Use of nanocellulose in fibre-based packaging: from barrier to active and intelligent packaging

Julien BRAS

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University Grenoble Alpes, Grenoble INP - LGP2
Institut Universitaire de France (IUF 2016-2021)

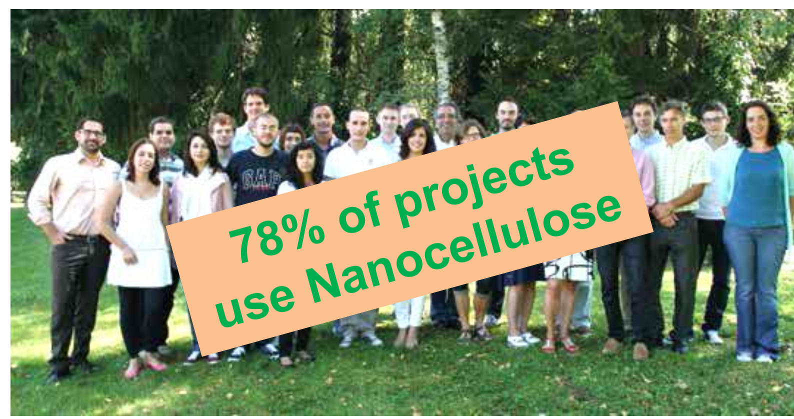
Julien.Bras@grenoble-inp.fr

AT THE CROSSROAD OF LEADING DISCIPLINES
CHEMISTRY, MATERIALS, PROCESSES

[www. pagora.grenoble-inp.fr](http://www.pagora.grenoble-inp.fr)

3 research departments

- Biorefinery: wood chemistry and eco-process
- Multi-scale bio-based materials
- Surface functionalization by printing



10 Permanent researchers, 5 technical staff, 25 PhD & Post-doc

OUTLINE

1. Nanocellulose & production
2. From barrier packaging…
3. To active & intelligent packaging

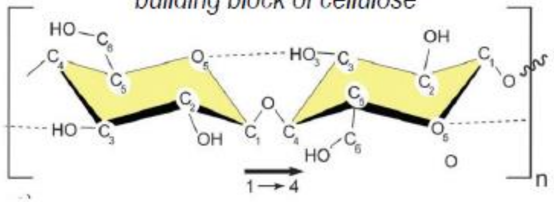
NanoCellulose

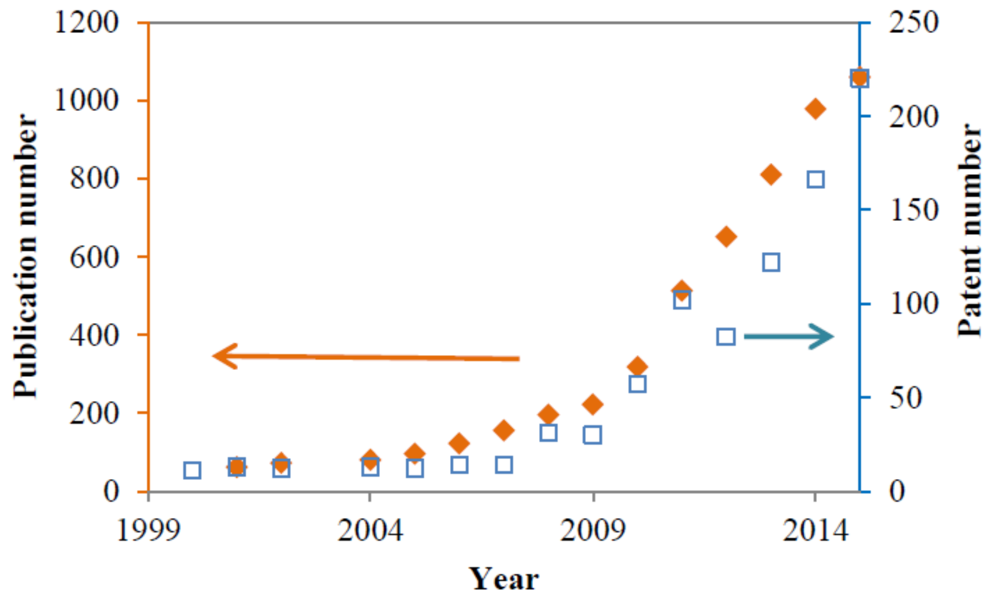
Nanocelluloses

Nanomaterials
- 1 dimension < 100 nm
- high surface area (>100 m² /g)
- novel characteristics

Cellulose
- most available biopolymer on earth
- 200 billion tons / year (3 % used)
- many sources available

building block of cellulose



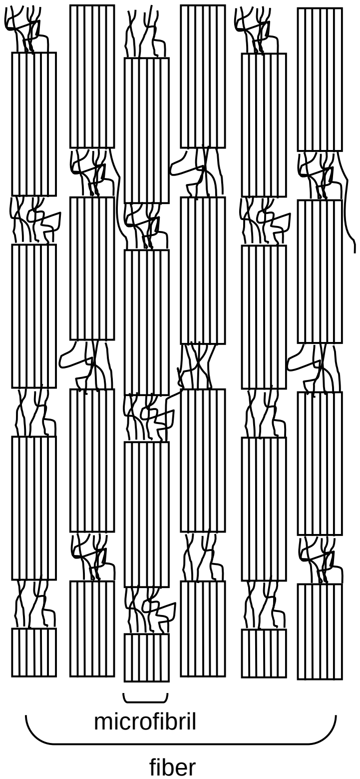


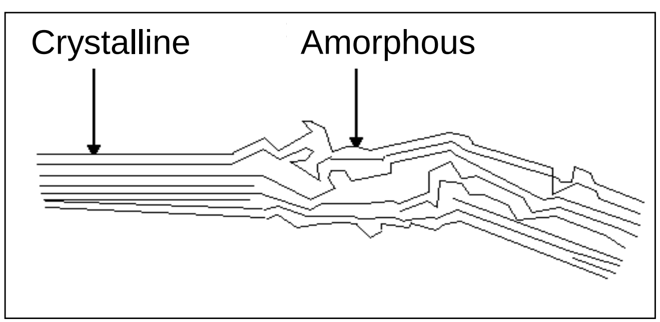
Evolution of annual non-cumulative number of publications and patents on nanocellulose

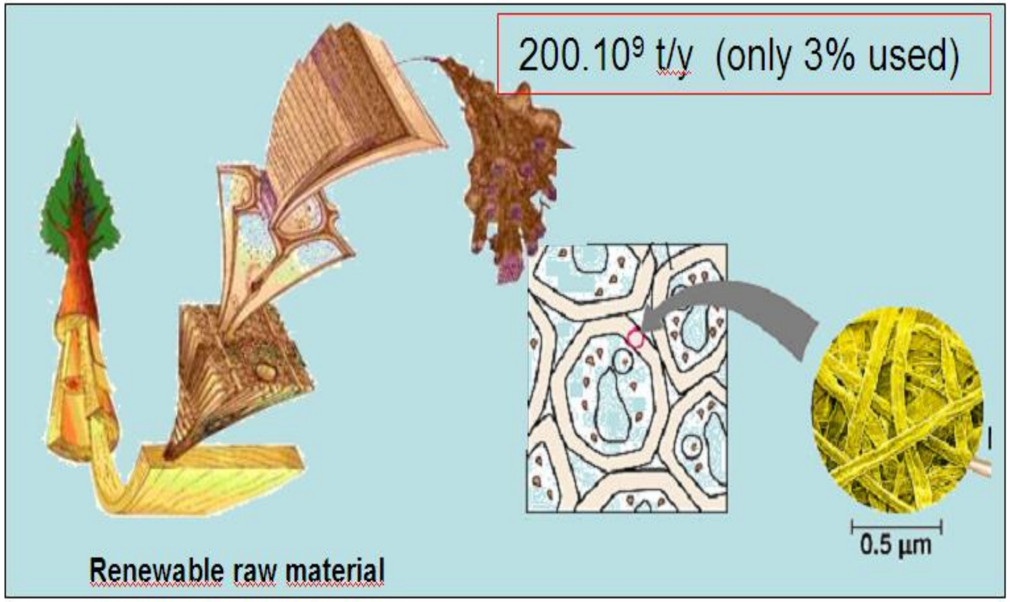
(Source: SciFinder, July 2016 – descriptors : cellulose nanofibrils, cellulose microfibrils, cellulose nanocrystals, cellulose nanowhiskers, microfibrillated cellulose)

(Nano)Cellulose

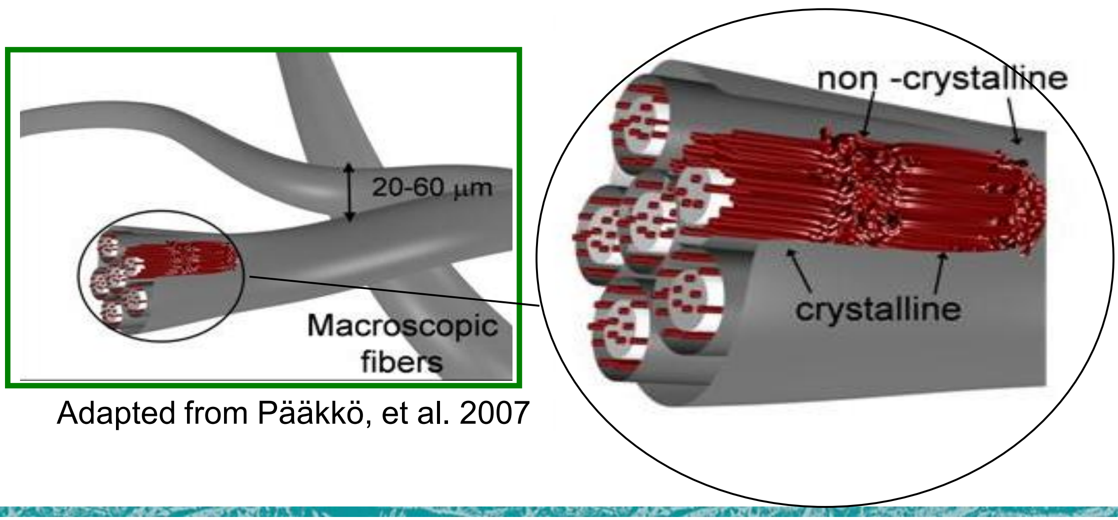
Hierarchical Structure





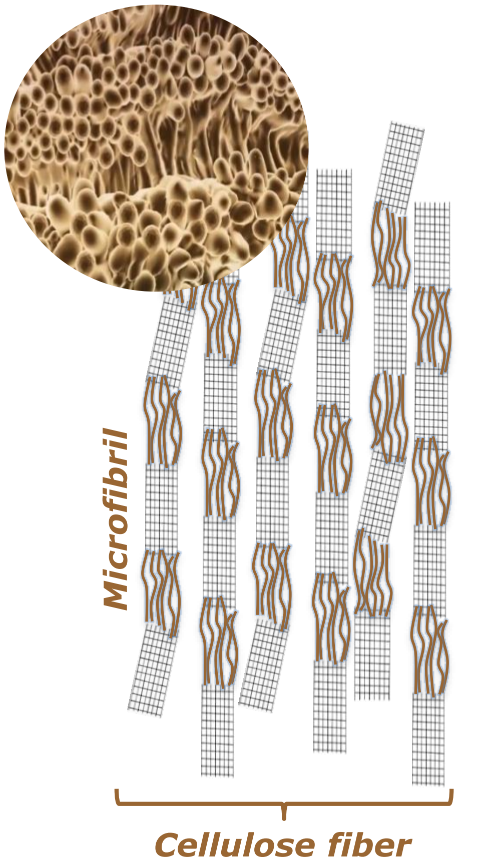


Multi-level Organization



Adapted from Pääkkö, et al. 2007

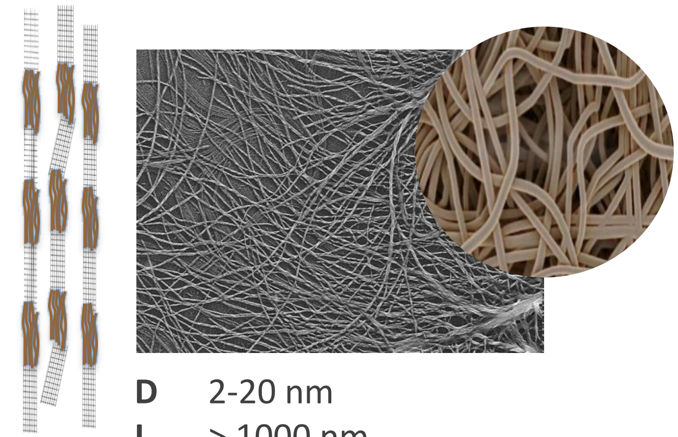
NanoCellulose



2. Mechanical
Homogenization
1. Defibrillation

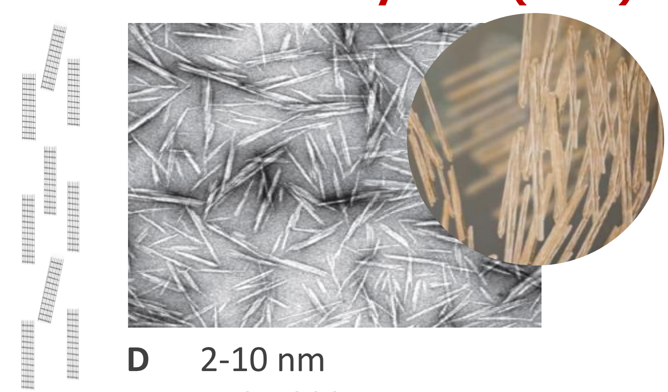
1. Hydrolysis
2. Dialysis /UF

Microfibrillated cellulose (MFC)



