

Nanocellulose: Is it really a good solution for Sustainable Packaging?

Julien BRAS

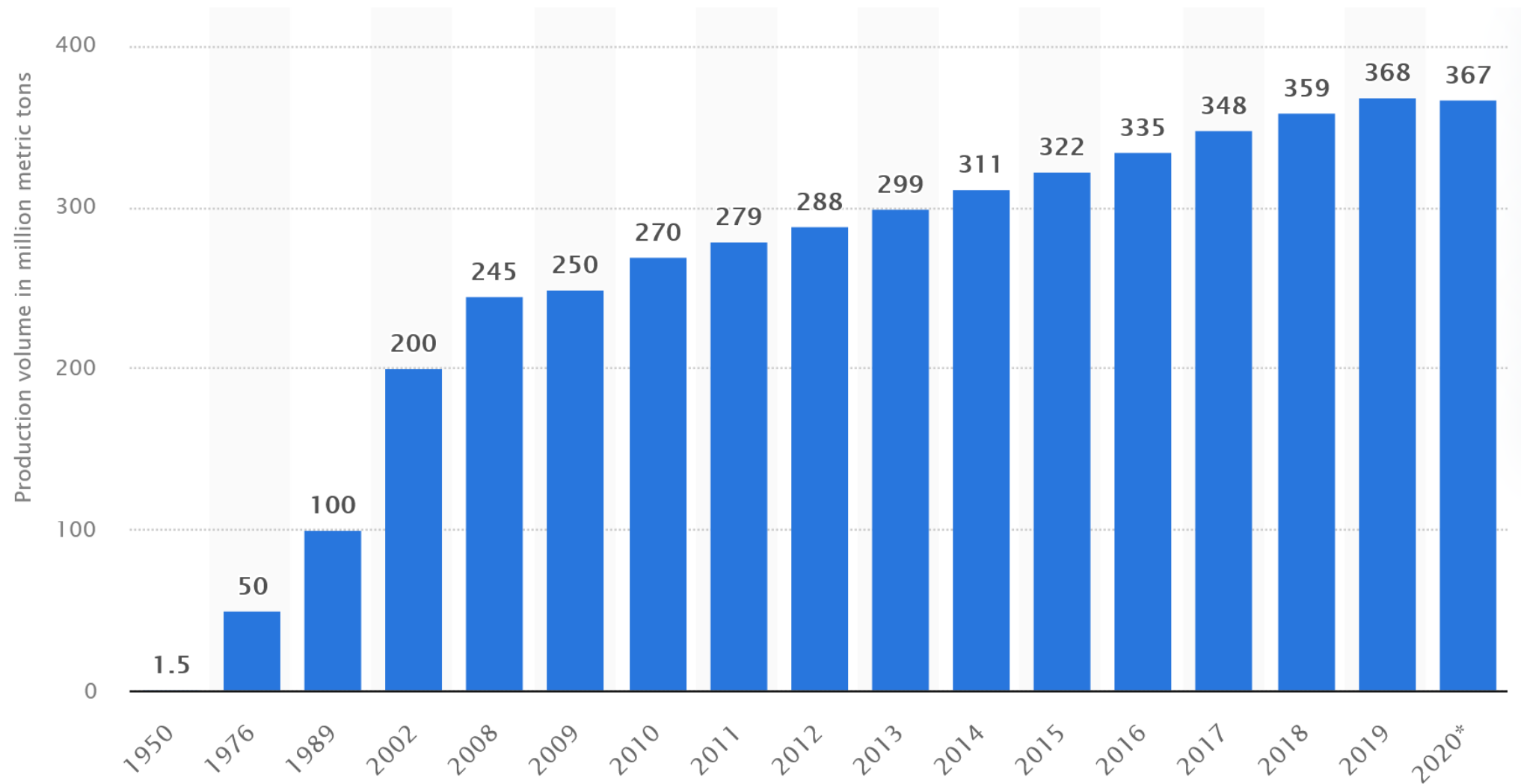
University Grenoble Alpes, Grenoble INP – Pagora, LGP2, 38000 Grenoble France
Institut Universitaire de France, 75000 Paris, France



12-16 JUNE 2023 • VANCOUVER, B.C. CANADA



Annual production of plastics worldwide from 1950 to 2020 (in million metric tons)



PLASTICS PRODUCTION

2014



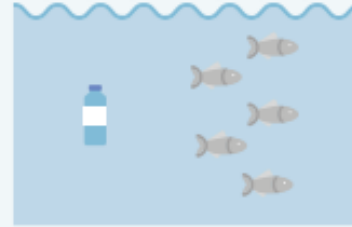
311 MT

2050

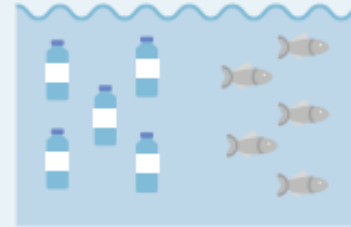


1,124 MT

RATIO OF PLASTICS TO FISH IN THE OCEAN¹ (BY WEIGHT)



