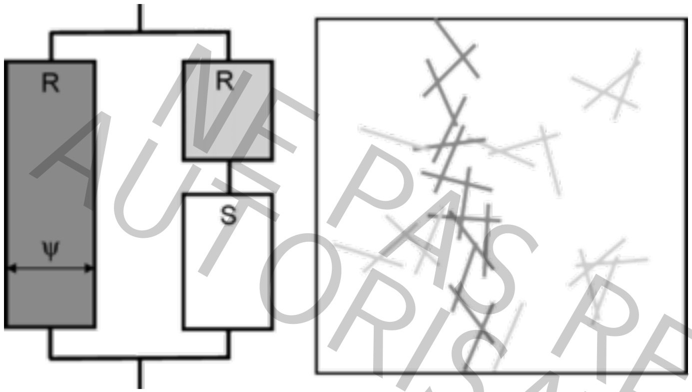
Polymer Matrix
HYDROPHILIC

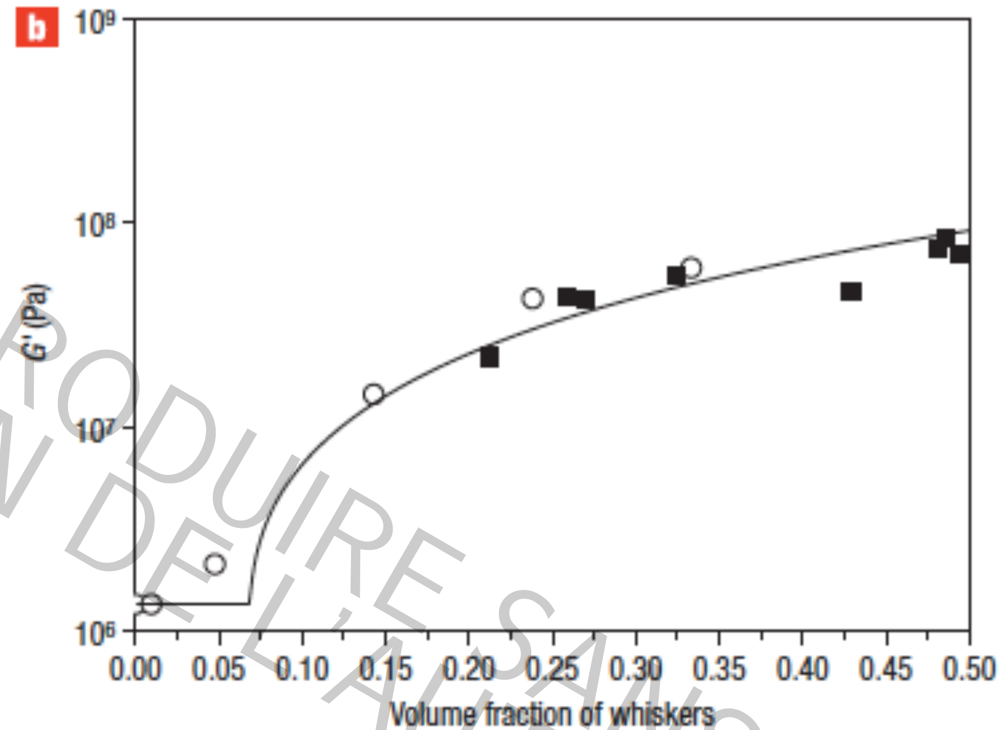


Processing methods:

- ✧ Solvent Casting
- ✧ Wet Spinning
- ✧ Electrospinning
- ✧ Gel templating

Nanocomposites





$$G' = \frac{(1 - 2\psi + \psi X_r)G'_s G'_r + (1 - X_r)\psi G'^2_r}{(1 - X_r)G'_r + (X_r - \psi)G'_s}$$

$$\psi = 0 \qquad \text{for} \quad X_r < X_c$$

$$\psi = X_r\left(\frac{X_r - X_c}{1 - X_c}\right)^b \qquad \text{for} \quad X_r > X_c$$

S and R for soft and rigid phase. X: volume fraction

Xc: critical percolation volume fraction = 0.7/A (where A is the aspect ratio).