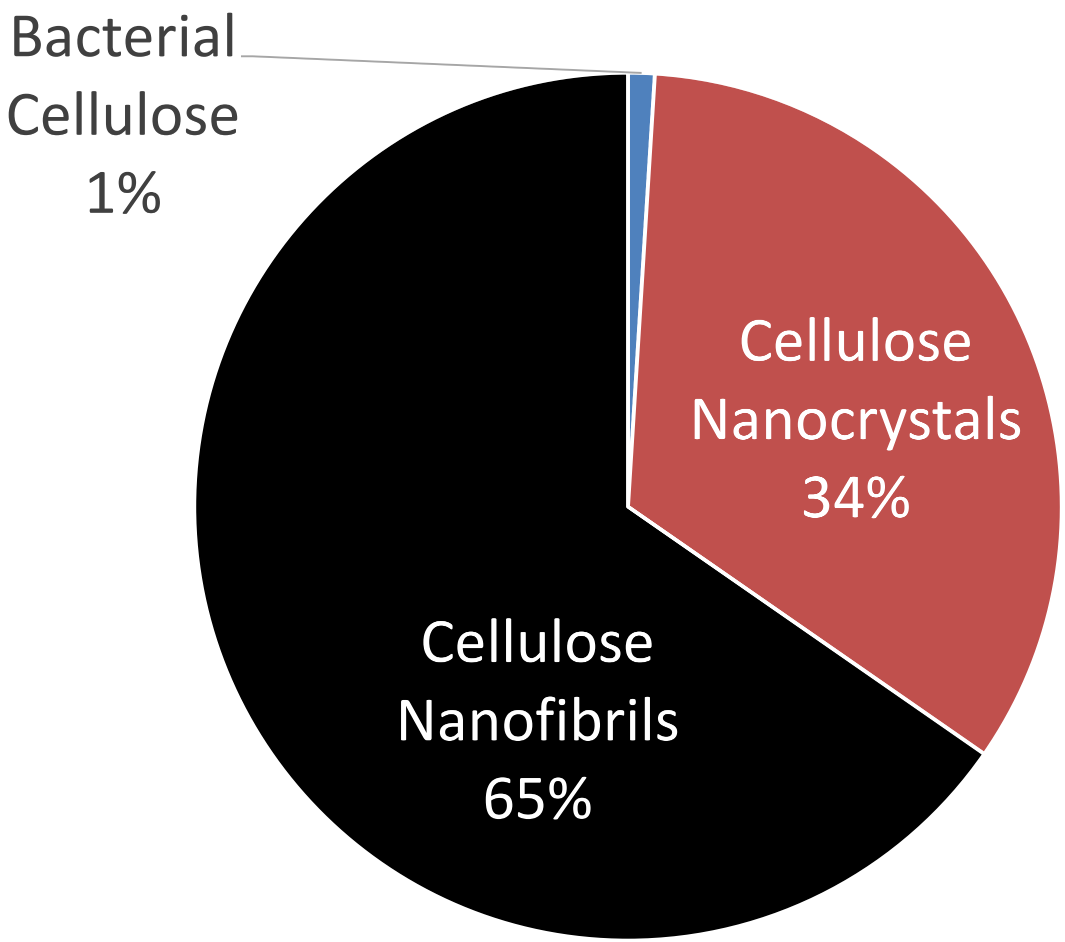
D 2-20 nm
L > 1000 nm

Cellulose Nanocrystals (CNC)



D 2-10 nm
L 150-1000 nm

Nanocellulose



USDA
Global production estimate: 34 million tons/year by 2050

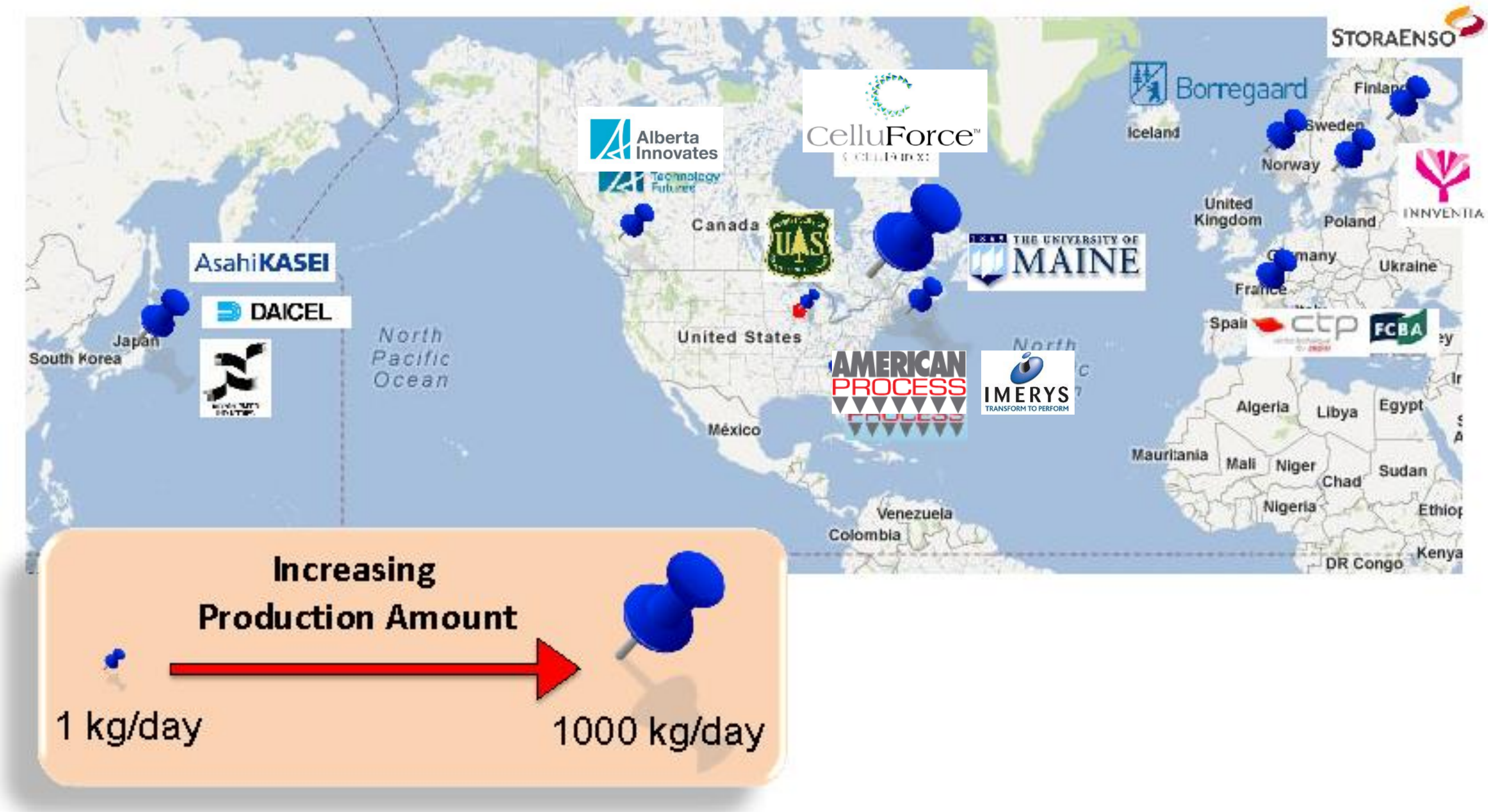
FPI market estimate: $250 million in North America by 2020

<u>Production cost:</u>
Pulp: $0.75-1.00/kg
Nanocellulose: $4-40/kg

Cranston 2015

Future Markets, *The global market for nanocellulose to 2020*, 2nd ed. Future Markets Inc, 2012

Nanocellulose



Slide provided by Robert Moon, USDA FPL

NanoCellulose

LGP2

Flagships in Call 2016

BBI

Objective: deployment of a technology, which has been already demonstrated leading to a system, which is complete and qualified (TRL8) for successful commercial operation (large scale production facility in Europe)

TOPIC	FOCUS
BBI.VC1.F1	BIOETHANOL: second generation bioethanol production built on lignocellulosic non-food feedstock (straw)
BBI.VC2.F2	Microfibrillar Cellulose (MFC): large-scale supply and market creation of MFC to demonstrate an industrial symbiosis between the biomass and the forest industry
BBI.VC1.F1	CELLULOSIC ETHANOL: Cellulosic ethanol from unused crop residues and crops grown on marginal lands

›rregaard / News / EUR 25 million in EU funding for Exilva

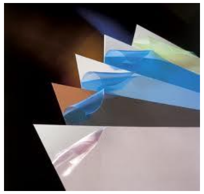
Borregaard Receives EUR 25 million for Commercialization of Microfibrillar Cellulose from the EU

Borregaard Receives EUR 25 million for Commercialization of Microfibrillar Cellulose from the EU

Borregaard has received a funding commitment of EUR 25 million (NOK 232 million), for the development and commercialization of

=> Nanocellulose = 2nd **priority** of european Bioeconomy
=> Not only fashionable but also **sustainable**

NanoCellulose




23 million tonne potential

(figure in ktons)


	Market Size	Potential Loading	Nano Cellulose Potential	Potential @ 5% Market Penetration	CNF Potential	CNC Potential	CNF	CNC
Paper and Paperboard	400,000	5.0%	20,000	1,000	95%	5%	950	10*
Paints and Coatings	40,000	2.0%	800	40	5%	95%	2	38
Composites	9,000	2.0%	180	9	5%	95%	0	9
Films and Barriers	9,670	2.0%	193	10		100%	0	10
Excipients	4,600	2.0%	92	5	10%	90%	0	4
Natural Textiles	34,500	2.0%	690	35		100%	0	35
Manufactured Textiles	56,300	2.0%	1,126	56		100%	0	56
Cement	15,000	0.5%	75	4	5%	95%	0	4
Oil and Gas	17,500	1.0%	175	9	10%	90%	1	8
Nonwovens	7,000	2.0%	140	7		100%	0	7
Adhesives	4,000	2.0%	80	4	5%	95%	0	4
TOTAL			**23,551**	**1,178**			954	184