1:5



>1:1

PLASTICS' SHARE OF GLOBAL OIL CONSUMPTION²



6%



20%

PLASTICS' SHARE OF CARBON BUDGET³



1%

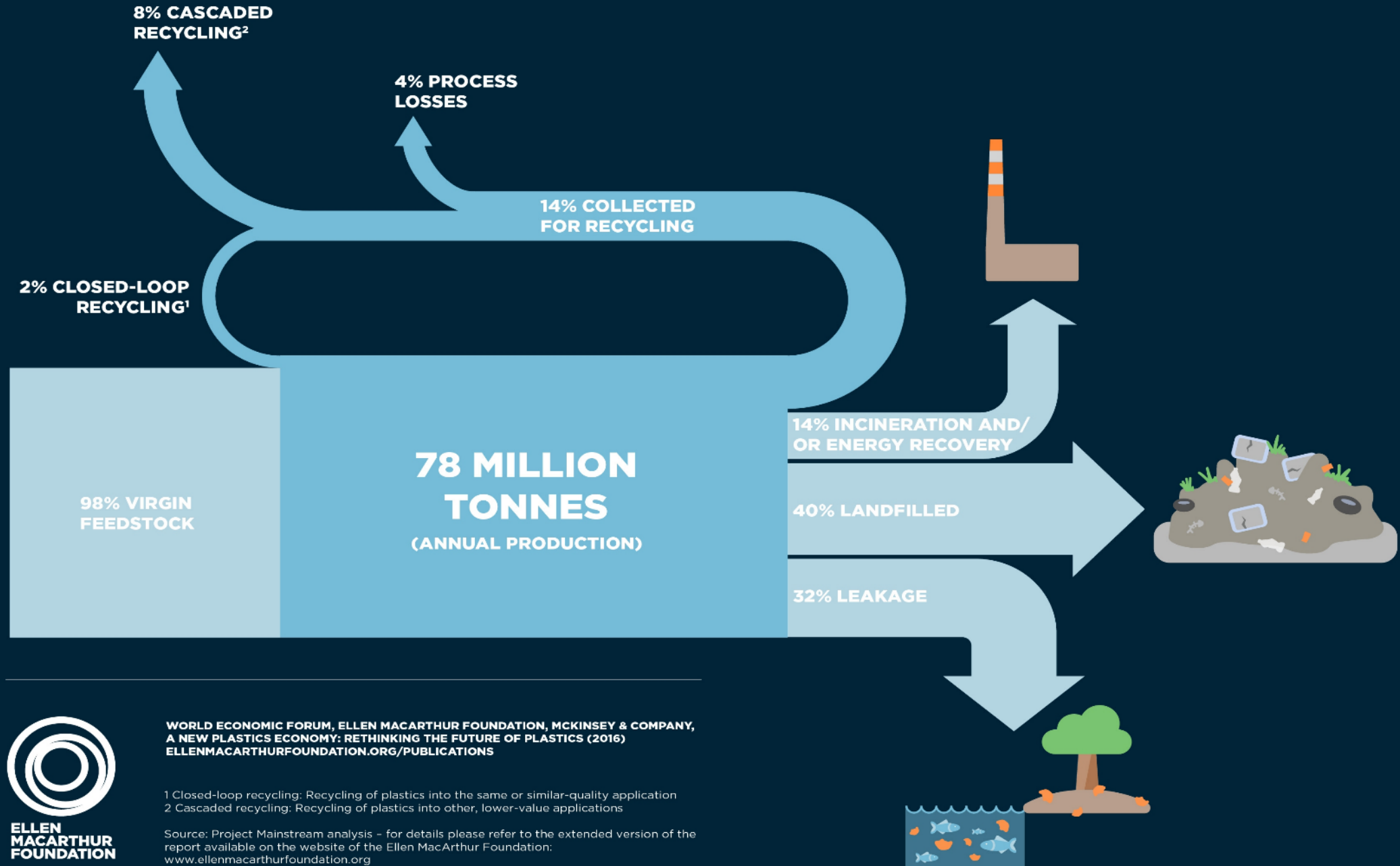


15%

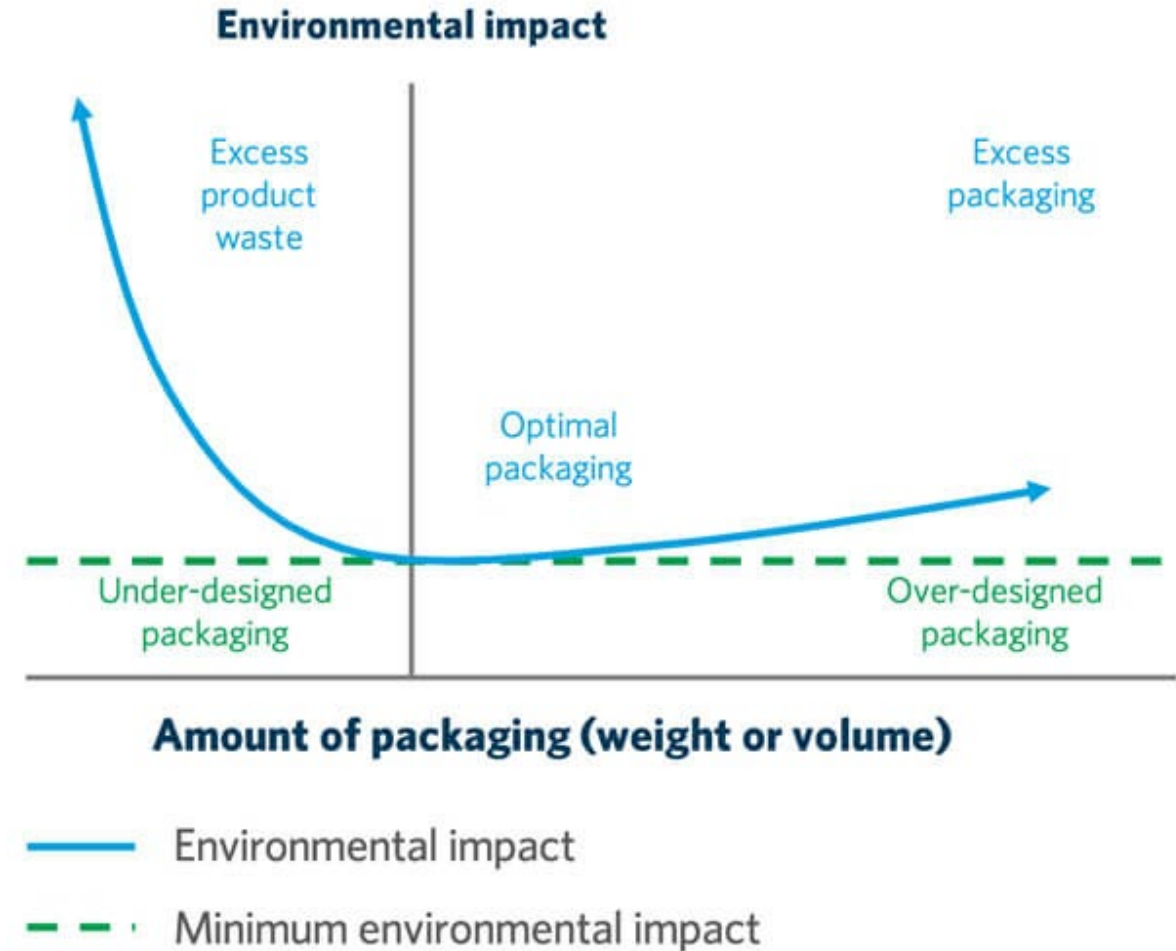
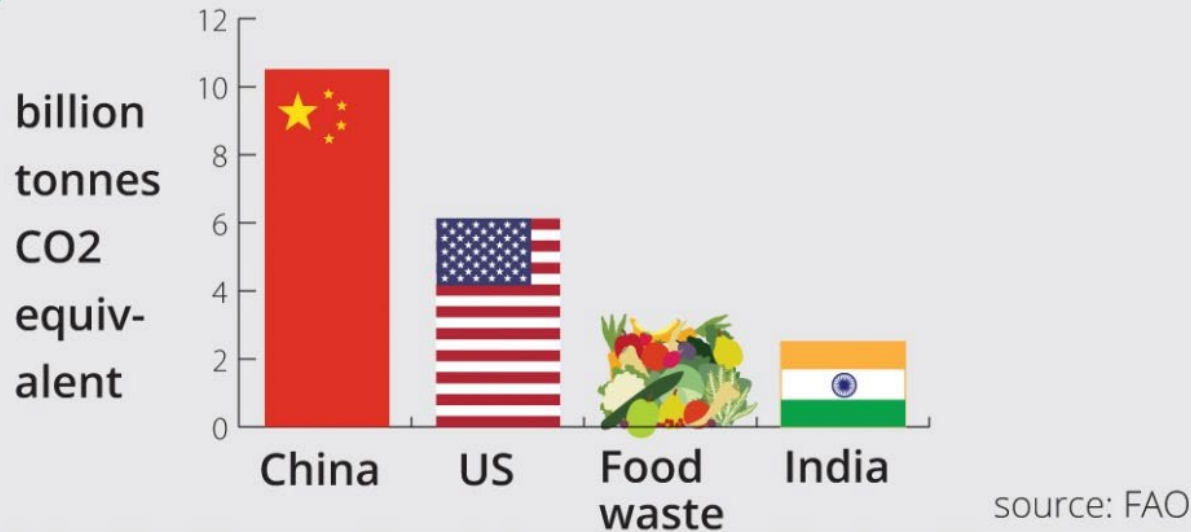
• Ellen MacArthur Foundation, *The New Plastic Economy – Rethinking the future of plastics*. 2014.



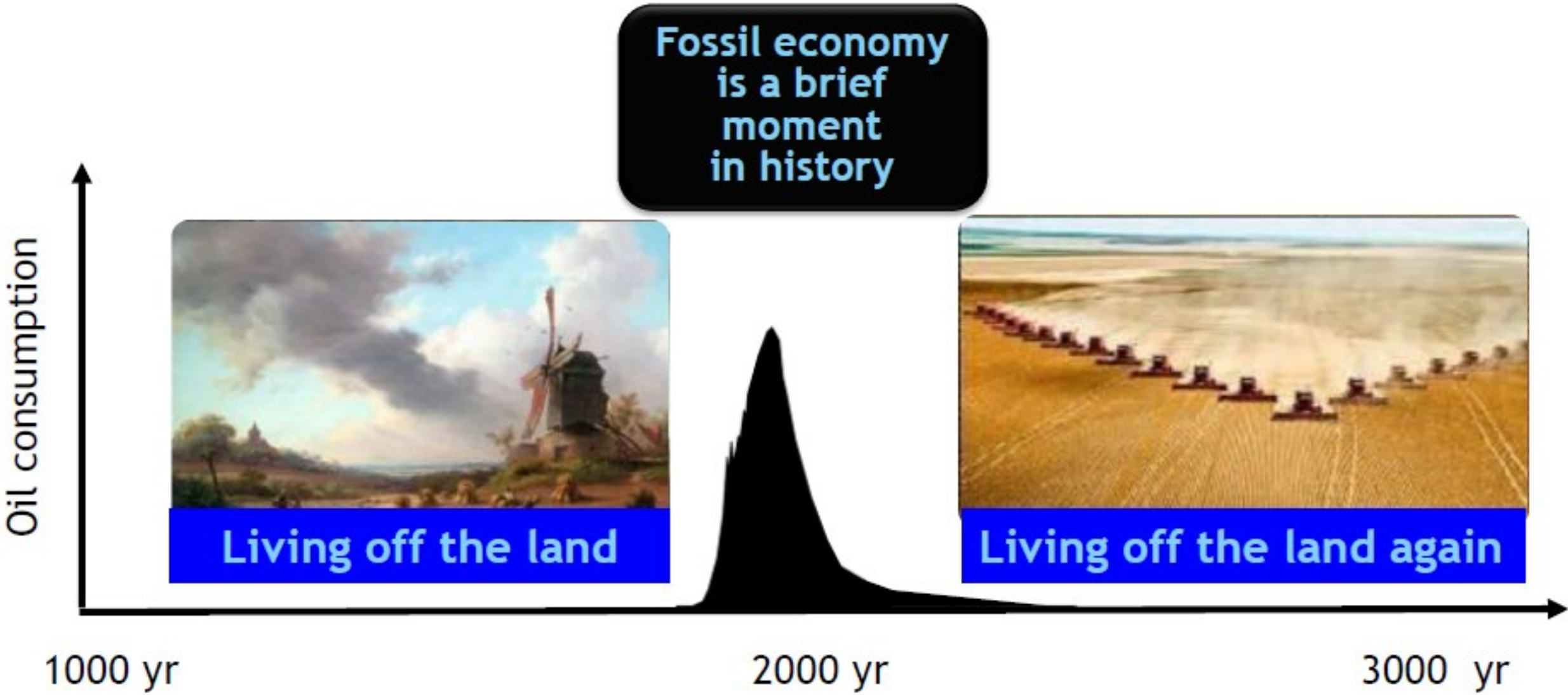
TODAY, PLASTIC PACKAGING MATERIAL FLOWS ARE LARGELY LINEAR



If global food waste was a country, it would be the third largest greenhouse gas emitter after the US and China

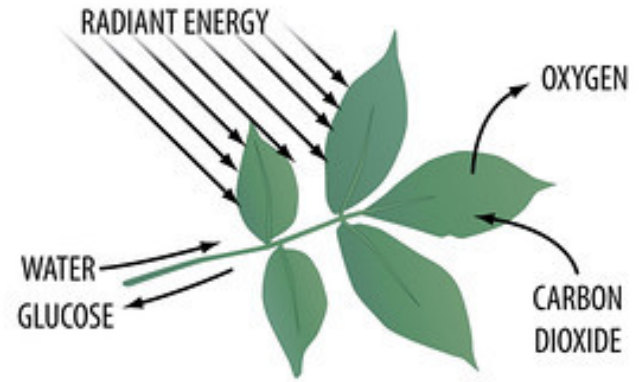
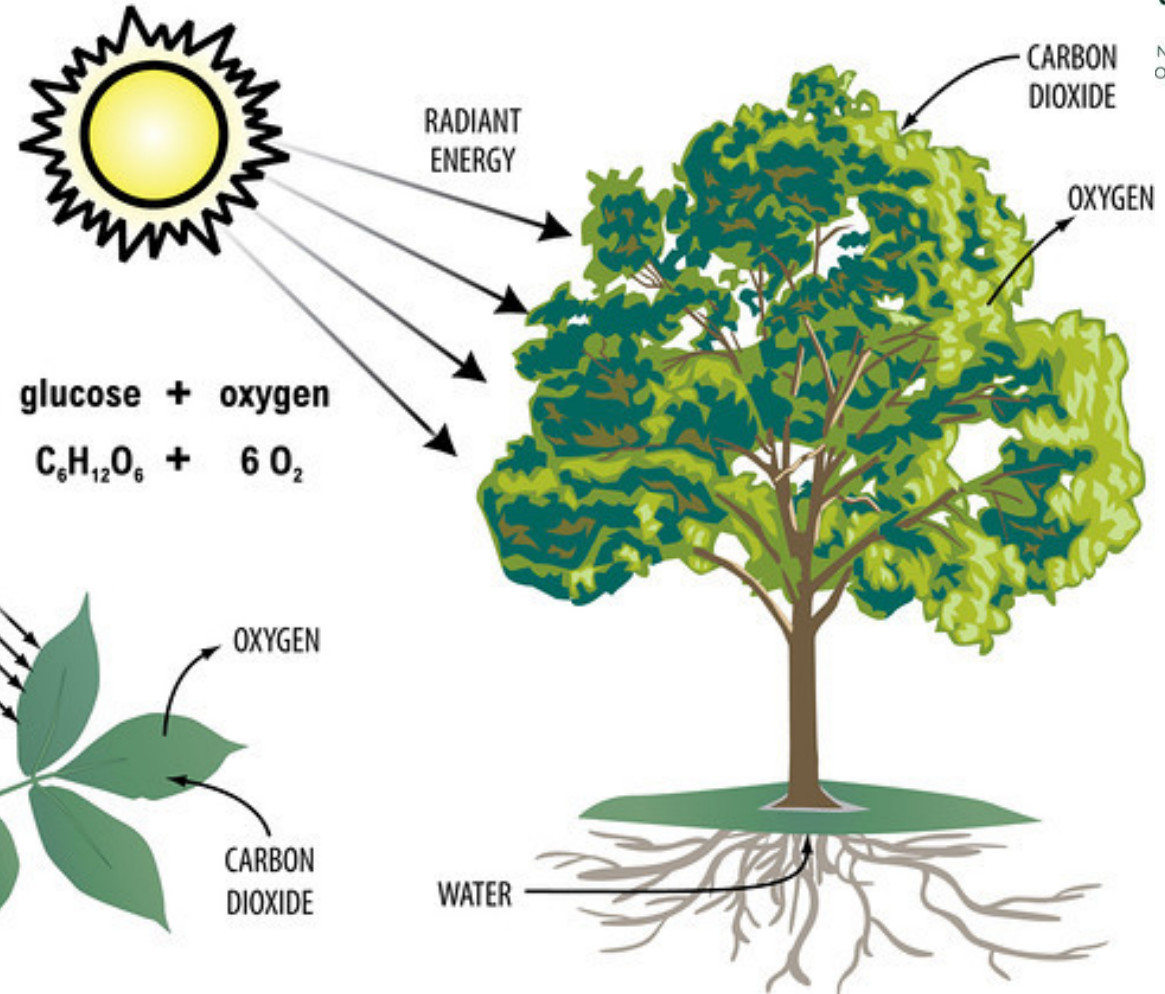
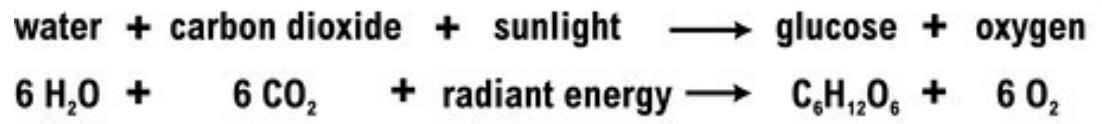


Packaging pollutes **BUT**
We need Packaging to limit food waste
and so to limit pollution



Photosynthesis

In the process of photosynthesis, plants convert radiant energy from the sun into chemical energy in the form of glucose (or sugar).