b:critical percolation exponent, for 3D network b=0.4

Habibi and Dufresne, Handbook of Nanophysics

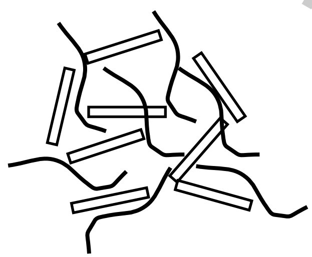
Nanocomposites

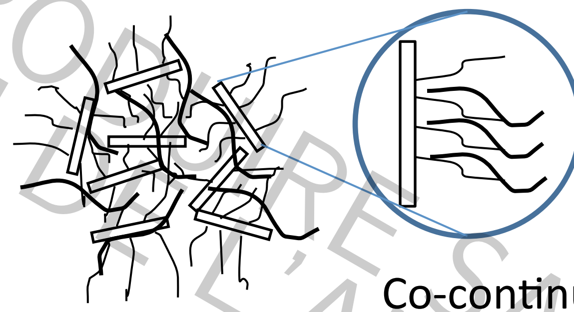
Nanocellulose
HYDROPHILIC

Polymer Matrix
HYDROPHOBIC

Interface Compatibility

Chemical Modification



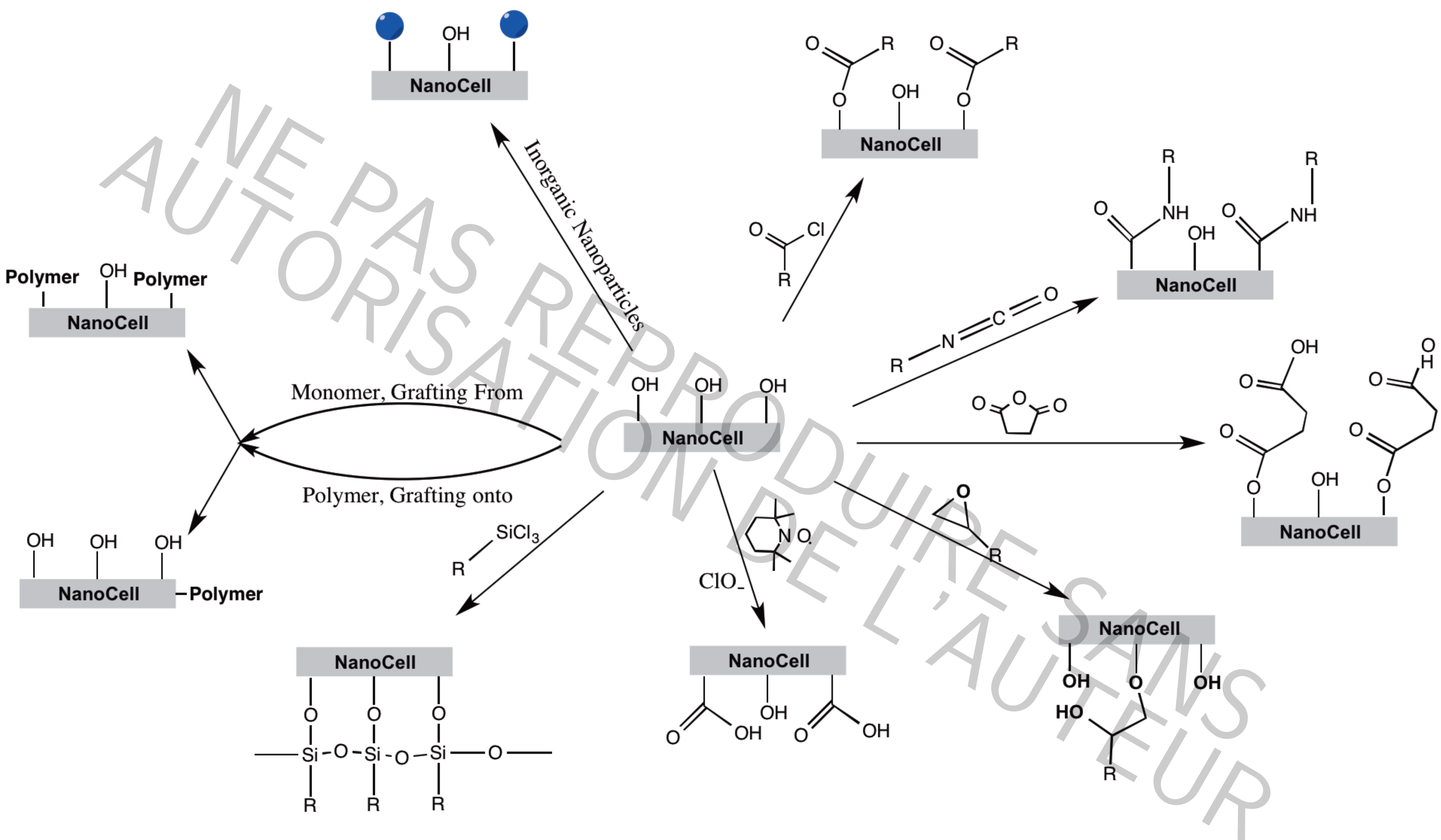


Co-continuous phase

++ Compatibilisation
-- poor adhesion
-- Poor mechanical properties

+++ Compatibilsation
+++ Good adhesion
+++ Good mechanical ppties

Chemical Modifications



WARNING

Preserve the native crystalline structure

Preserve the morphological integrity

Conclusions

NanoCellulosic Substrates have unique mechanical, optical, and chemical properties that can be used in diverse applications

Successful and positive advances have been achieved through the efforts of many dedicated studies

However,

- the scaling-up of nanocellulose production
- Solid-state processing and the long term durability of the nanocellulose-based composites

remain as challenges

Reading Documents

Habibi et al. Cellulose Nanocrystals: Chemistry, Self-assembly and Applications
Chem Rev, 2010, 110, 3479-3500.

Moon et al. Cellulose nanomaterials review: structure, properties and nanocomposites.
Chem Soc Rev, 2011, 40, 3941-3994.

Siró & Plackett. Microfibrillated cellulose and new nanocomposite materials: a review
Cellulose, 2010, 17, 459-494.

Habibi. Key advances in the chemical modification of nanocelluloses. 2014, Chem Soc Rev, ASAP.
DOI: 10.1039/C3CS60398A


Thank you!