Source: RISI, *Nanocellulose: Technology Applications, and Markets*

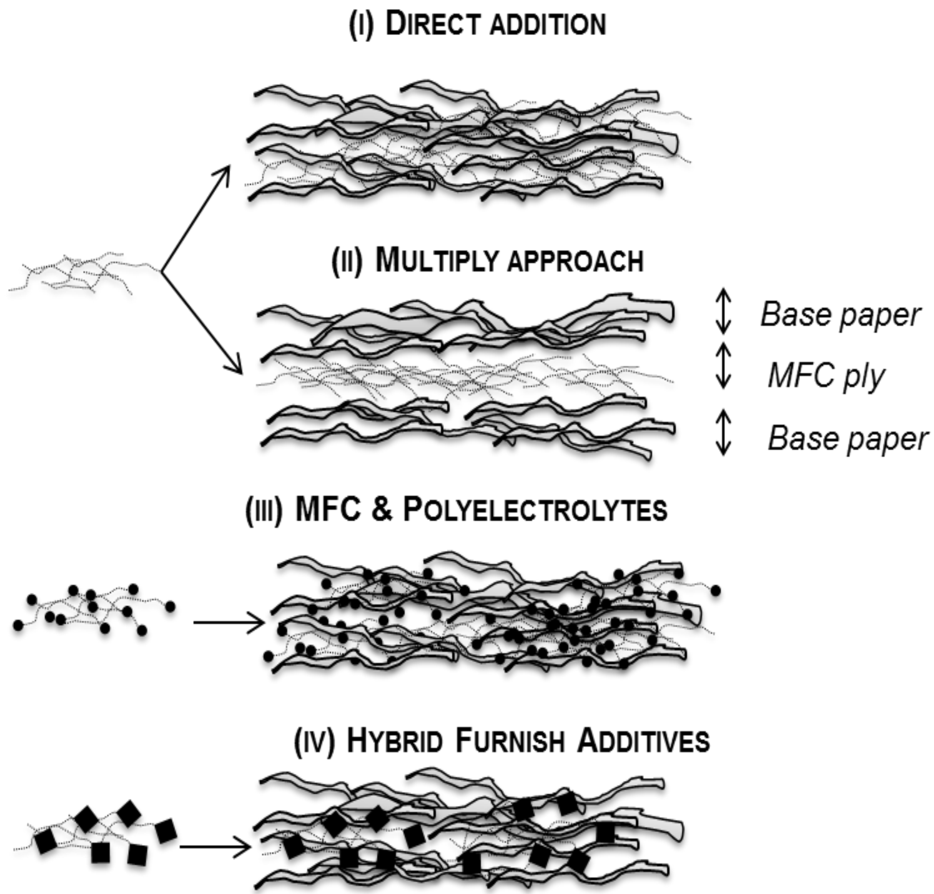
OUTLINE

1. Nanocellulose & production
2. From barrier packaging…
3. To active & intelligent packaging

Paper & Nanocellulose: In Bulk

Several strategies

BUT not with NCC

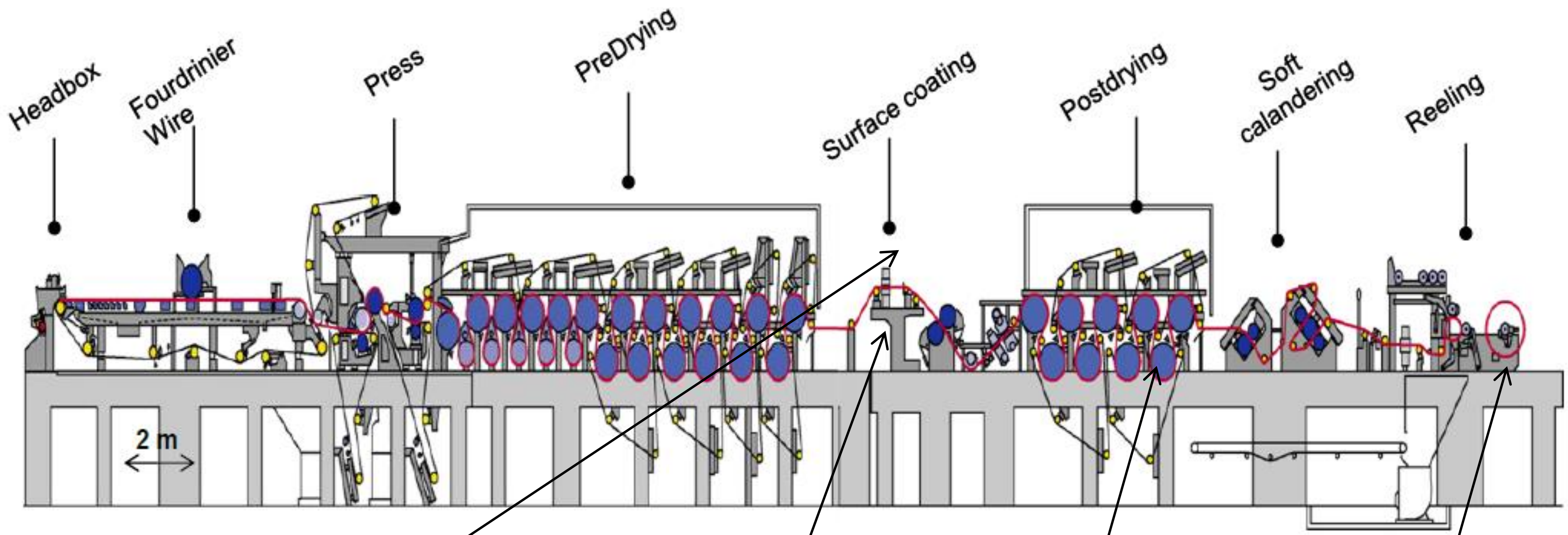


« CNF is dry strength additives
BUT not the magic pill »
T. Lindstrom, Tokyo Paper, 2015

Bardet R.., Bras J., MFC in Paper, 2014, Handbook of Green Materials, K.Oksman,

Paper & Nanocellulose : On Surface

Why not coating nanocellulose ?



Coating Formula & rheology process

Coating process

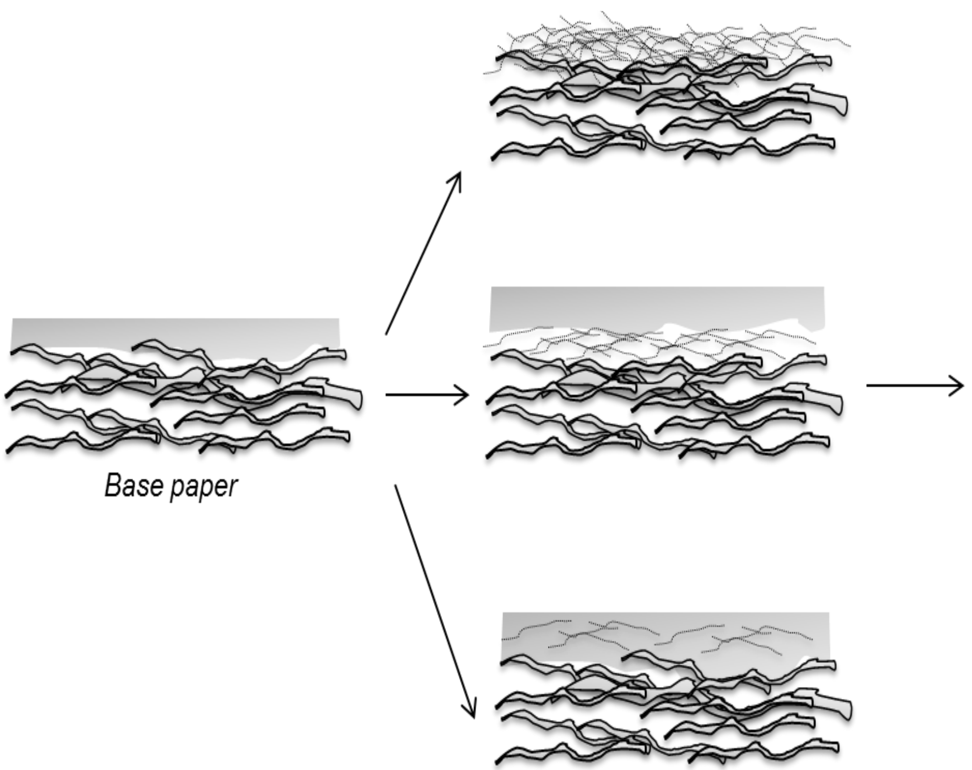
Drying

Properties

Adapted from Voith, 2013

Paper & Nanocellulose : On Surface

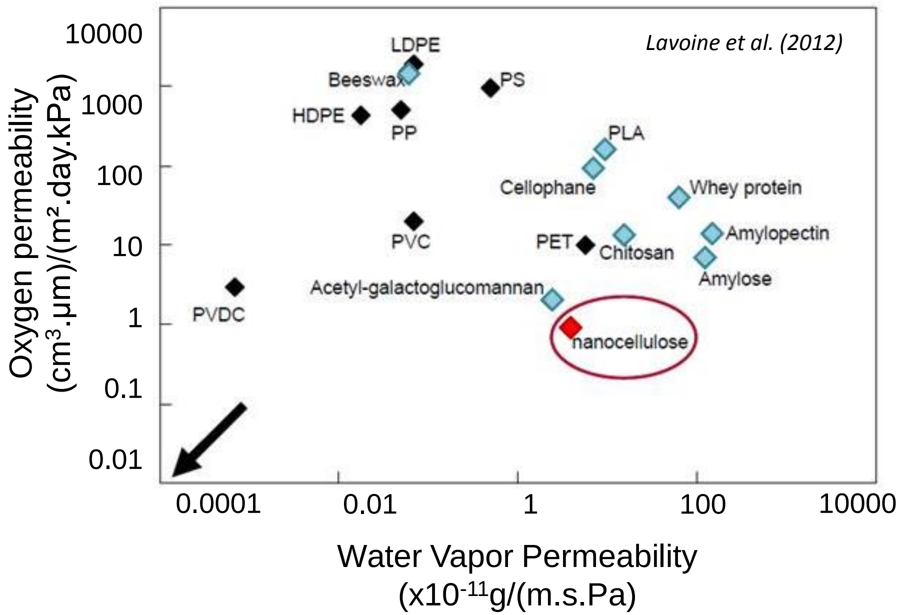
STRATEGIES | **APPLICATIONS TARGETED**

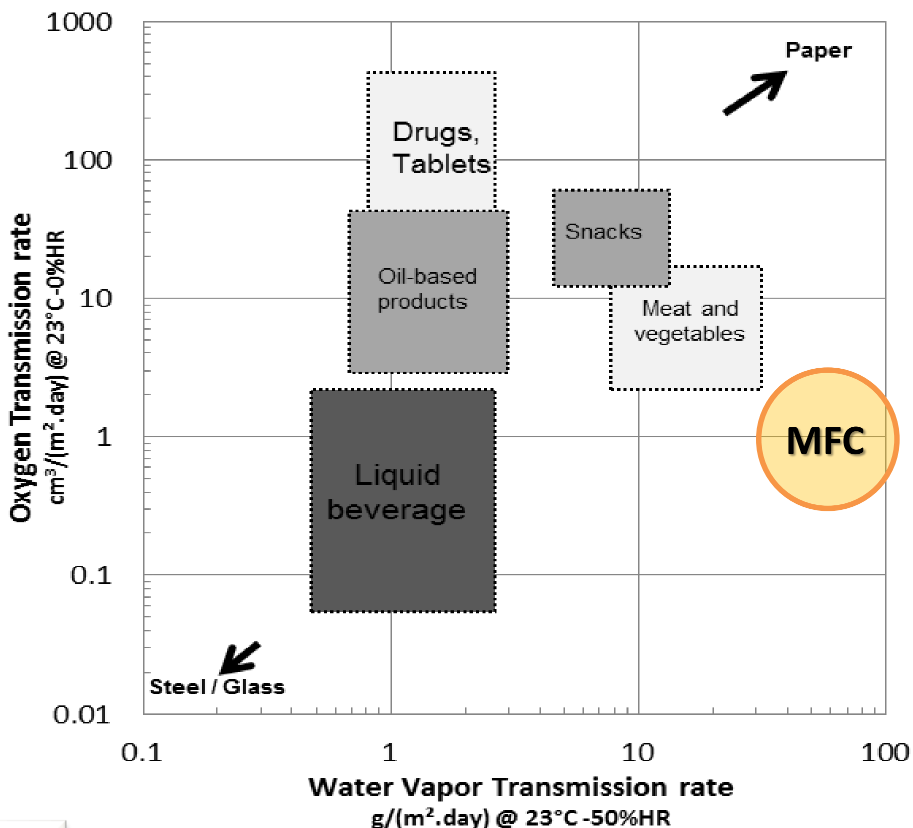


- **(I) BARRIER PROPERTIES**
  Air, Oxygen, Grease, Water vapor ,...
- **(II) PRINTING PROPERTIES**
  Flexography, offset, inkjet
- **(III) FUNCTIONNAL PROPERTIES**
  Antimicrobial , hydrophobic paper , conductive paper