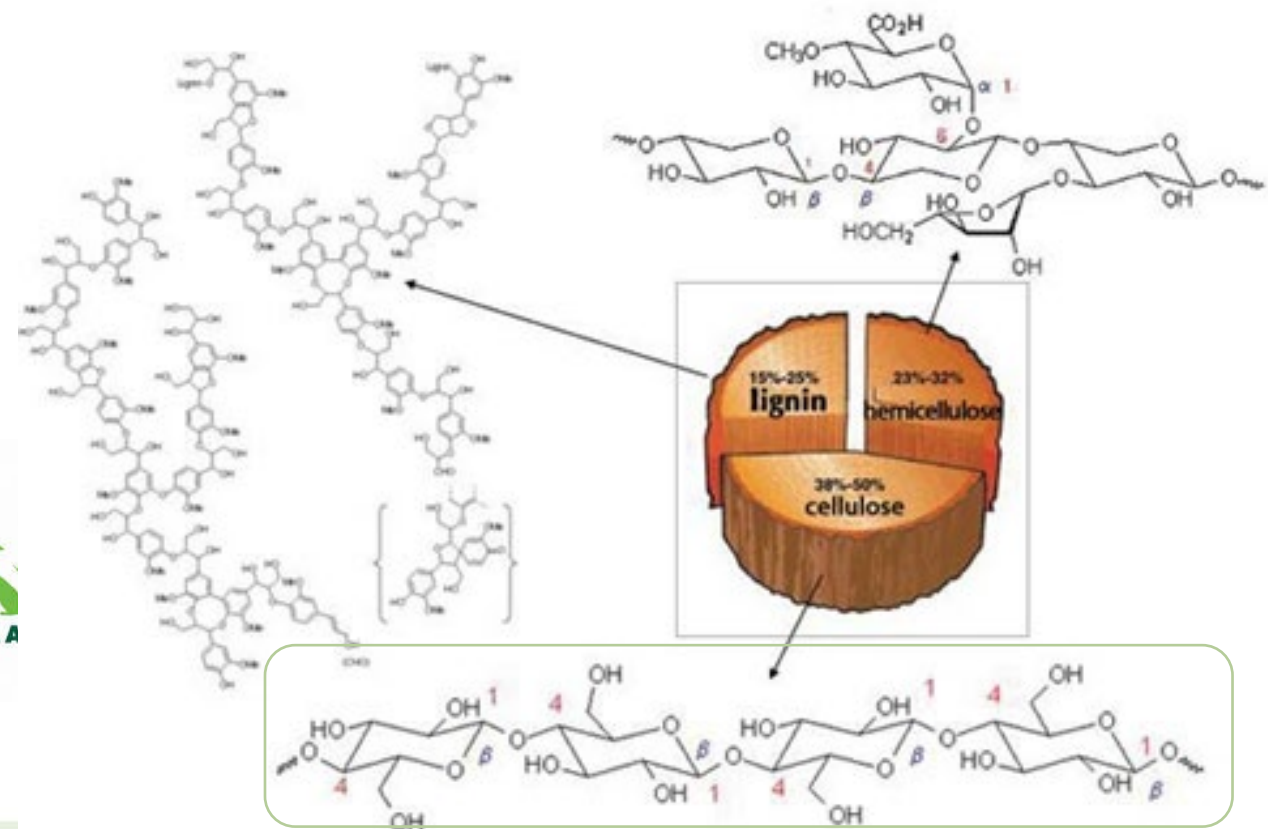


→ BIOMASS = 300-500 Billions tons product every year

Cellulose IS the SUPERSTAR



→ So many sources everywhere



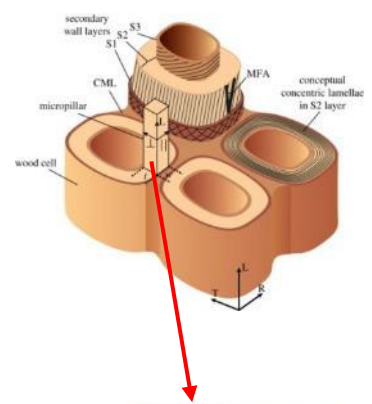
ab. 10-15 t/ha
Dried biomass



Industry= 300-400 Millions t/y



NanoCellulose IS also the SUPERSTAR



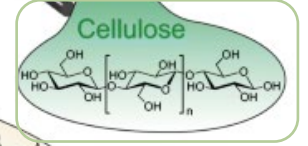
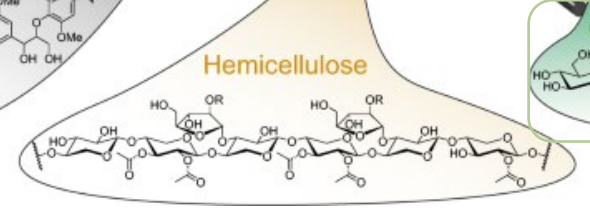
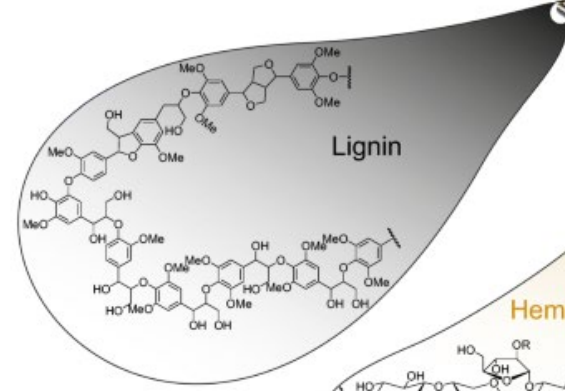
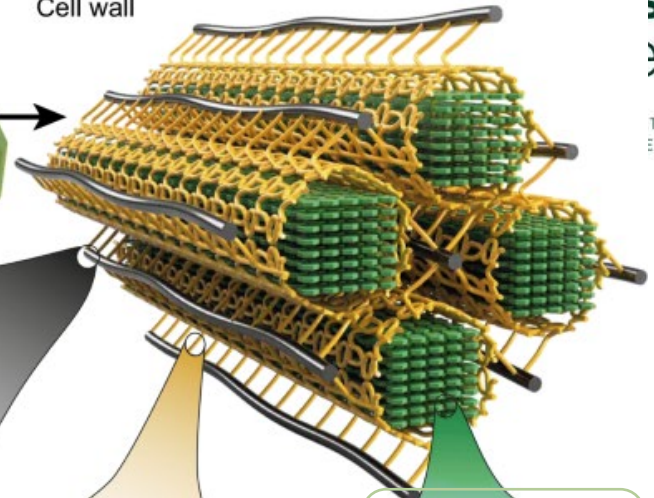
Lignocellulosic substrates



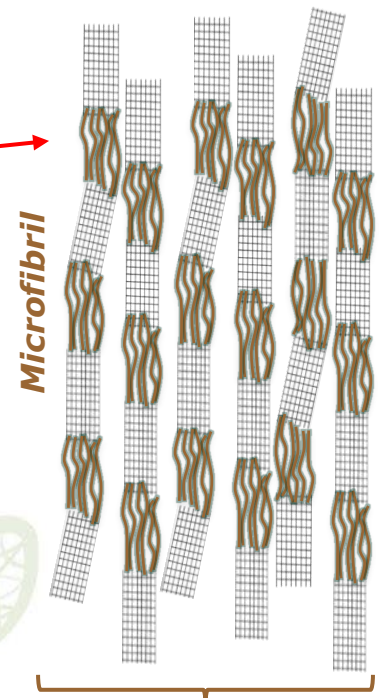
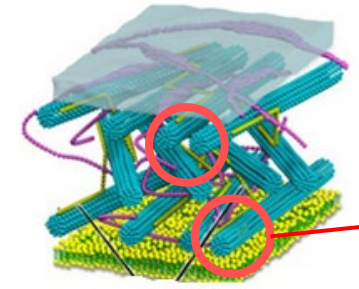
Plant cells



Cell wall



Ab. 50% of wood



Cellulose fiber

Microfibrillated cellulose (MFC)

D 5-50 nm
L > 1000 nm

SSP= 50-100m²/g

Cellulose Nanocrystals (CNC)

D 5-10 nm
L 150-1000 nm

SSP= 150-200m²/g

Nanocellulose:
Is it really a good solution
for Sustainable Packaging?



What means **sustainable
packaging** ?



Sustainable design check list

- Choose the most suitable packaging material for each product
 - Use recycled or biobased plastic
 - Choose the right packaging size & functionalities
 - Ensure product protection to minimise waste
 - Ensure hygiene and food safety
- Ensure reusability or recyclability
 - Make LCA calculations to ensure your packaging is truly sustainable
 - Communicate your sustainability message on your packaging
 - Inform the used raw materials and communicate recycling instructions on the packaging

Source: Amerplast 2023



Source: ecoart 2023

Nanocellulose: Is it really a good solution for Sustainable Packaging?



PRELIMINARY ASUMPTION:

Sustainable production of Nanocellulose
Low carbon footprint and low price



My group research topics



BIOMASS

T1: Nanocellulose preparation process optimization
(Deconstruction)

→

→

200 nm EHT = 3.00 kV Grenoble INP - CMTC

NANO-CELLULOSE

T2: Nanocellulose surface functionalization
(activation)

→

MATERIALS

T3: Material preparation processes for high performance (nano)cellulose materials
(reconstruction)

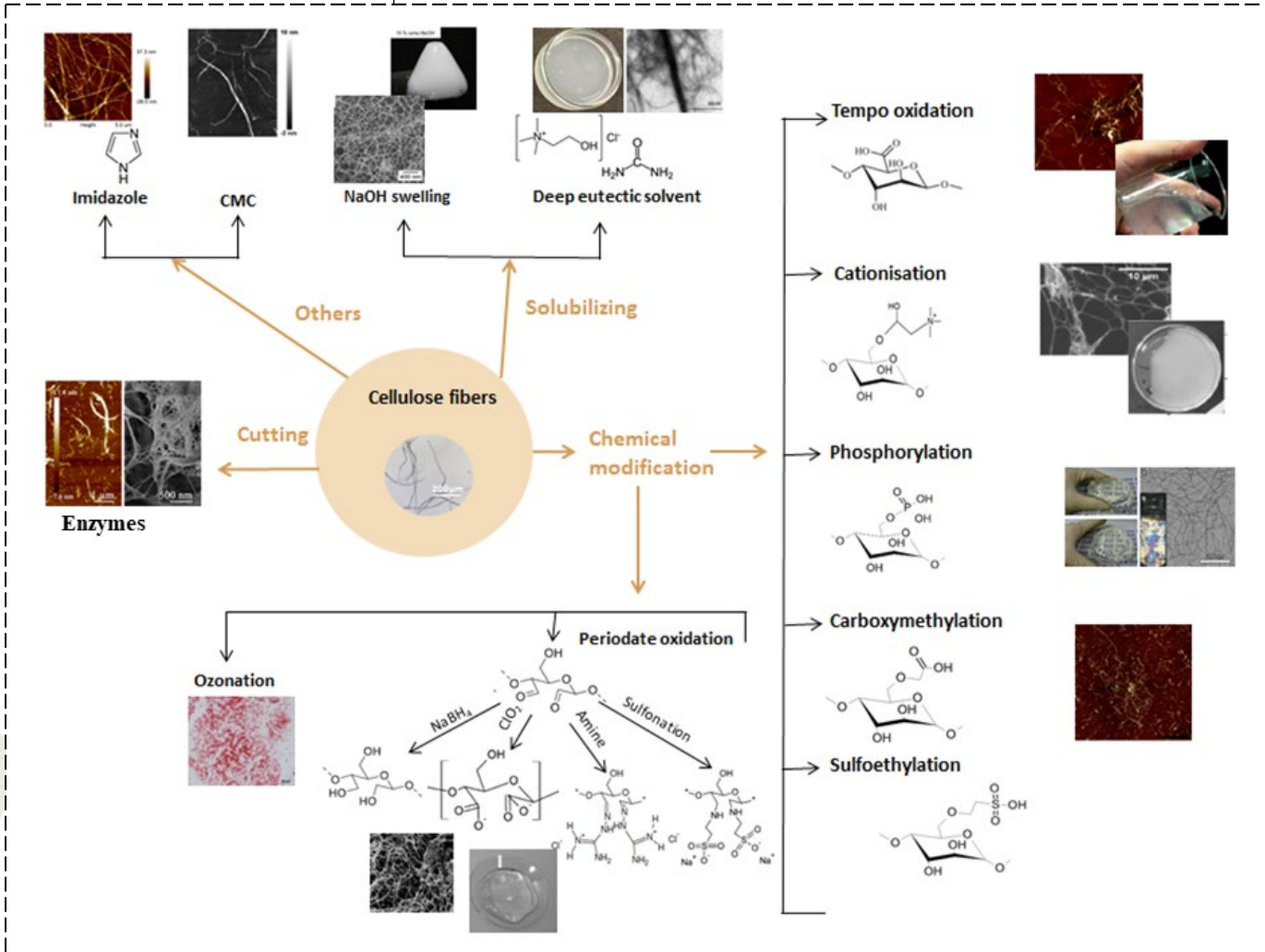
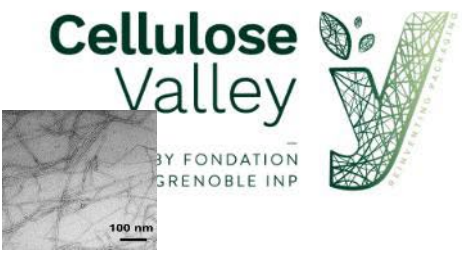
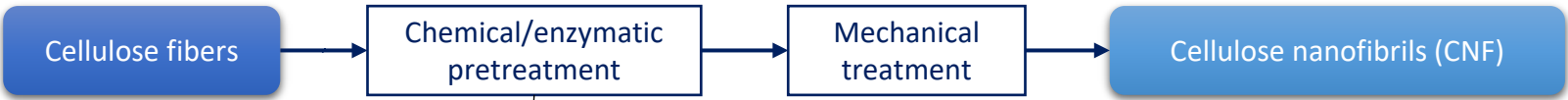
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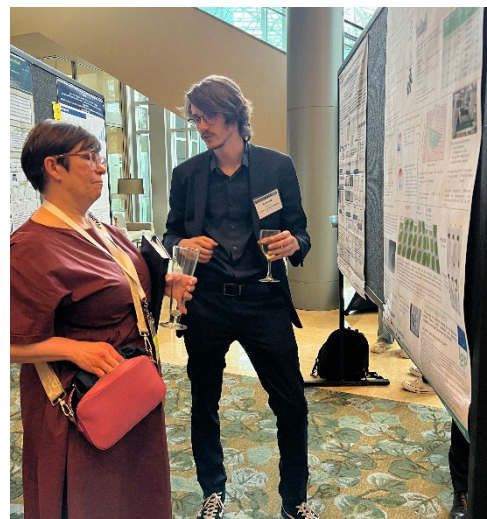
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Nanocellulose & Sustainable production

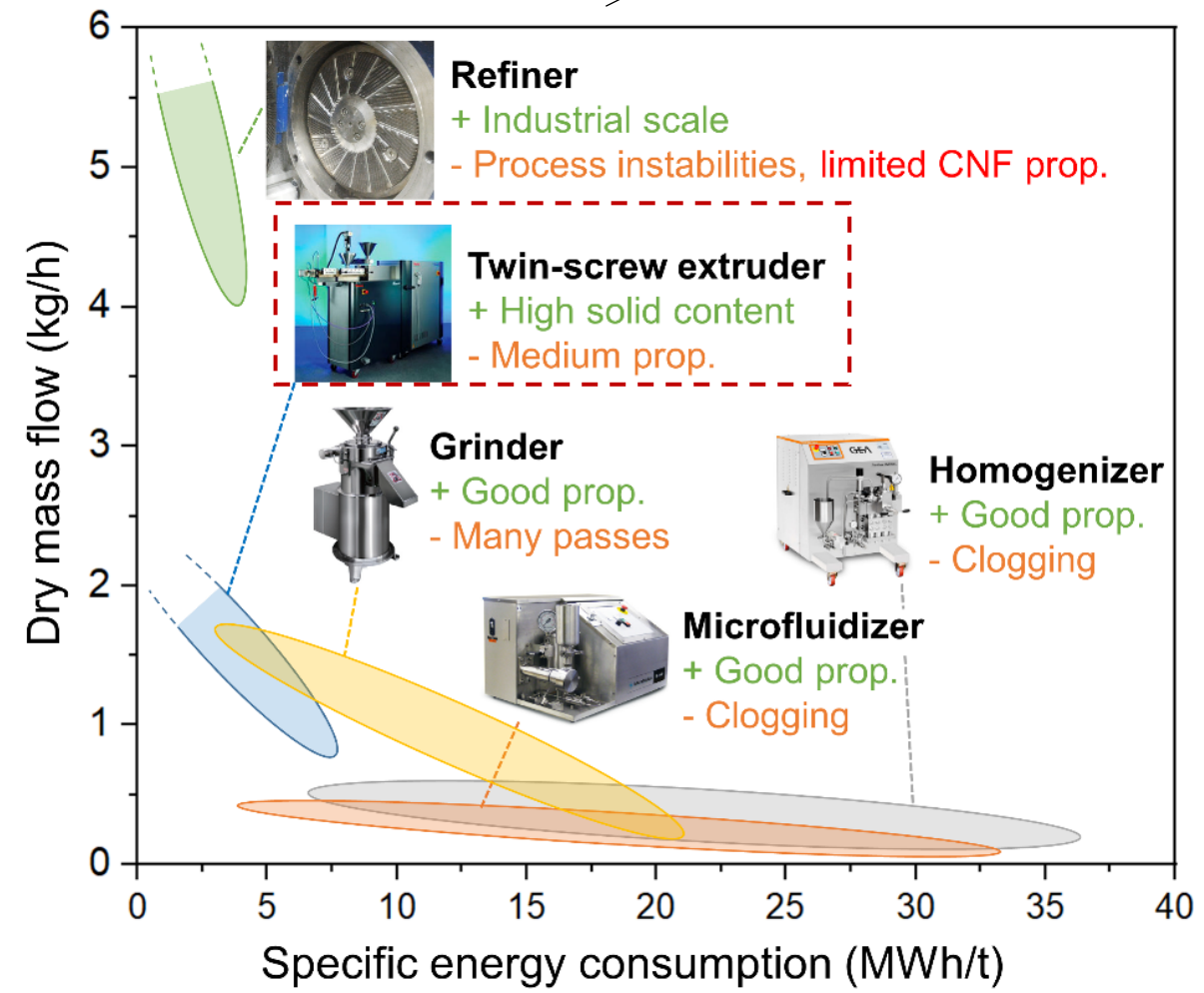
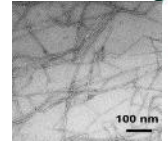
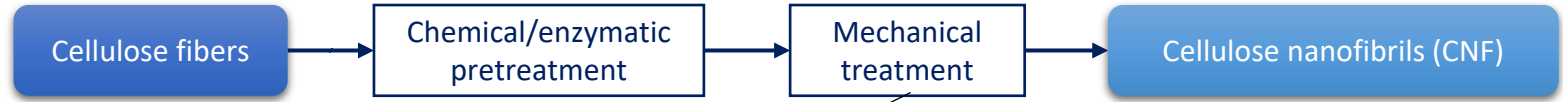


Mechanochemistry



R2R phosphorylation

Nanocellulose & Sustainable production



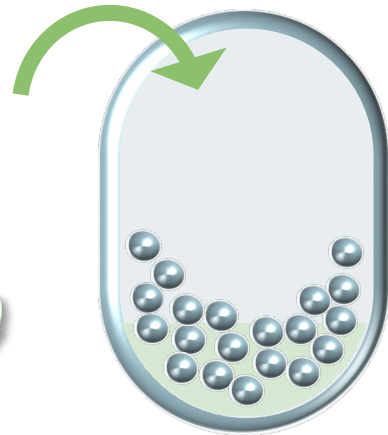
Twin screw extrusion



Nanocellulose & Sustainable production

Fibres addition

Cotton cellulosic fibers
Consistency (65 wt%)