Bardet R.., Bras J., MFC in Paper, 2014, Handbook of Green Materials, K.Oksman

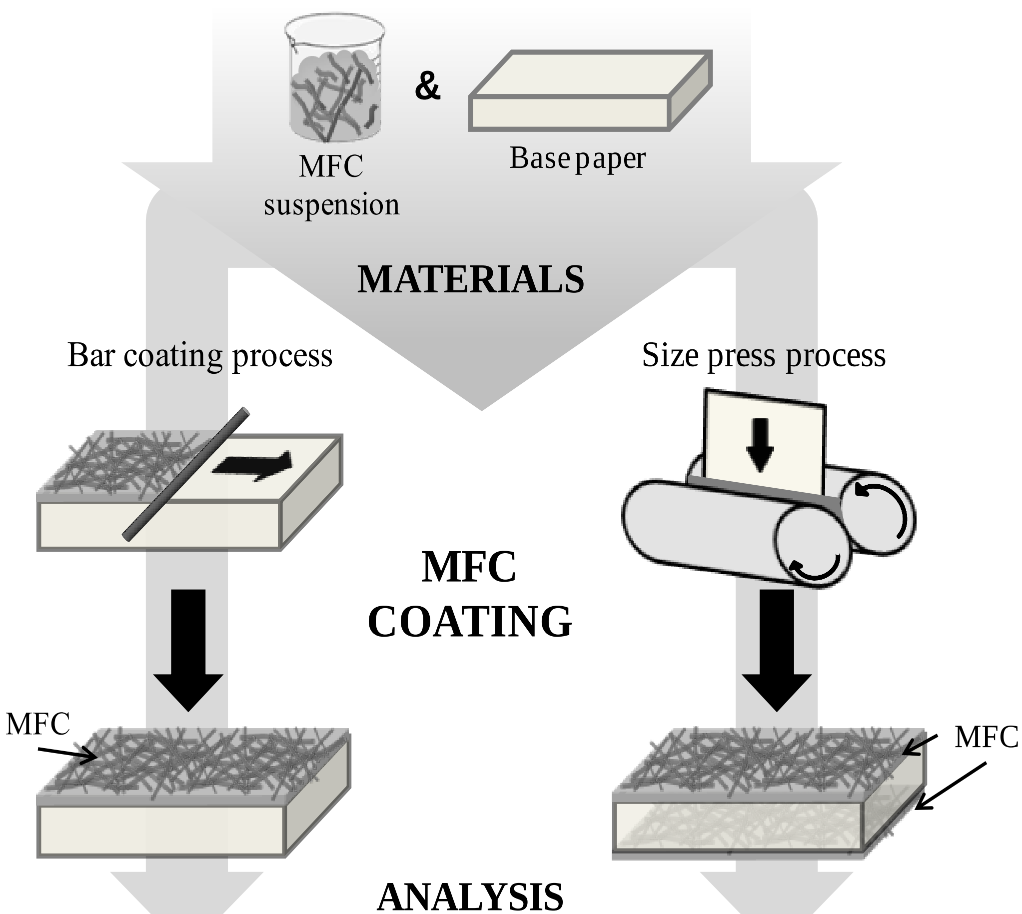
Paper & Nanocellulose : Barrier





=> CNF = The best bio-based barrier …at low HR

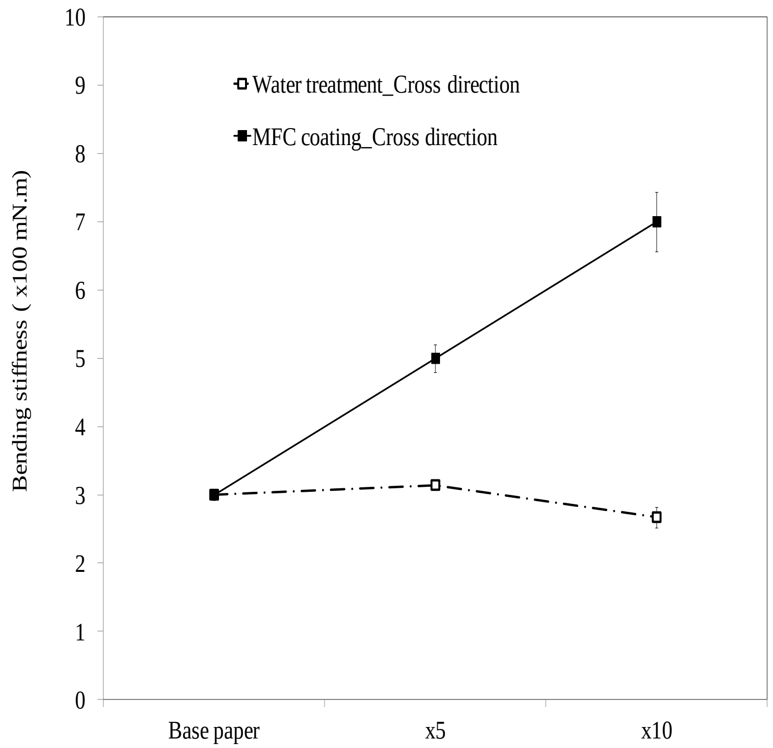
Paper & Nanocellulose : Barrier

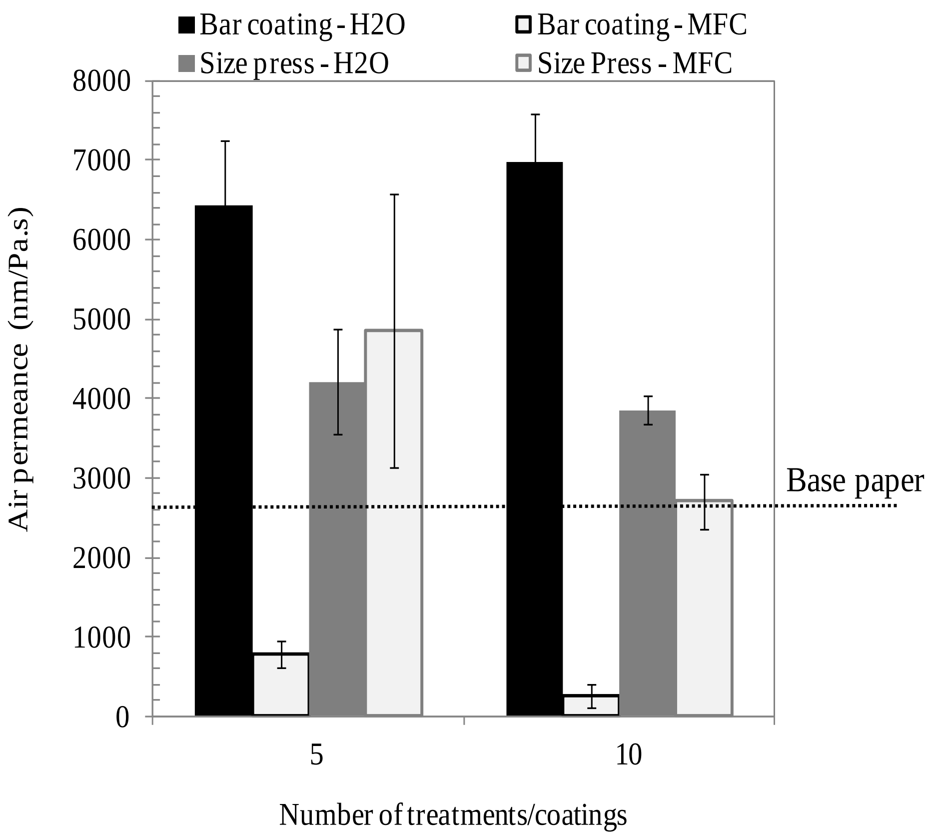


Structure properties (SEM, coat weights, thickness)
Mechanical properties (Young modulus, strength, elongation at break, burst index, bending stiffness)
Barrier properties (Air permeability, grease resistance, water absorption)

Lavoine N.,et al (2014), Impact of different coating processes of microfibrillated cellulose on the mechanical and barrier properties of paper, J. Mater. Sci., 49, 2879-2893.

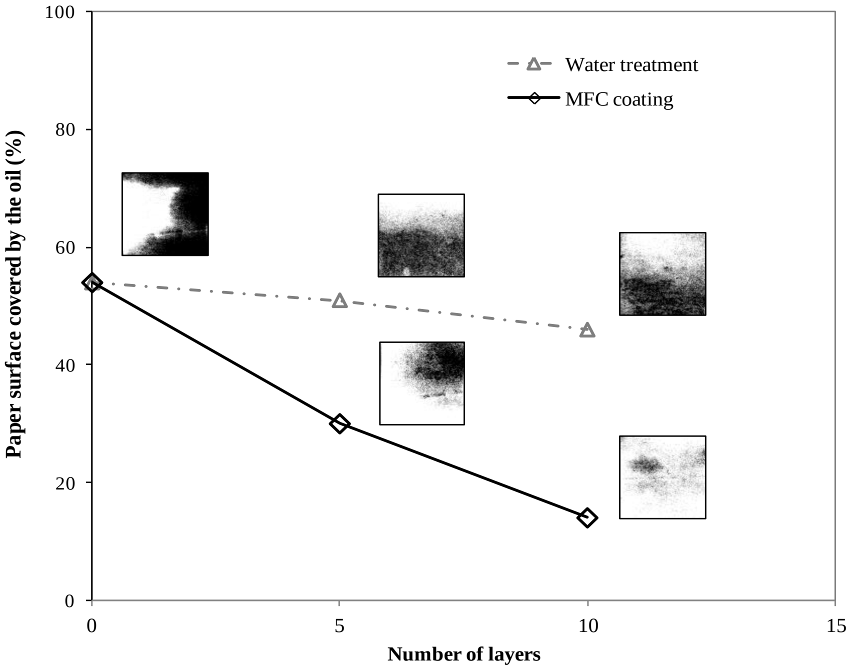
Paper & Nanocellulose : Barrier





=> Positive impact on air barrier & stiffness only for bar coating

Paper & Nanocellulose : Barrier



Paper

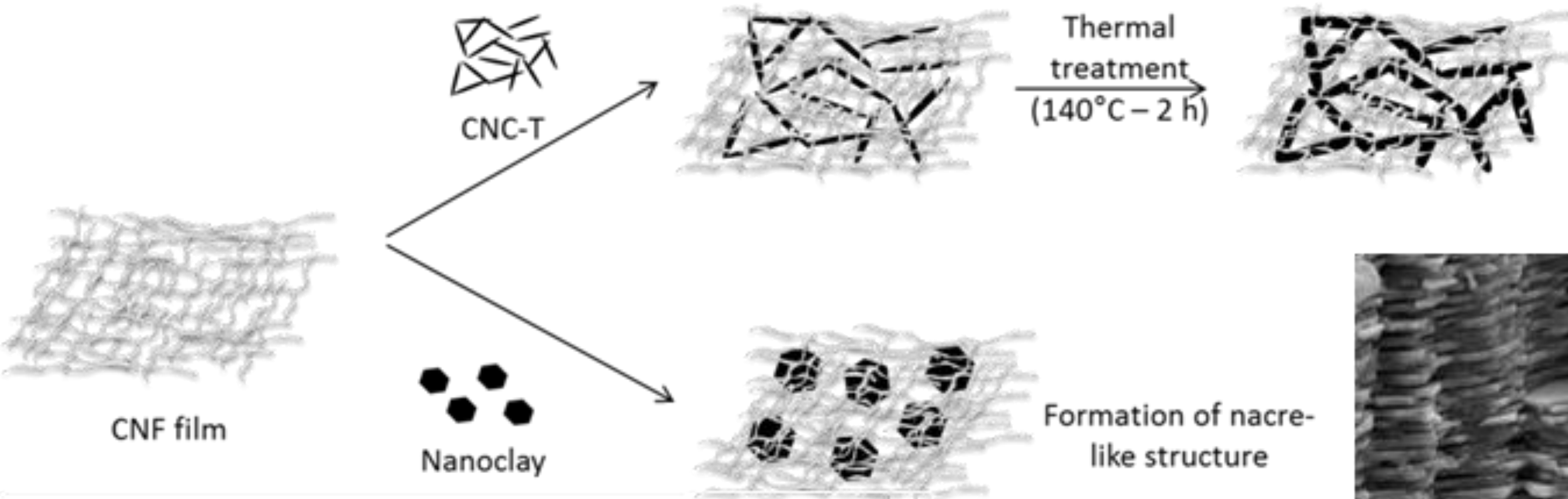
Paper+MFC

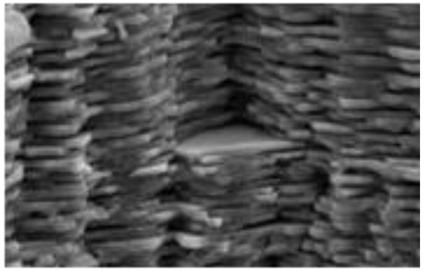
GREASE BARRIER

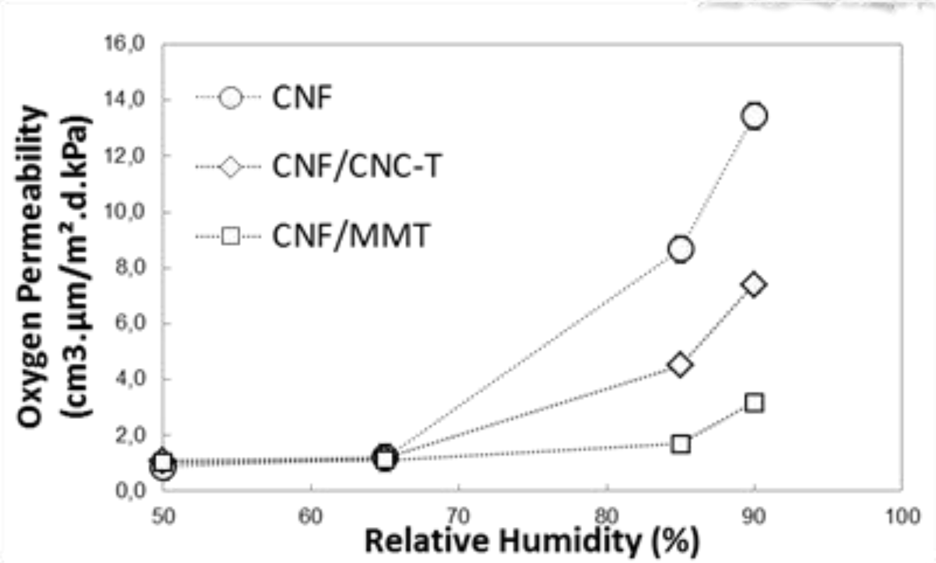
=> Interesting grease barrier of MFC coating

Lavoine N.,et al (2014), J. Mater. Sci., 49, 2879-2893.