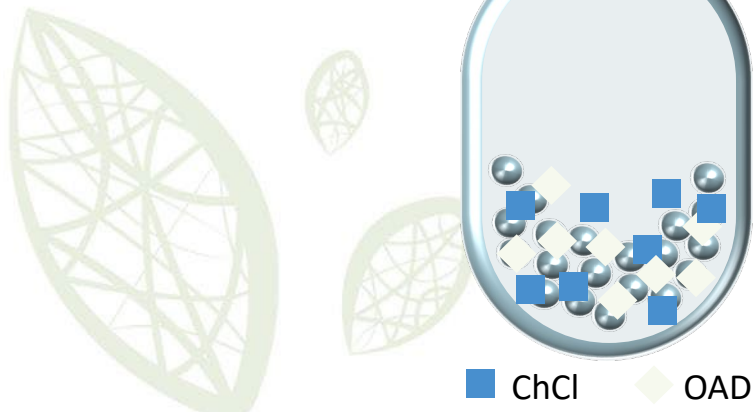
Mechanical treatment

Ball milling
30 Hz – 1 h 30 min
Ambient temperature

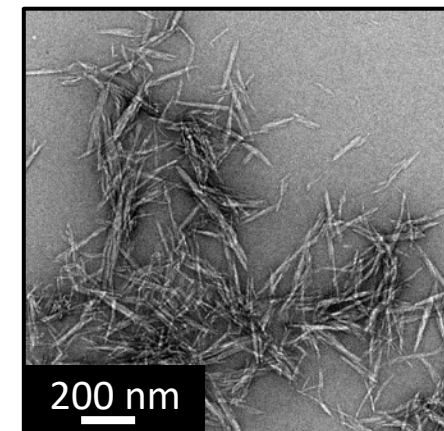


NADES obtention

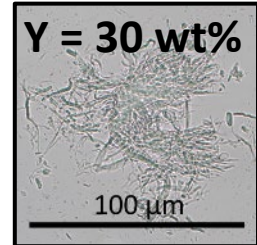
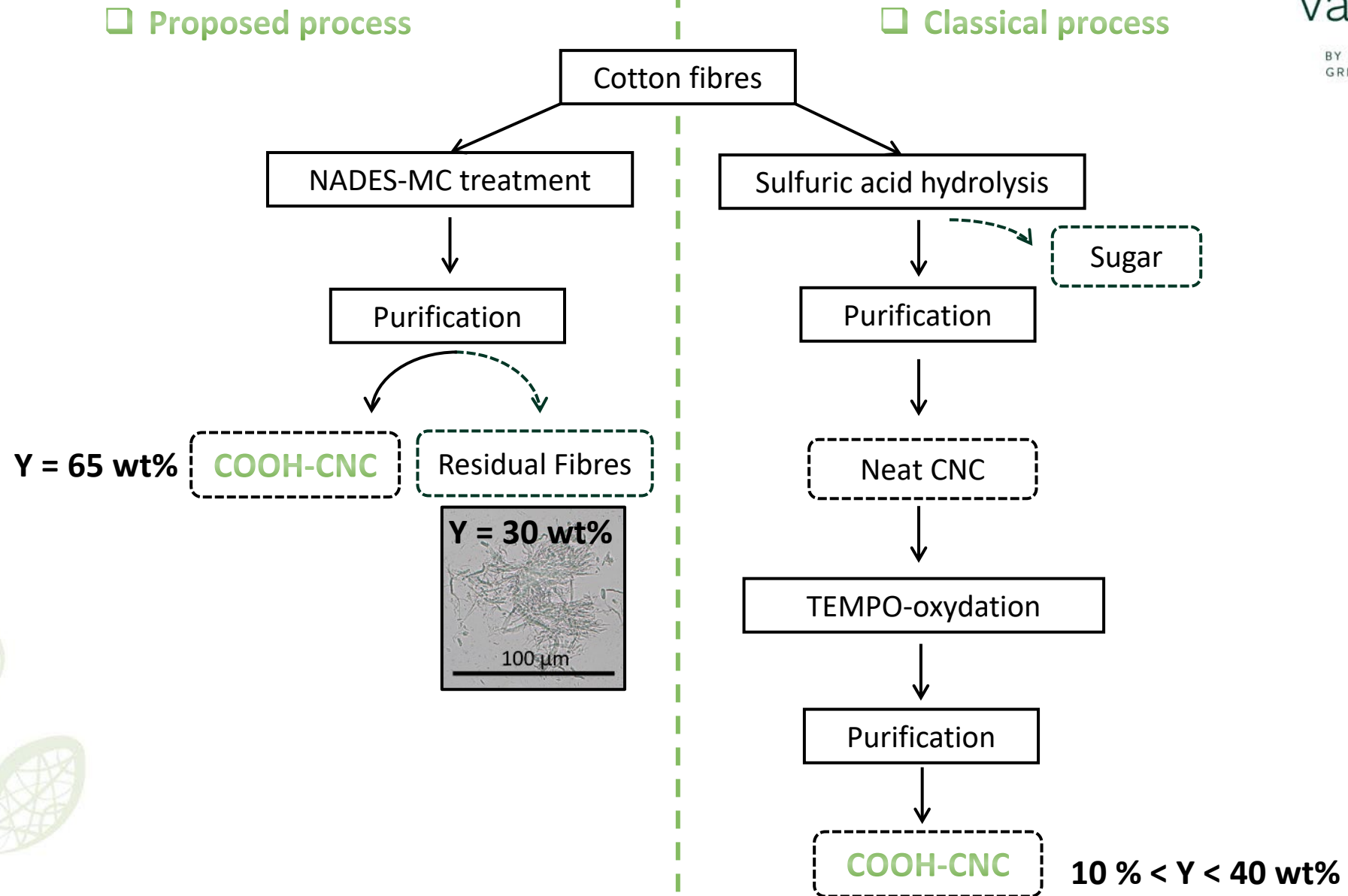
30 Hz - 15 seconds



Anionic CNC with High yield



Nanocellulose & Sustainable production



Nanocellulose & Sustainable production

□ Need more public Life Cycle Assessment

Impact Category	Unit	Enzymatic Treatments & Homogenisation (ENZHO)		TEMPO-Oxidation and Homogenisation (TOHO)		TEMPO-Oxidation and Ultrasonication (TOSO)	
		Virgin Materials (Hardwood Kraft Pulp)	Recycled Materials (Industrial Waste Sludge)	Virgin Materials (Cotton linters)	Recycled Materials (Industrial Waste Sludge)	Virgin Materials (Cotton Linters)	Recycled Materials (Industrial Waste Sludge)
Climate change	kg CO ₂ eq	1.86×10^{-1}	1.77×10^{-1}	6.32×10^{-1}	6.78×10^{-1}	8.80×10^{-1}	7.84×10^{-1}

— ENZHO Virgin fibres (Short Fibre Eucalyptus)
 — ENZHO Recycled materials (industrial waste sludge)
 — TOHO Virgin fibres (Cotton linters)
 — TOHO Recycled materials (industrial waste sludge)
 — TOSO Virgin fibres (Cotton linters)
 — TOSO Recycled materials (industrial waste sludge)

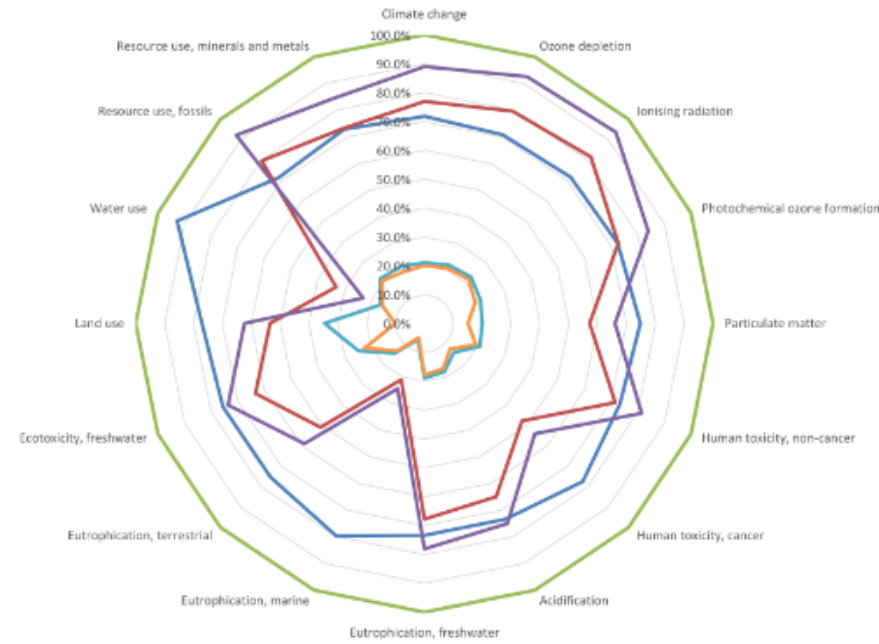


Figure 4. Relative environmental performances of the six CNFs based on the results of the characterisation step. The highest impact per each category is given 100% of the impact.

Nanocellulose & Sustainable production

□ Need more public Life Cycle Assessment

Step of the LCA	Strategies for Reduction of Energy Demand	Strategies for the Development of Low-Carbon Materials
Extraction of raw materials	1. Usage of fruit and vegetable wastes reduces energy consumption [83].	1. Usage of fruit and vegetable wastes reduces environmental impacts [83].
Cellulose products manufacturing	<ol style="list-style-type: none"> Using better insulation and heat recovery during the process. Burning some by-products for using the generated energy [87]. Reducing solvent consumption can decrease energy consumption for the reaction indirectly. Reducing the reaction time can decrease power consumption [99]. 	<ol style="list-style-type: none"> Recovery of excessive solvents, especially in pretreatment reaction processes for reducing the environmental impact. Using by-products as inputs for other processes, specifically in large-scale processes [85]. Reusing of water used in the production of cellulose products, especially in the washing stage, for other processes [86].

Foroughi, Firoozeh et al. "A Review on the Life Cycle Assessment of Cellulose: From Properties to the Potential of Making It a Low Carbon Material." Materials 14 (2021)

Nanocellulose: Is it really a good solution for Sustainable Packaging?



PRELIMINARY ASUMPTION:

Sustainable production of Nanocellulose
Low carbon footprint and low price



IN WHICH PACKAGING APPLICATIONS ?



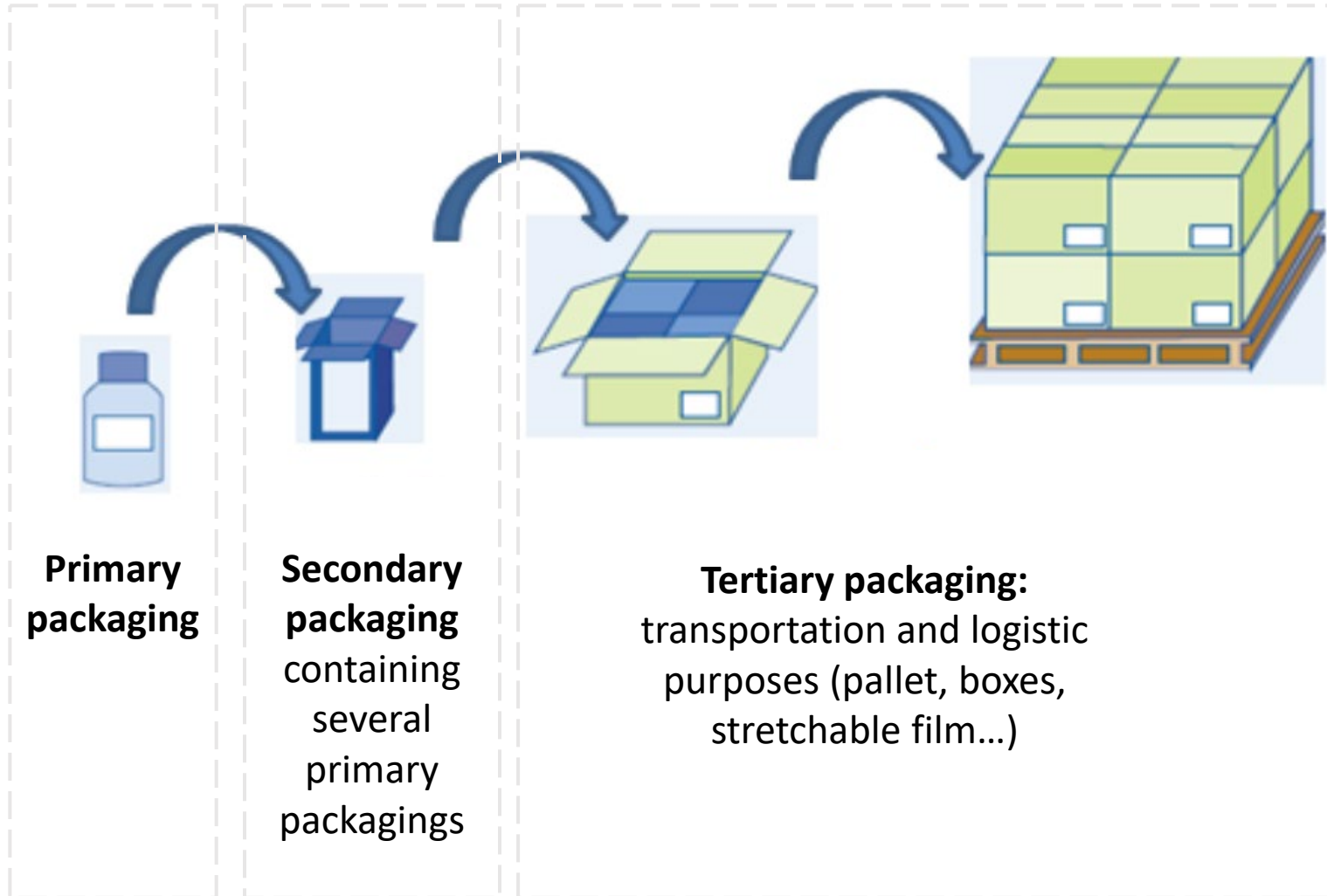
Orientations

REDUCE



Social responsibility
Change of the consumption habits

Understand the packaging



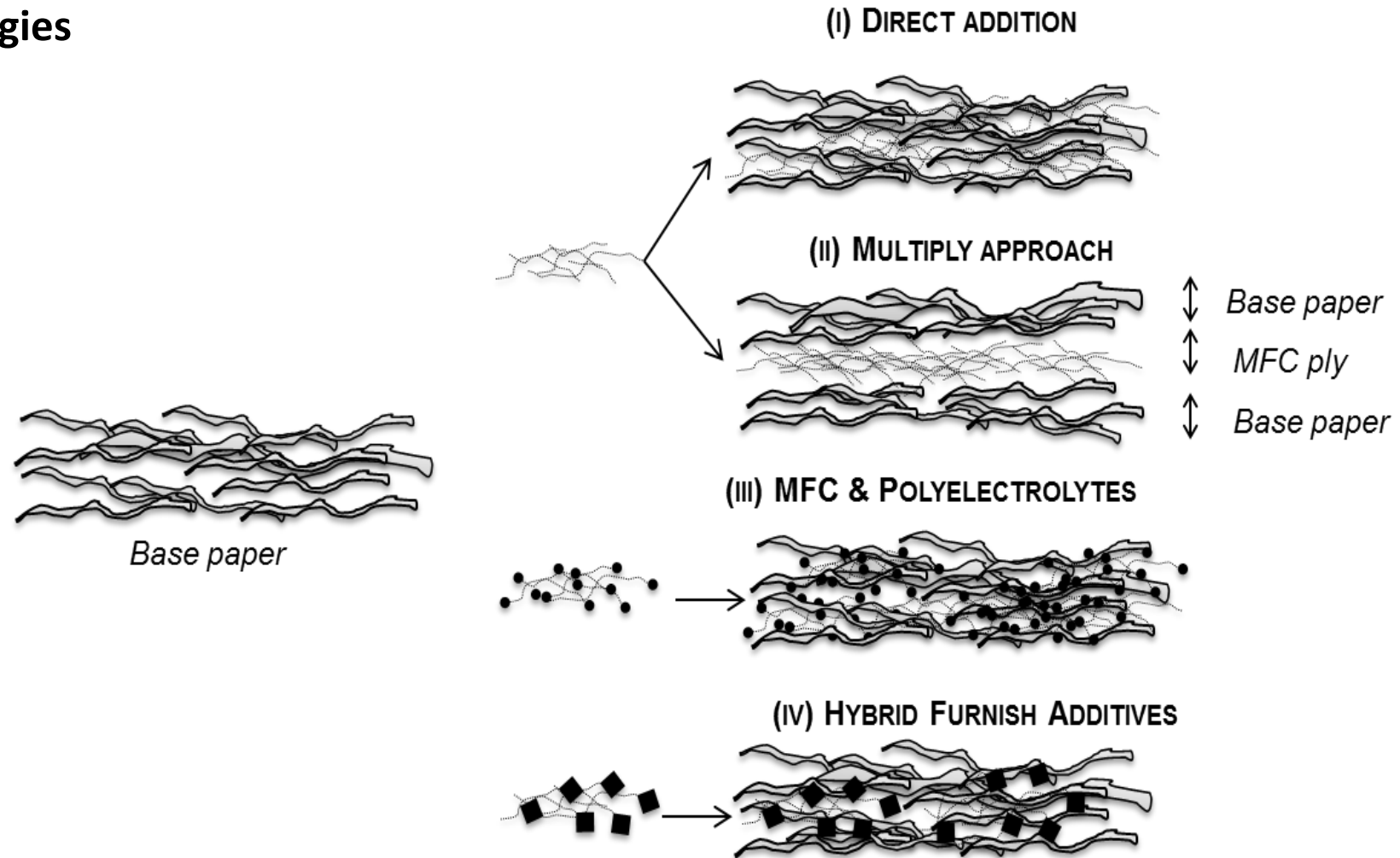
=> Development of Barrier shift concept (in progress)

PACKAGED FOOD CONCENTRATE WITH BARRIER PROPERTIES PROVIDED BY AN EDIBLE PACKAGING, Niederreiter, Bras et al, WO2022043072

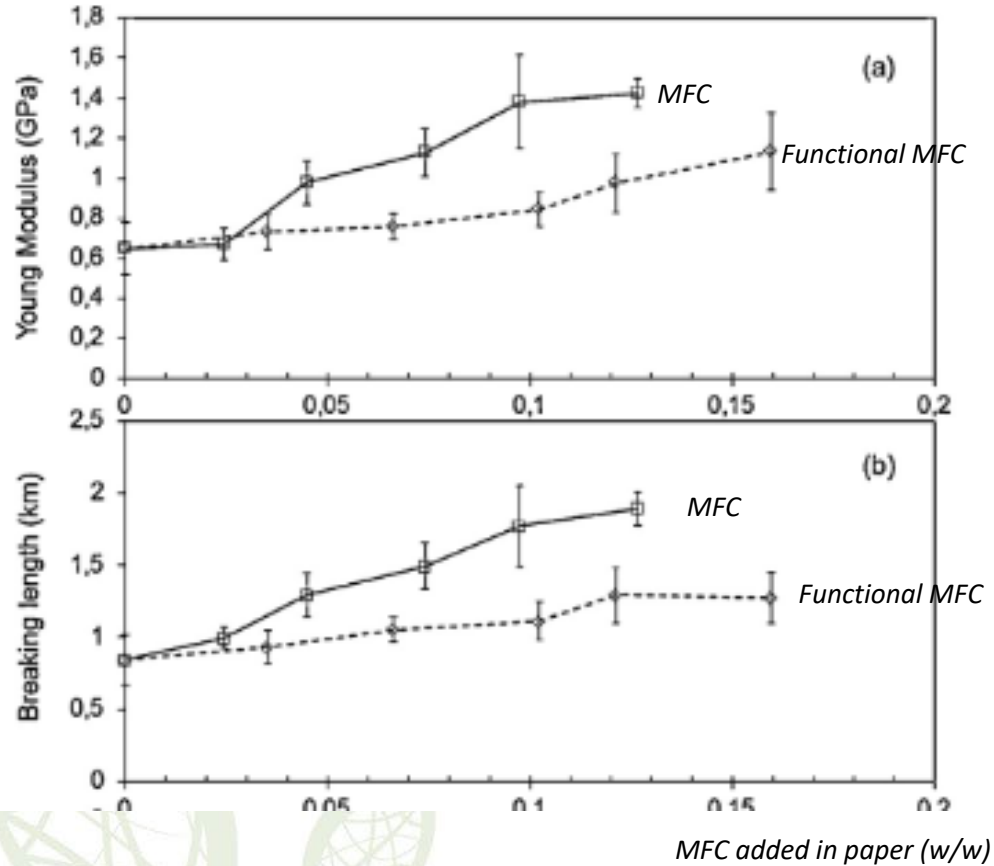
BARRIER PACKAGING MATERIAL COMPRISING A CARDBOARD-BASED MOISTURE SCAVENGER, Wyser, Giardiello et Bras, WO2022135986

Nanocellulose to reduce weight

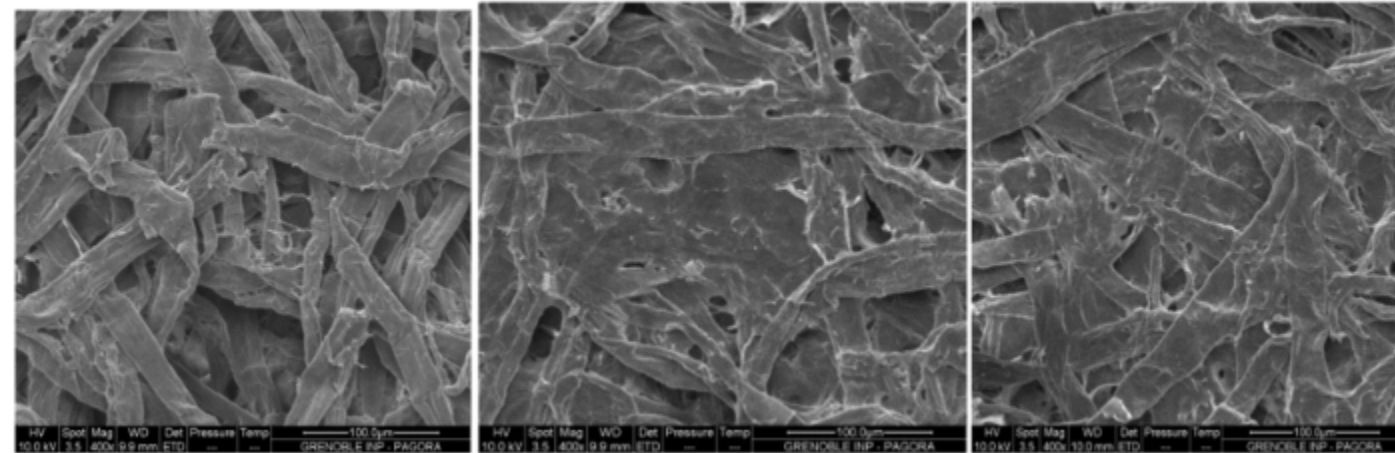
Several strategies



Nanocellulose to reduce weight



Missoum K., Bras J., et al, *Industrial Crops and Products* 48 (2013) 98–105,

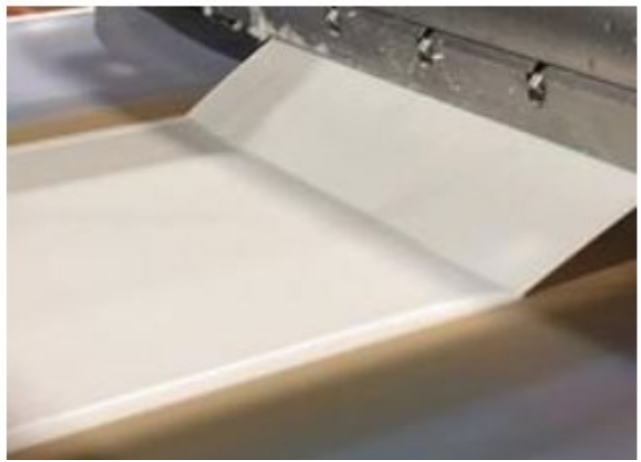
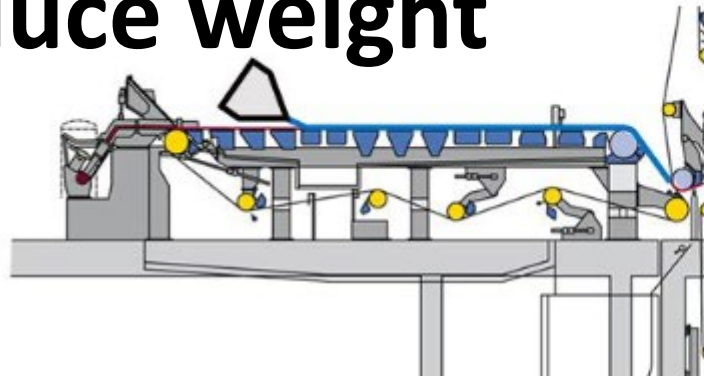
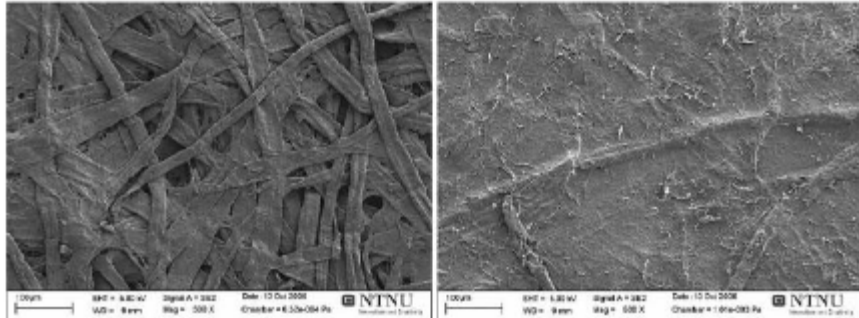


Effect of addition of MFC and TEMPO-MFC on the mechanical properties of paper sheets prepared from unbeaten bagasse.