Paper & Nanocellulose : Barrier

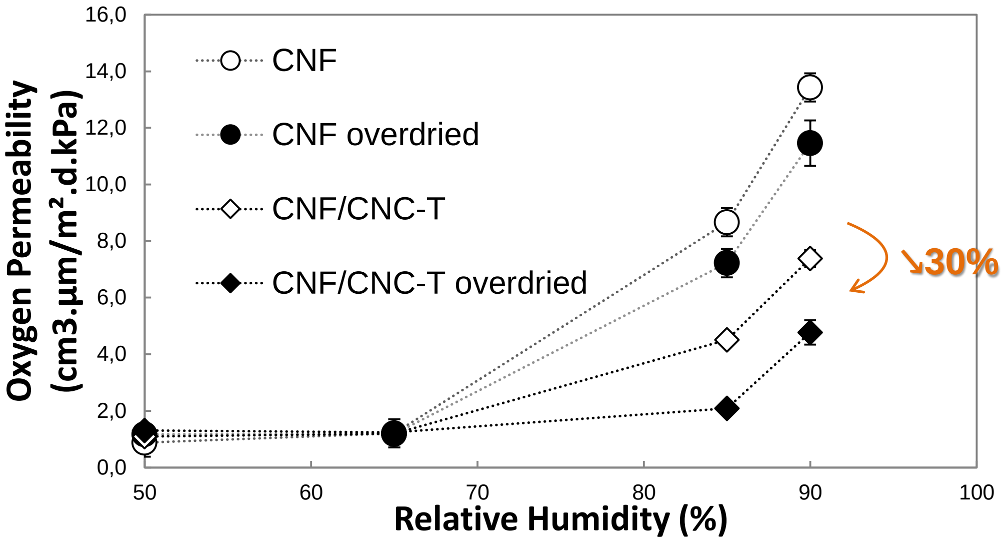


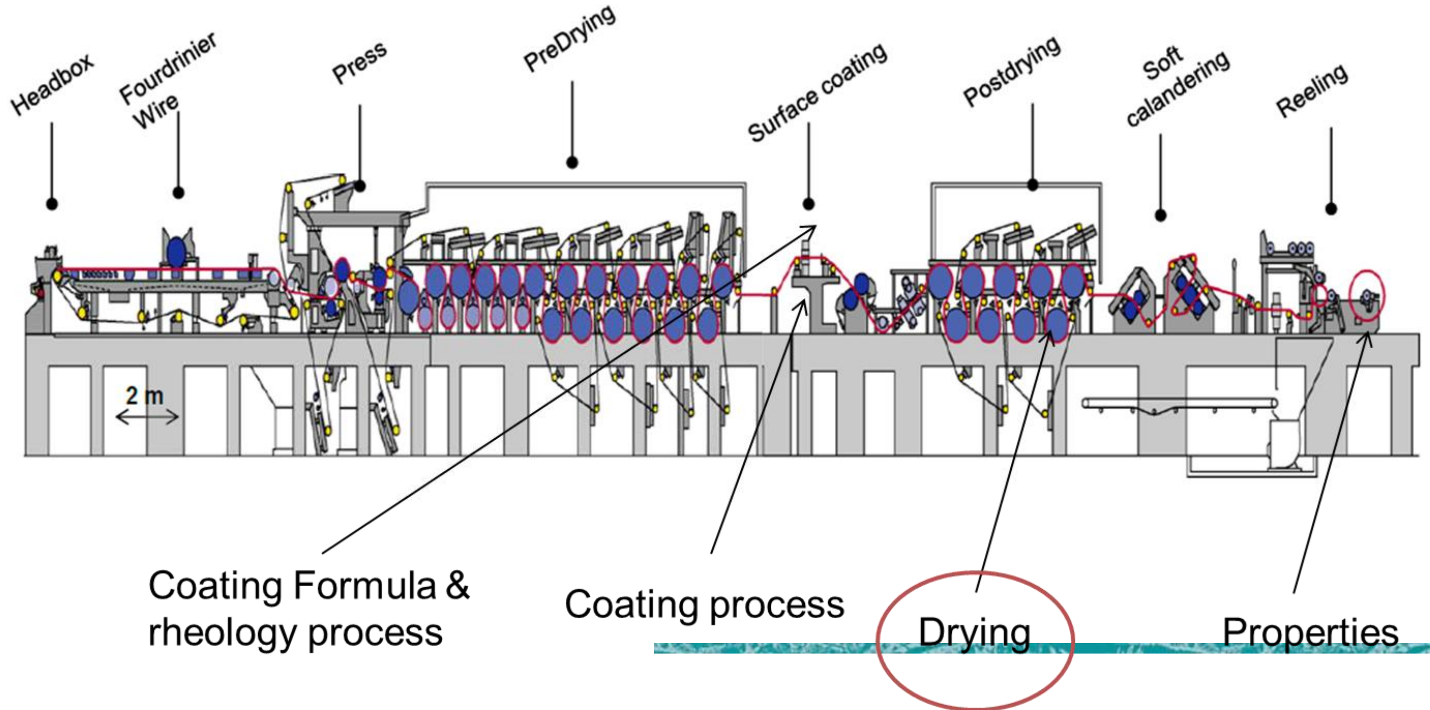




Bardet, Reverdy, Belgacem, Leirset, Syverud, Bras, J
(2015) Cellulose, 22(2), 1227-1241

Paper & Nanocellulose : Barrier





Adapted from Voith, 2013

Paper & Nanocellulose : Barrier

- **Study of the influence of MFC introduction in PVOH layer**
  - Coating of $10 g/m^2$ of PVOH
  - Coating of $10 g/m^2$ of PVOH/MFC 5p
  - Coating of $10 g/m^2$ of PVOH/MFC 10p

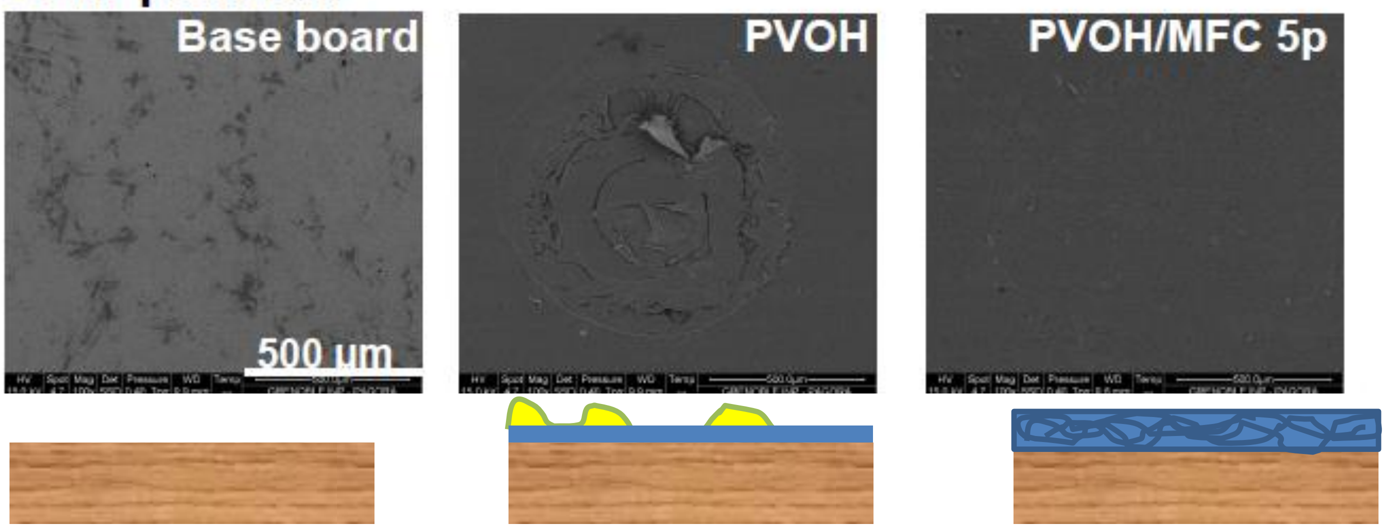
- **Pilot trials**
  - Coating with Soft-Tip blade equipment
  - Applicator roll
  - Drying: electric IR + Forced hot air
  - Speed: 70 m/min

SUNPAP

Guezennec et al, SunPap conference, 2013

Paper & Nanocellulose : Barrier

- **Drying behaviour**
  - Drying strategy very hard to monitore with PVOH:
    - ✓ Blistering
  - Improvement of the layer drying with PVOH/MFC
    - ✓ Blistering reduction
- **SEM pictures**



=> CNF = network controlling-dispersing drying energy
=> No more Blistering

Adapted from Guezennec et al, SunPap conference, 2013

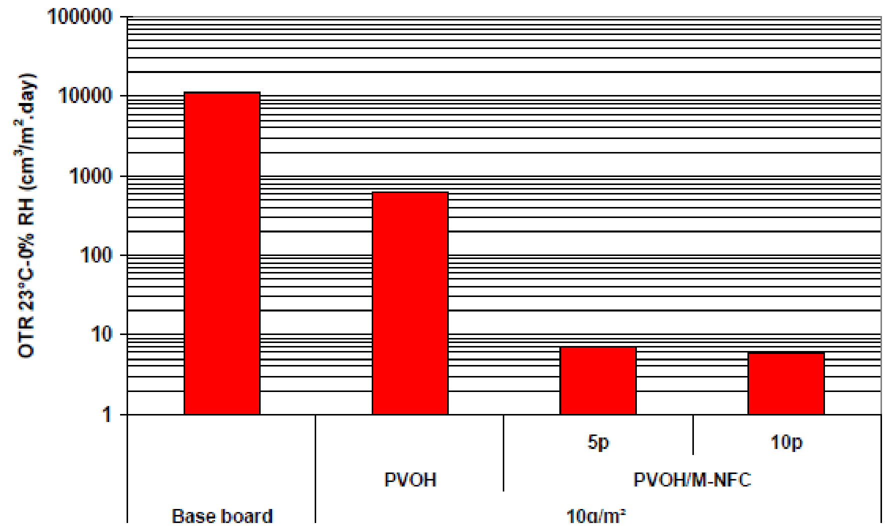
Paper & Nanocellulose : Barrier

- **Oil and grease resistance**
  - Cobb index 24H with coloured peanut oil

Base board **PVOH/MFC 5p - 10g/**

Cobb index: 200 g/m² **Cobb index: 2 g/**

- **Oxygen transmission rate 23°C-0% RH**



Adapted from Guezennec et al, SunPap conference, 2013

OUTLINE

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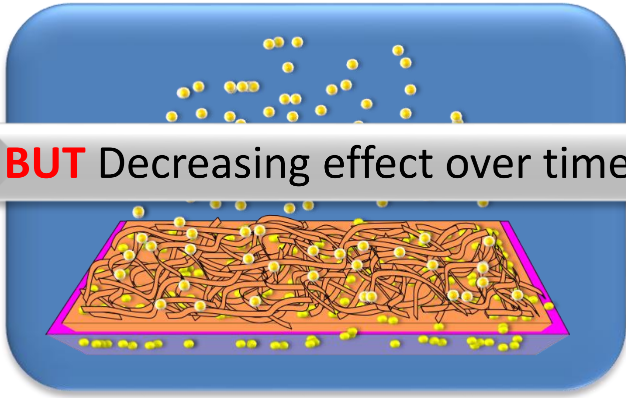
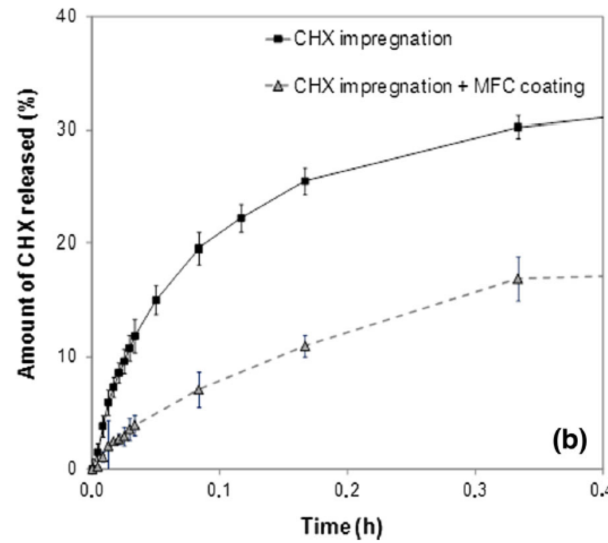
Antimicrobial packaging

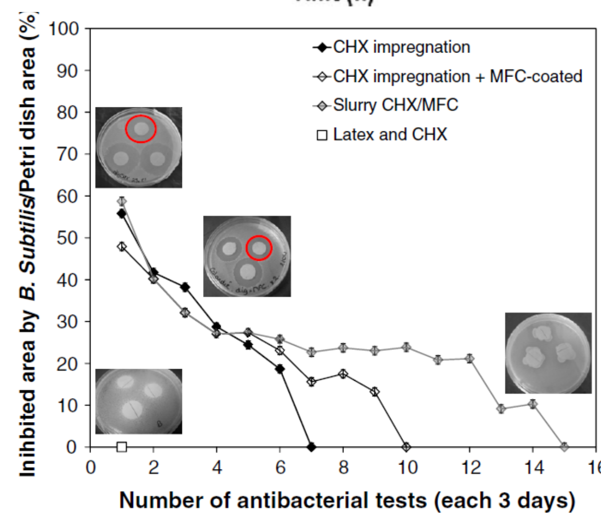
(i) Incorporation into CNF network



BUT Decreasing effect over time.