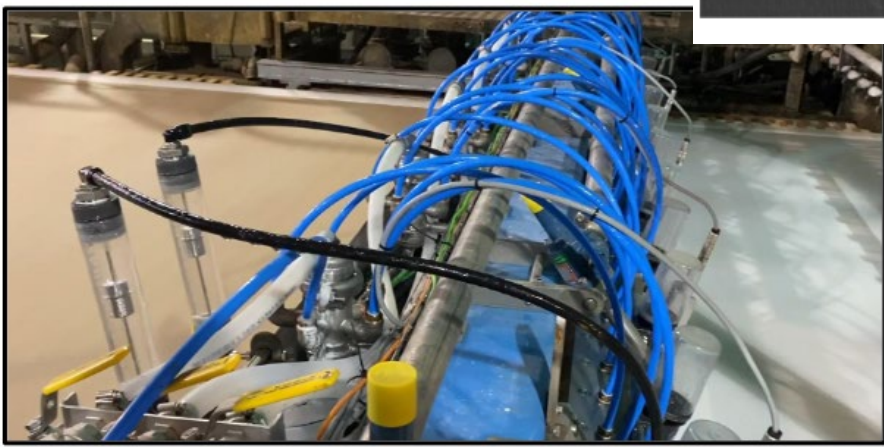
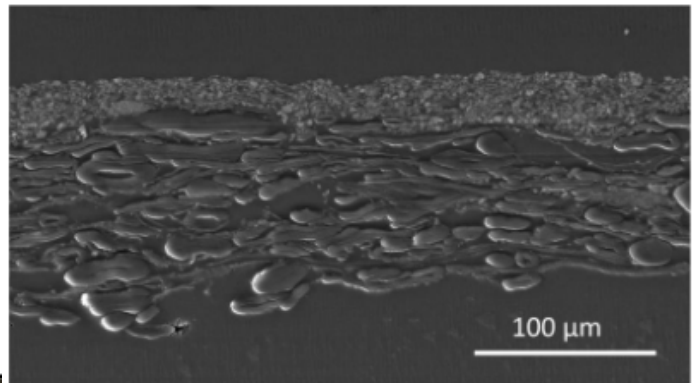
Sample	Breaking length (km)	Wet breaking length (km)
Unbeaten bagasse	2.97 (0.15)	0.078 (0.009)
Beaten bagasse (B)	4.83 (0.49)	0.16 (0.02)
B + 2.5% MFC	3.61 (0.18)	0.13 (0.01)
B + 2.5% TMFC	3.49 (0.36)	0.12 (0.01)
B + 5% MFC	4.63 (0.68)	0.14 (0.01)
B + 5% TMFC	4.51 (0.23)	0.18 (0.03)
B + 10% MFC	4.9 (0.41)	0.17 (0.02)
B + 10% TMFC	4.87 (0.29)	0.29 (0.05)
B + 20% MFC	4.23 (0.29)	0.18 (0.02)
B + 20% TMFC	4.22 (0.59)	0.42 (0.05)

Values between brackets are the standard deviation.

Nanocellulose to reduce weight



- MFC suspension is applied at the wet end of a papermachine, just after the 'wet line'
- Dewatering is achievable with existing elements – vacuum boxes, presses and dryers



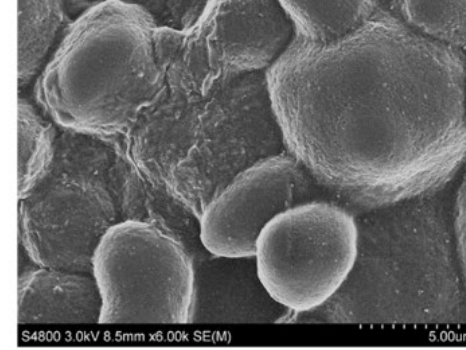
Nanocellulose to reduce weight

- Better bond strength

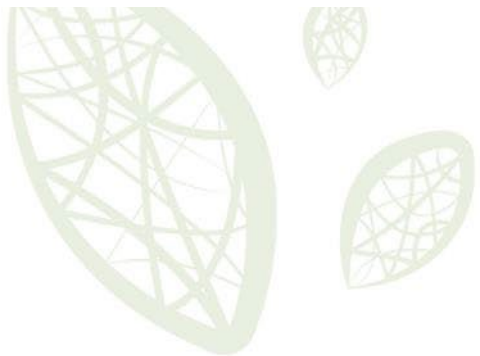
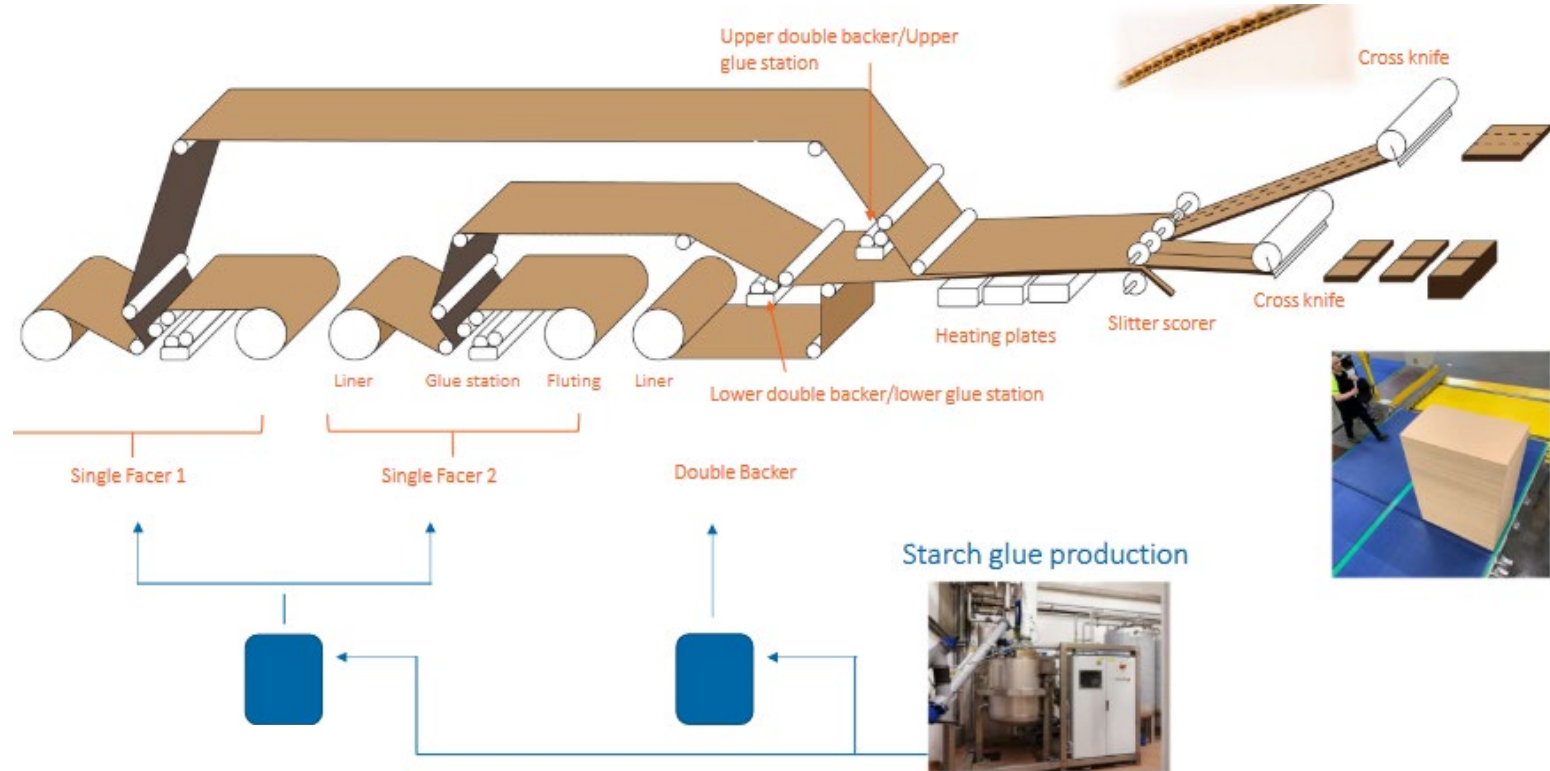
%Difference with Exilva in glue B-flute, Double Backer (DB)



Starch adhesive without Exilva



Starch adhesive with Exilva



Orientations



REDUCE



Social responsibility
Change of the
consumption habits

REUSE



Refill and Reuse

Bulk products

Eliminate Single Use Packagings

CIRCULAR DELIVERY



- Refill container delivered to consumer
- Collaboration with LOOP/ TerraCycle

REFILL SYSTEMS



- Water system to refill consumers container
- Piloted in US, France and Switzerland

SINGLE-DOSE DISPENSERS



- Dosing system for powdered beverages
- Rolled out in 39 markets globally

IN-STORE DISPENSERS



- Bulk dosing system for petcare and soluble coffee
- Piloted in Switzerland

Source: Nestlé Press release, Sept 2020

Bulk products





=> Development of Cellulose Nacre concept (in progress)