Lavoine, N.; Desloges, I.; Sillard, C.; Bras, J. (2014)
Controlled release and long-term antibacterial activity of chlorhexidine digluconate through the nanoporous network of microfibrillated cellulose, Cellulose, 21(6), 4429-4442.





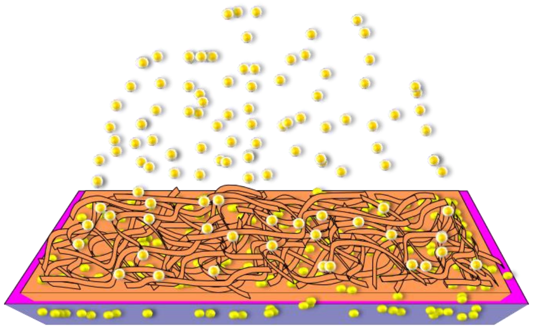
Release mechanism

- ✓ Antimicrobial agents incorporated in the packaging.
- ✓ Migrate into food through diffusioning and partitioning.
- ✓ Very positive impact of MFC for release monitoring

=> prolonged antimicrobial activity whatever molecules

Antimicrobial packaging

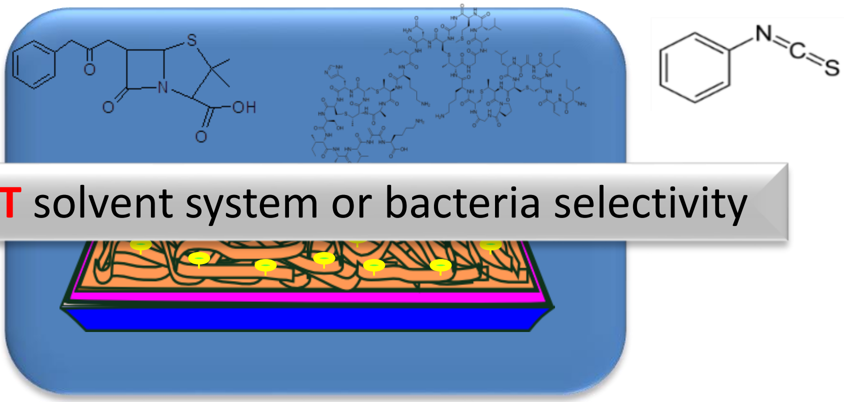
(i) Incorporation into CNF network



Release mechanism

- ✓ Antimicrobial agents incorporated in the packaging.
- ✓ Migrate into food through diffusioning and partitioning.
- ✓ Decreasing effect over time.

(ii) Immobilisation onto CNF



BUT solvent system or bacteria selectivity

Contact mechanism

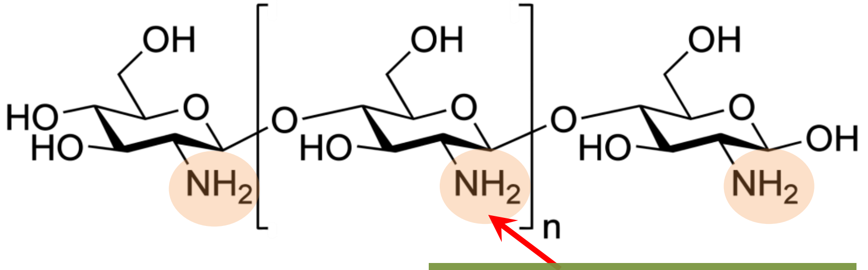
- ✓ Antimicrobial agents immobilized on the packaging.
- ✓ Microbial suppression at the contact surface without diffusion.
- ✓ Prolong effect.

- Saini, ; Belgacem, N; Mendes, J; Elegir, G; Bras, J
Contact Antimicrobial Surface Obtained by Chemical Grafting of Microfibrillated Cellulose in Aqueous Solution Limiting Antibiotic Release, ACS Applied Materials & Interfaces (2015), 7(32), 18076-18085

-Saini, M. N. Belgacem, K. Missoum, J. Bras,
Natural active molecule chemical grafting on the surface of microfibrillated cellulose for fabrication of contact active antimicrobial surfaces, Industrial Crops and Products (2015), Accepted-in press.

Antimicrobial packaging

Chitosan - (1, 4)-linked 2-amino-deoxy-b-D glucan units



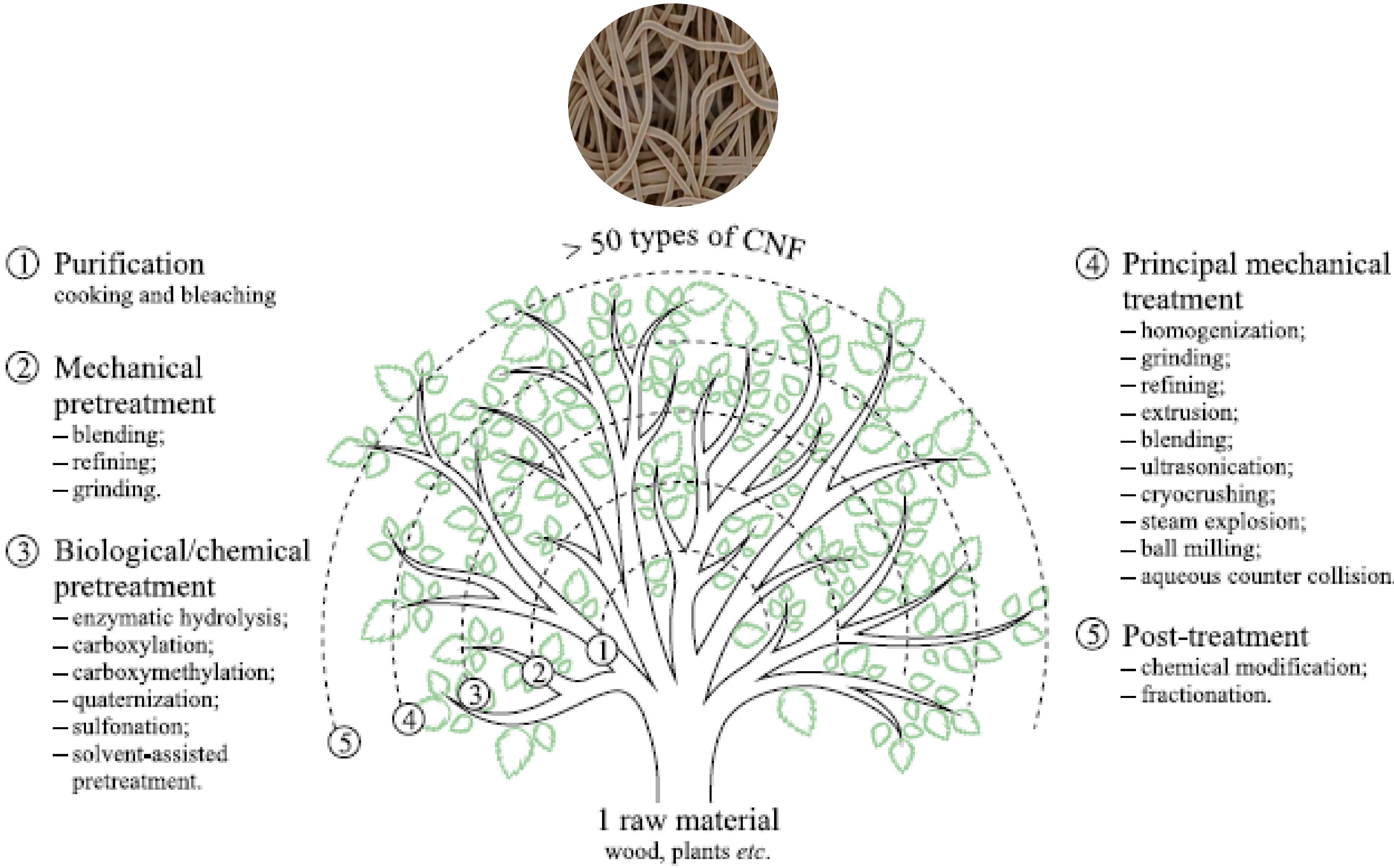
Responsible for antibacterial activity

Sources in the form of chitin : Sea crustaceans

Limited applications due to:

- insolubility in water
- high viscosity
- tendency to coagulate with proteins
- difficulties to obtain high specific area nanofibre (cost)

CNF functionnalization

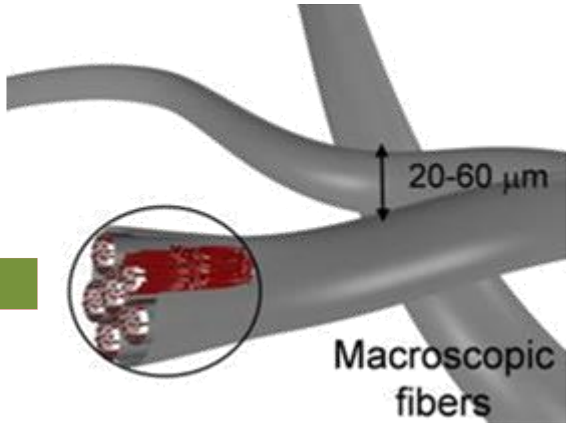


Nechyporchuk, Belgacem, Bras
Production of cellulose nanofibrils: a review of recent advances,
Ind crops (2016), in press

CNF Pre-treatment

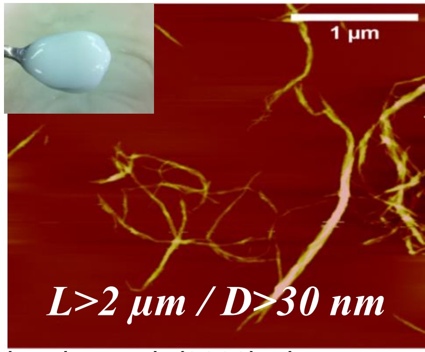
Mechanical Treatment
(Homogeniser, Microfluidiser, Grinding)

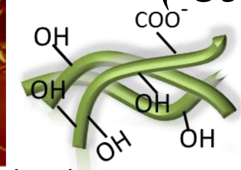
Pretreatment



*Pääkkö et al. (2007) Biomacromolecu

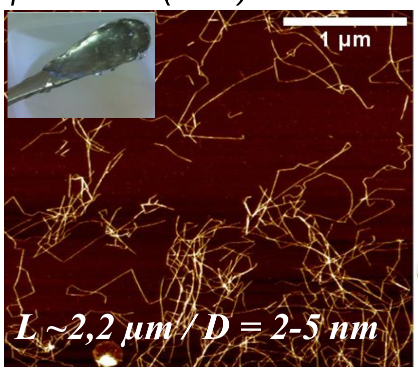
Enzymatic Hydrolysis
(Cellulase or endoglucanase)

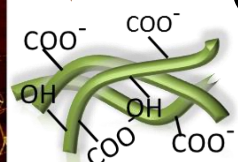




*Siqueira et al. (2009) Biomacromolecules

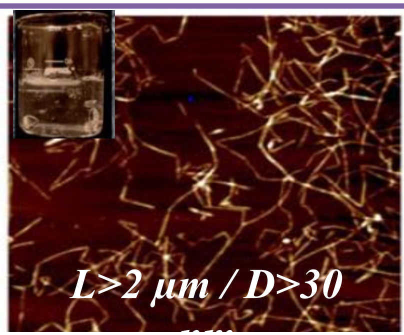
Tempo oxidation
(Tempo/NaBr/NaClO)

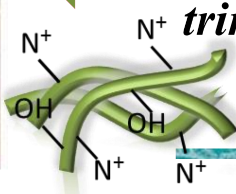




*Saito et al. (2006) Biomacromolecules

Cationization
(2,3-epoxypropyl trimethylammonium chloride or chlorocholine chloride)

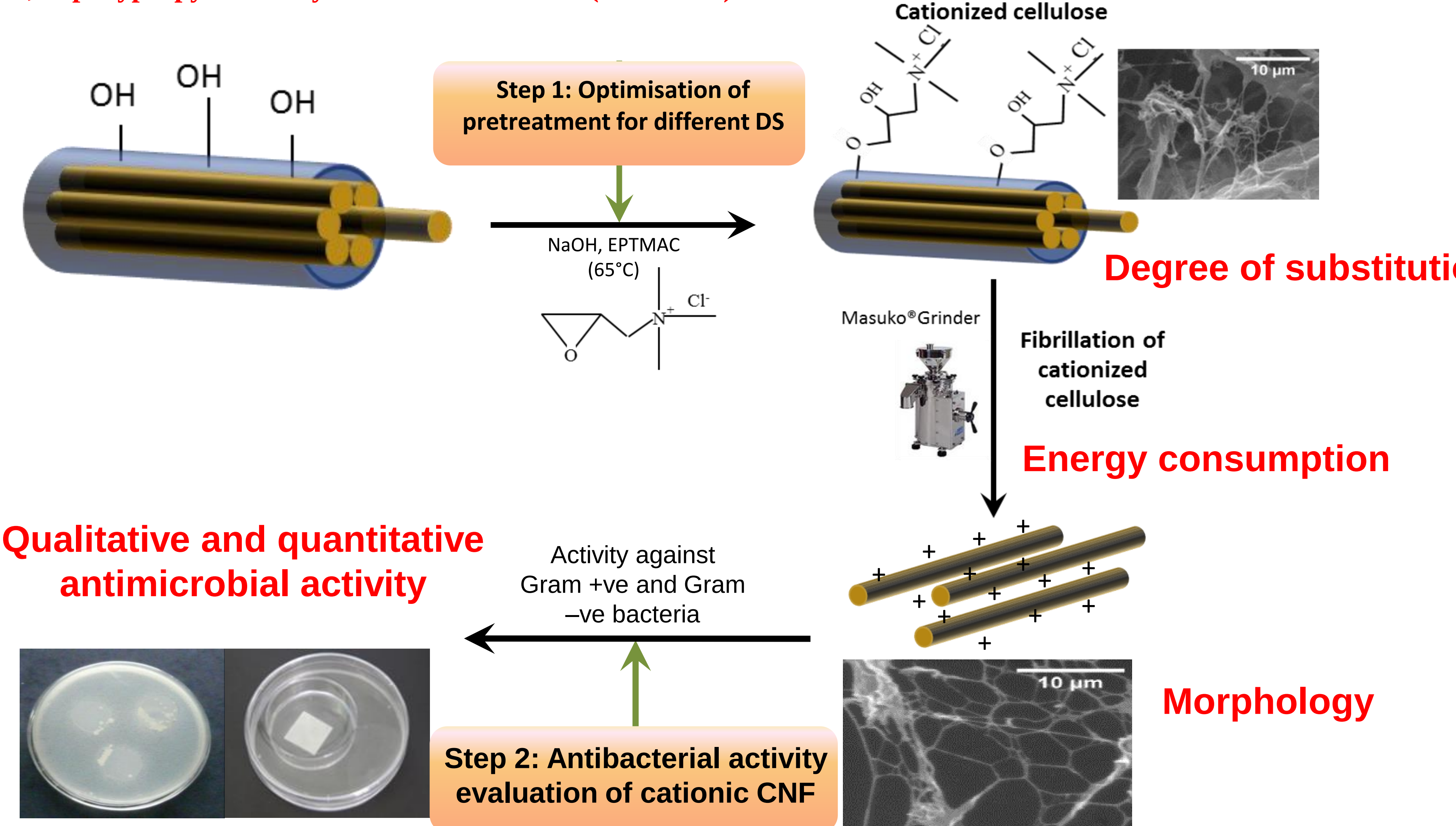




*Pei et al. (2013) Soft matter

CNF Pre-treatment

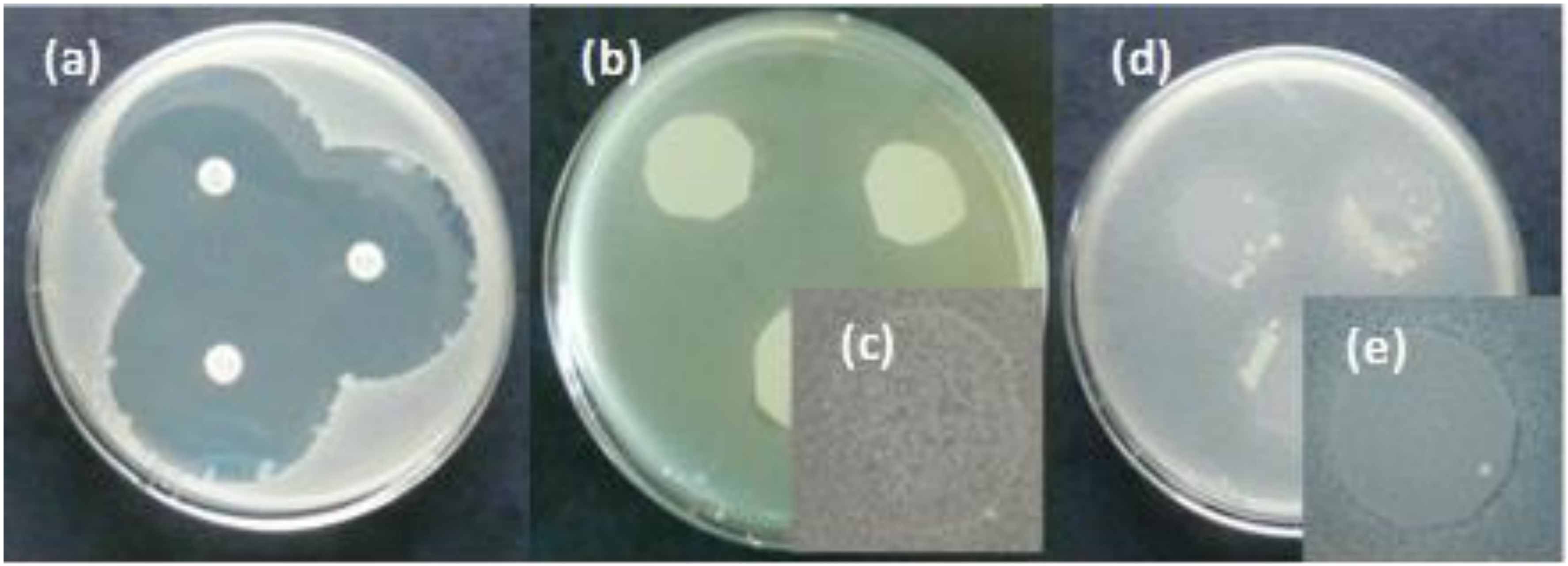
2,3-epoxypropyl trimethylammonium chloride (EPTMAC)



Surface cationized cellulose nanofibrils for the production of contact active antimicrobial surfaces ,
S. Saini, C. Yucel-Falco, M. N. Belgacem, J. Bras Carbohydrate polymers (2015), 135, pp 239-247.

Antimicrobial packaging

Bacteria: *Bacillus subtilis (Level 1) Gram +ve*



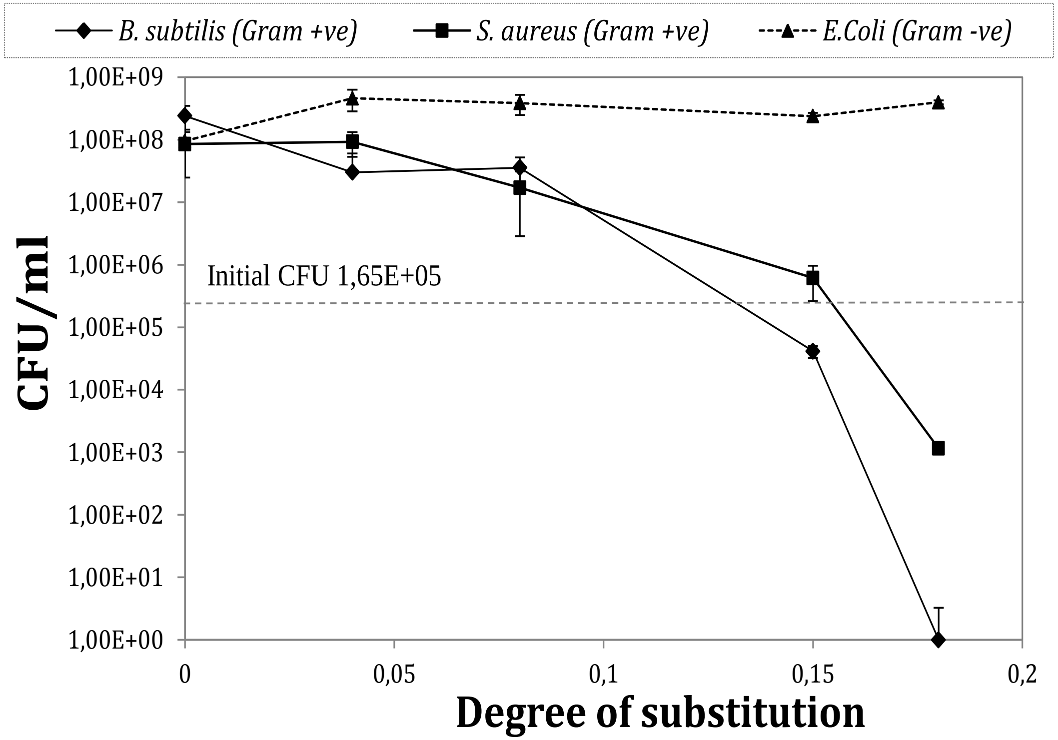
PENICILLIN: Positive Control

ENZY MFC: Negative Control

CAT-MFC DS= 0.18

- No Zone of inhibtion: No free EPTMAC leaching
- Antimicrobial by contact

Antimicrobial packaging



- ✓ CATMFC DS=0,04: Antimicrobial agents lower than Minimum inhibitory concentration.
- ✓ CATMFC DS=0,18: 3 log reduction with high SD => samples are heterogenous.
- ✓ E.coli – need to increase degree of substitution.

S. Saini, C. Yucel-Falco, M. N. Belgacem, J. Bras, « Surface cationized cellulose nanofibrils for the production of contact active antimicrobial surfaces », Carbohydrate polymers (2015), 135, pp 239-247.

LGP2

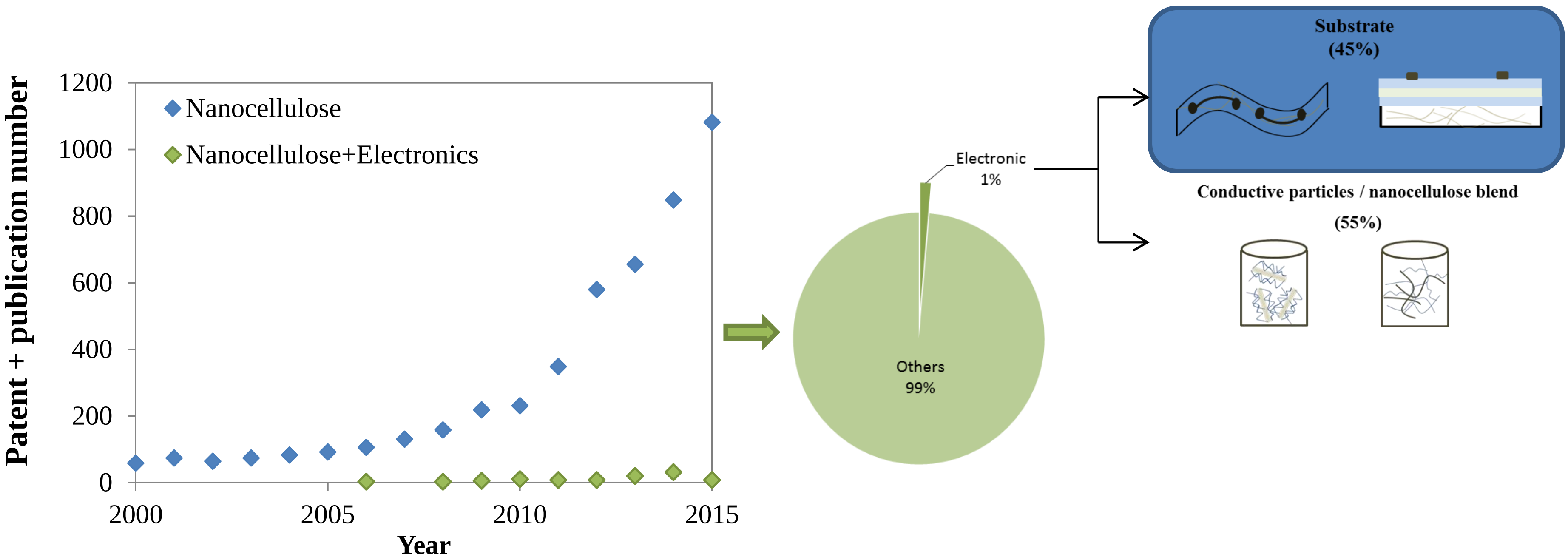
Industrial Pilot trial at Multipackaging Solutions

Multi Packaging Solutions

Towards demonstrator

NewGenPak

Nanocellulose & printed electronics

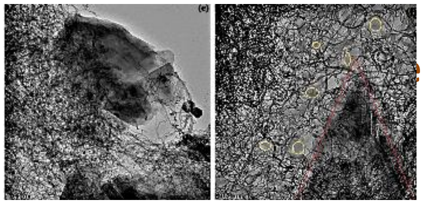


- High value added expectations
- Less than 10 years
- Very new field: only few research groups and companies

Hoeng , Denneulin, Bras, Use of Nanocellulose in printed electronics, Nanoscale, 2016

Nanocellulose for printed electronics

Nanoce



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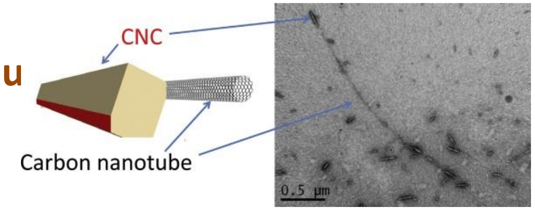
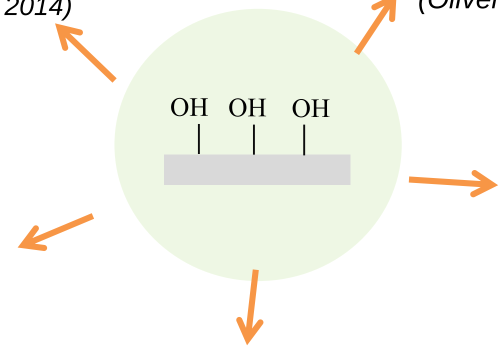
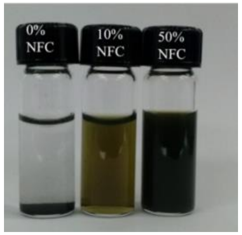


Carbon nanotubes –CNF
(Koga et al. 2013, Tang et al. 2014)

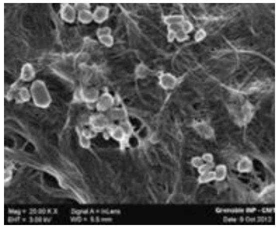
Carbon nanotubes –CNC
(Oliver et al. 2012, Moreau et al. 2016)



Polypyrrole- CNF
(Sasso et al. 2010Wu et al. 2014)



MoS_2 and BN - CNF
(Li et al. 2015)



TiO_2 - CNF
(Bardet et al. 2013)

No work with silver nanowires

Conductive ink based on nanocelluloses: process

Materials and methods

Cellulose microfibrils
L= 1 µm
d= 20 nm

→ **Adapted Mixing** ←

Silver nanowires
L= 50 µm
d= 150-200 nm

Cellulose microfibrils gel

↓

Stable silver nanowires ink

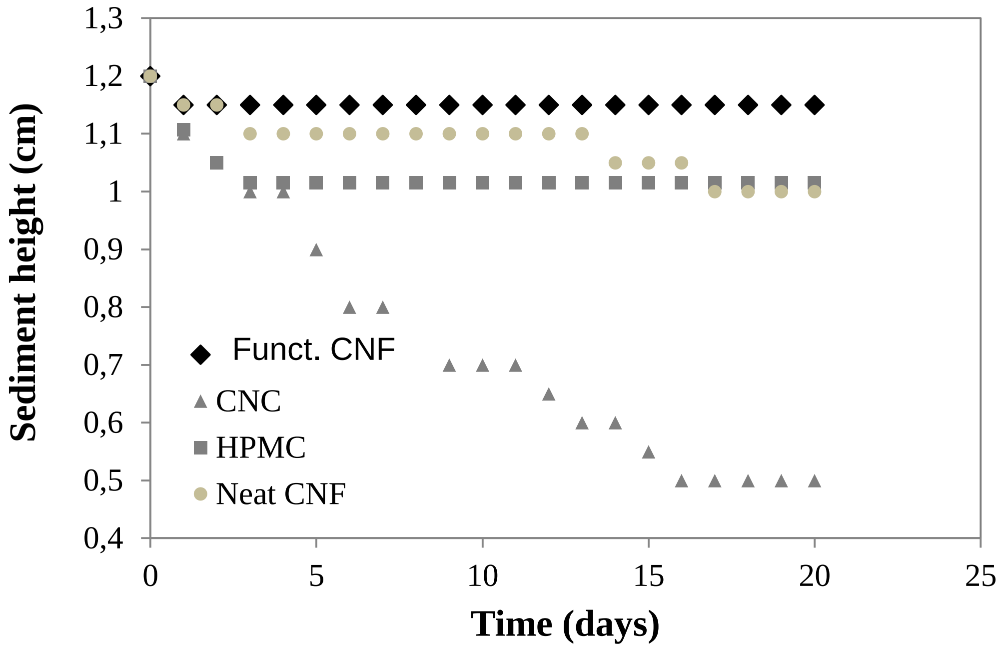
Silver NW in solvent

PolyBioWire® Ink
(Patent protected – FR1553131)

- **Easy process**
- No addition of others chemicals

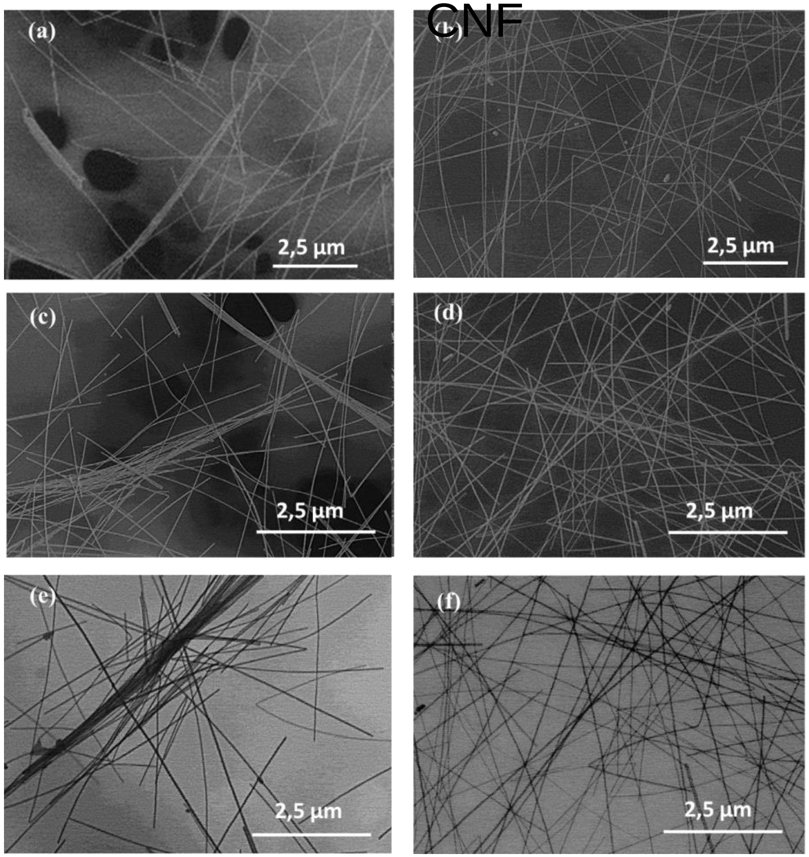
Stable aqueous silver nanowires ink based on renewable materials

Conductive ink based on nanocelluloses: process



Neat CNF

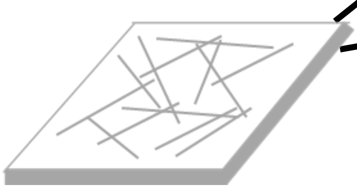
Functionnalized CNF



Stable aqueous silver nanowires ink only with Functionnalized CNF

PolyBioWire®: opto-electrical properties

PolyBioWire®



PolyBioWire® coated film

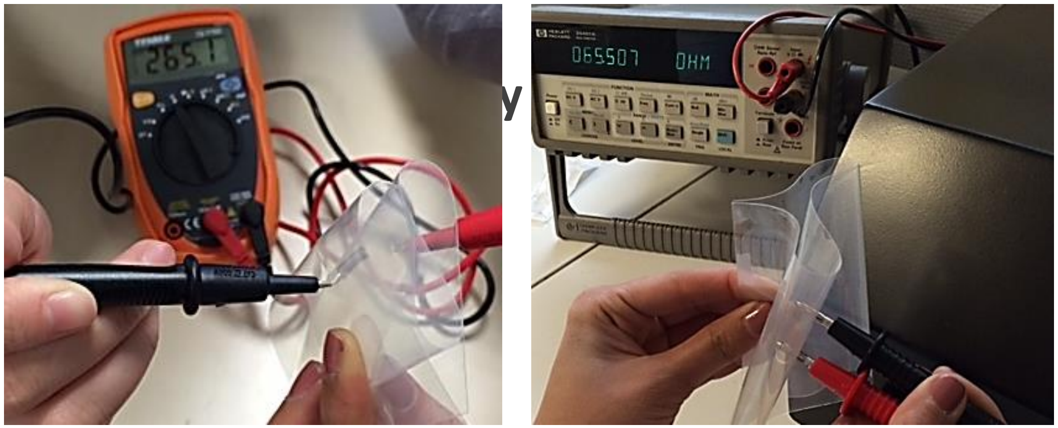
PolyBioWire® film patent protected FR1553131)

PolyBioWire® film	
Substrate	PET
R_{sh} (Ω/□)*	22 ± 3
T% (%)*	88 ± 0,4
ΔL*	3,1 ± 1,8
Δa*	0,56 ± 0,08
Δb*	0,78 ± 0,31

**Best compromise in opto-electrical properties*

- **No color deviation**
- High transmittance
- Low resistance

PolyBioWire®: PolyBioWire® film properties



PolyBioWire® film flexibility (patent protected FR1553131)

- **Conductive properties** even under flexion
- **PolyBioWire® is flexible**

PolyBioWire® adhesion on substrate

	R_{sh} (Ω/□)	
	Before scotch test	**After scotch test**
Silver nanowires	61 ± 22	/
MFC-Silver nanowires	22 ± 2	23 ± 4

- **Increase adhesion** thanks to MFC
- **No change in conductive properties**

Flexible conductive film with no need of protection layer

Hoeng et al , PE-US, 2015

OUTLINE

1. Nanocellulose & production
2. From barrier packaging…
3. To active & intelligent packaging

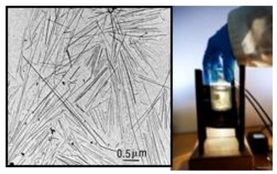
Conclusions

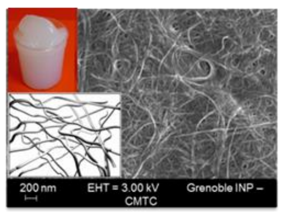
Nanocellulose in MatBio

BIOMASS → **NANO-CELLULOSE** → **MATERIALS** → **APPLICATIONS**

T1: Nanocellulose preparation **process optimization**

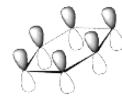
(Deconstruction)





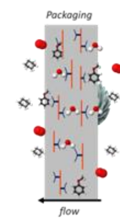
T2: Nanocellulose surface **functionnalization**

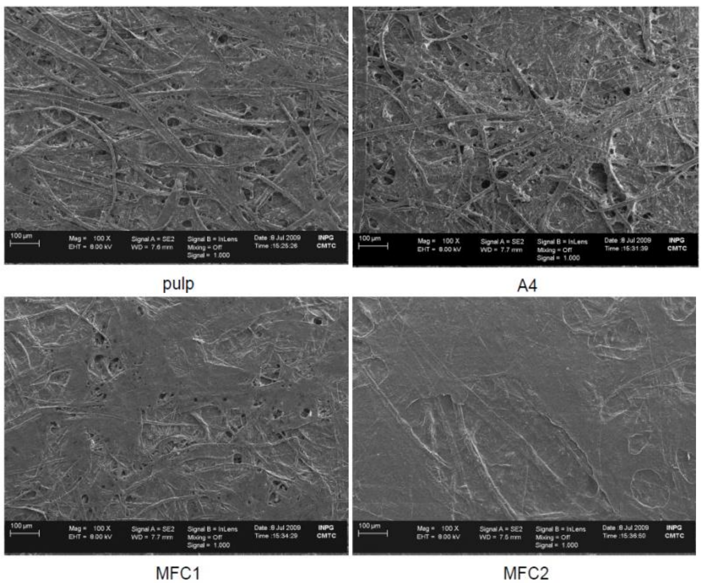
(activation)



T3: Material preparation **processes** for Transfer and **interactions**

(reconstruction)





Lab scale trials from CTP (Dynamic handsheets)

CTP's curtain coater located above Grenoble INP Pagora's paper machine

THANK YOU FOR YOUR ATTENTION

Julien.Bras@grenoble-inp.fr

Acknowledgement to my collaborators in this work:

Seema, Charlene, Oleksander, Nathalie, Isabelle, Naceur

Join us in the LinkedIn group « Nanocellulose Materials »

2 Post-doc positions open: Contact me

institut universitaire de France

Grenoble INP pagora

tec21 the engineering of complexity

INSTITUT CARNOT PolyNat