Orientations



REDUCE



Social responsibility
Change of the
consumption habits

REUSE



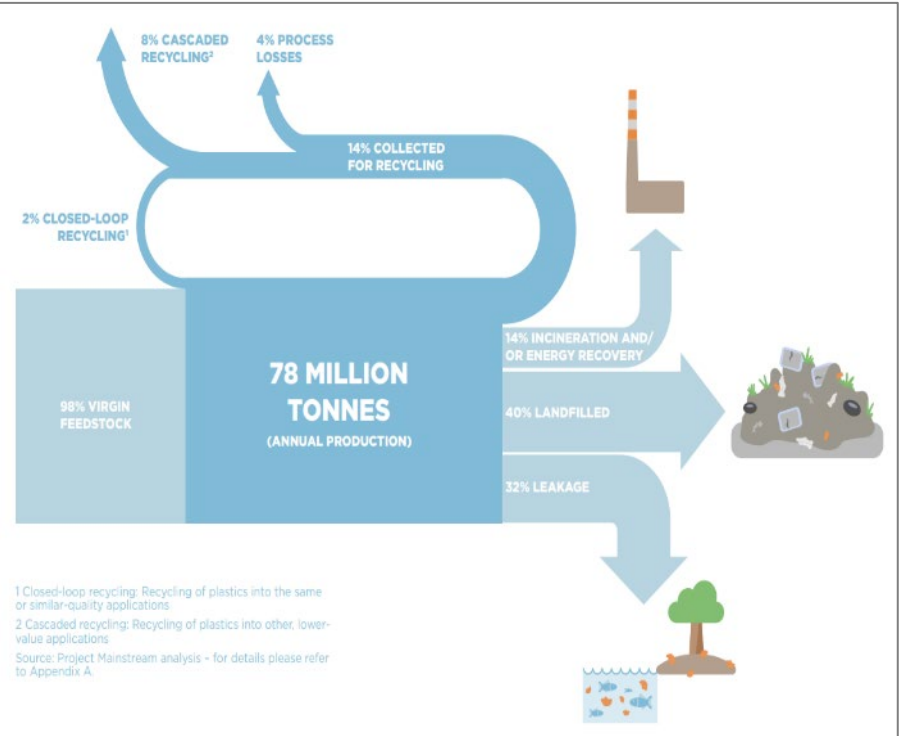
Refill and Reuse

RECYCLE

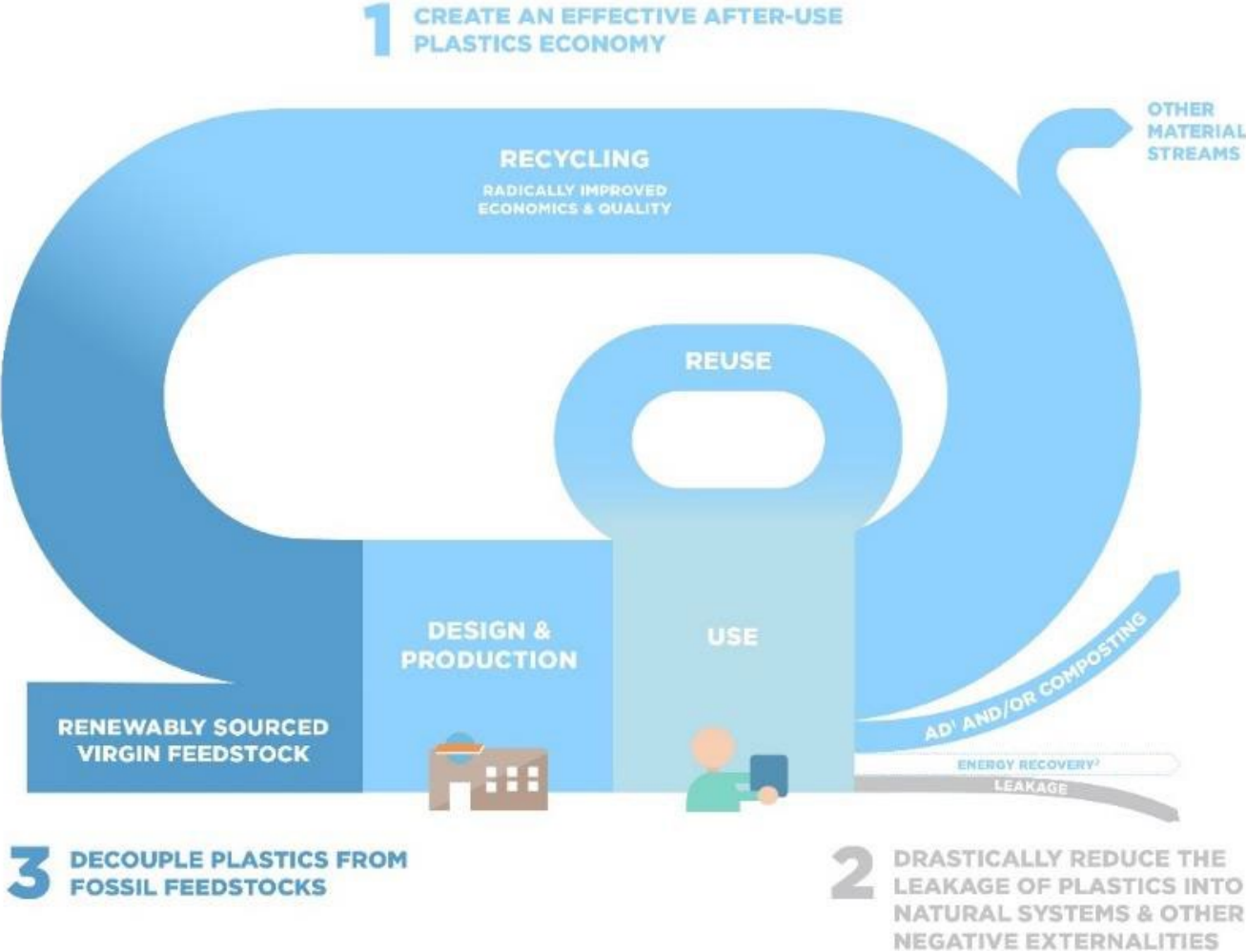


Recyclability for a better
feedstock management

Circular economy



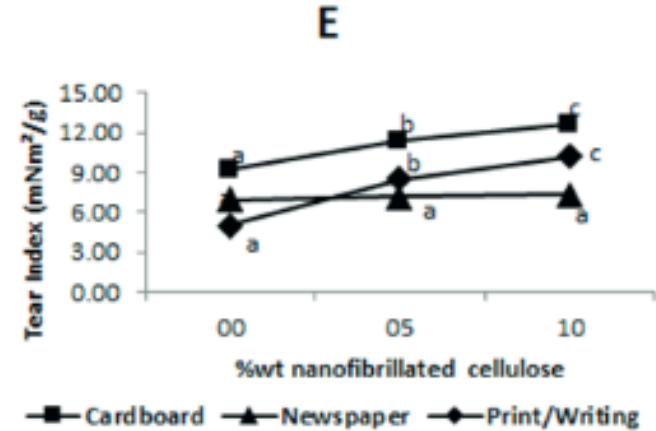
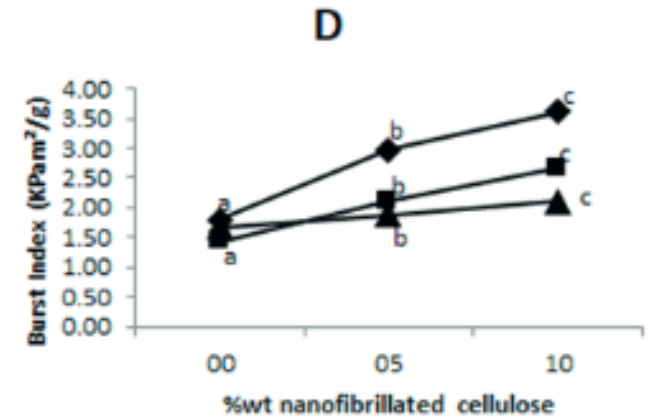
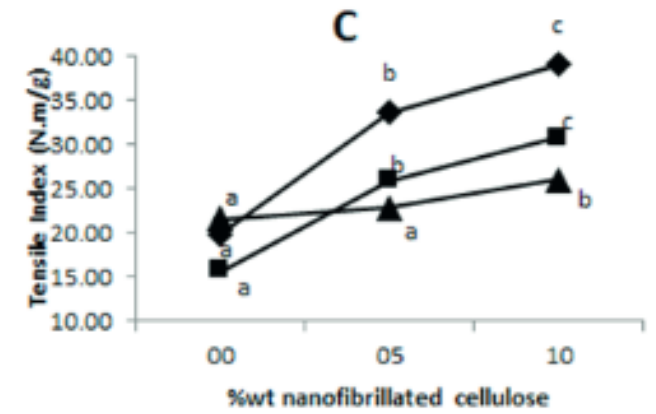
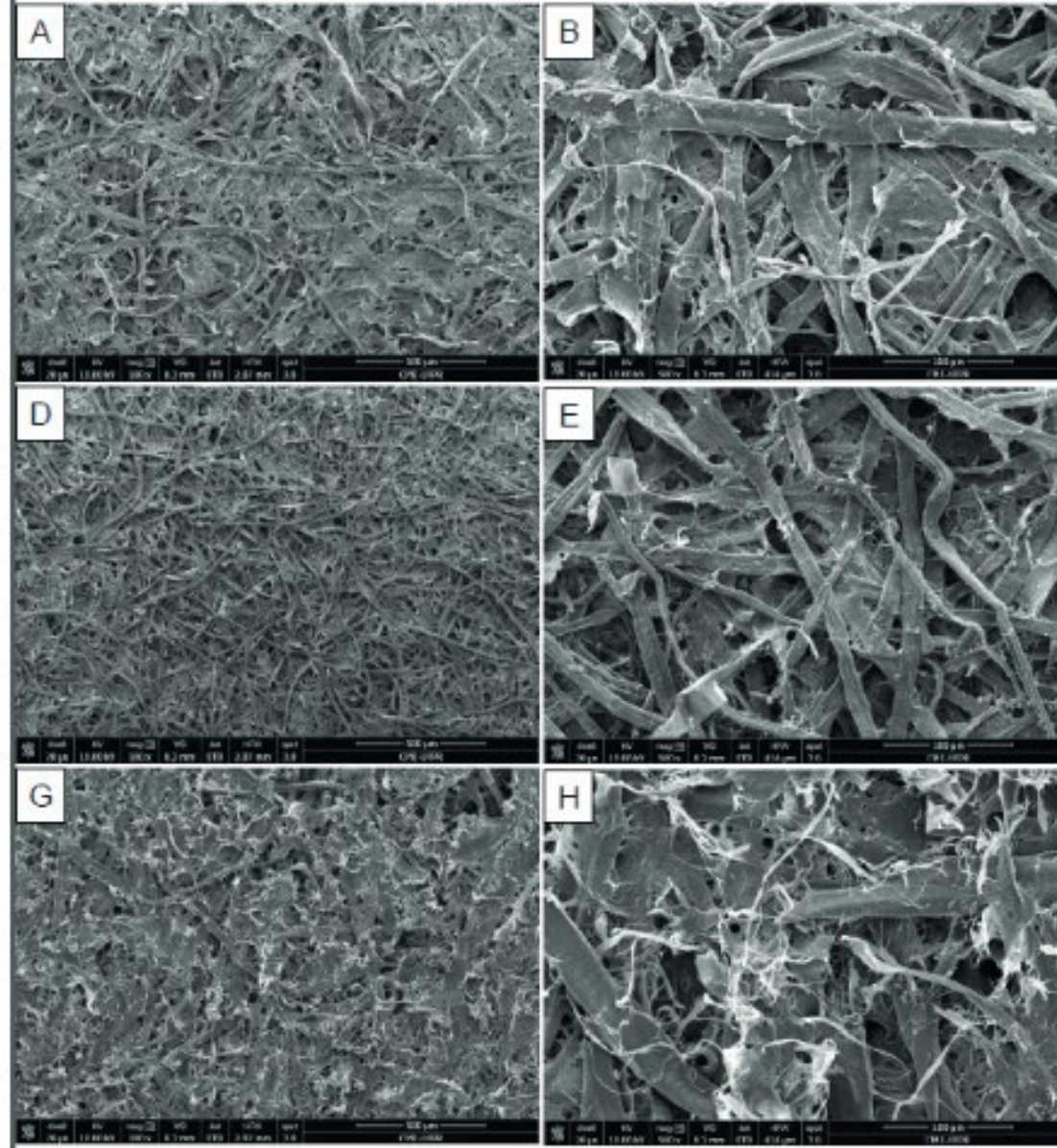
Linear economy



Circular economy

• Ellen MacArthur Foundation, *The New Plastic Economy – Rethinking the future of plastics*. 2014.

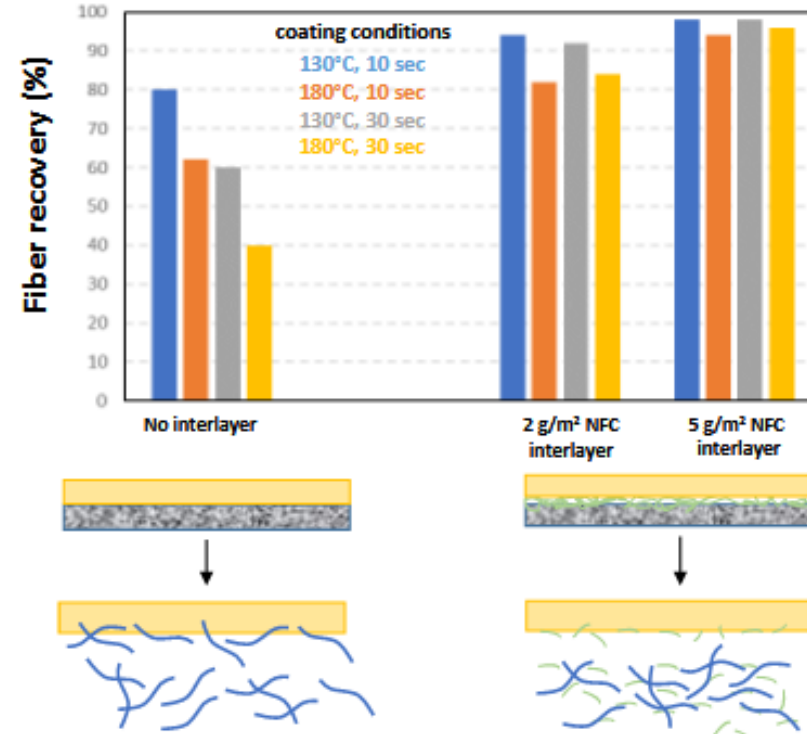
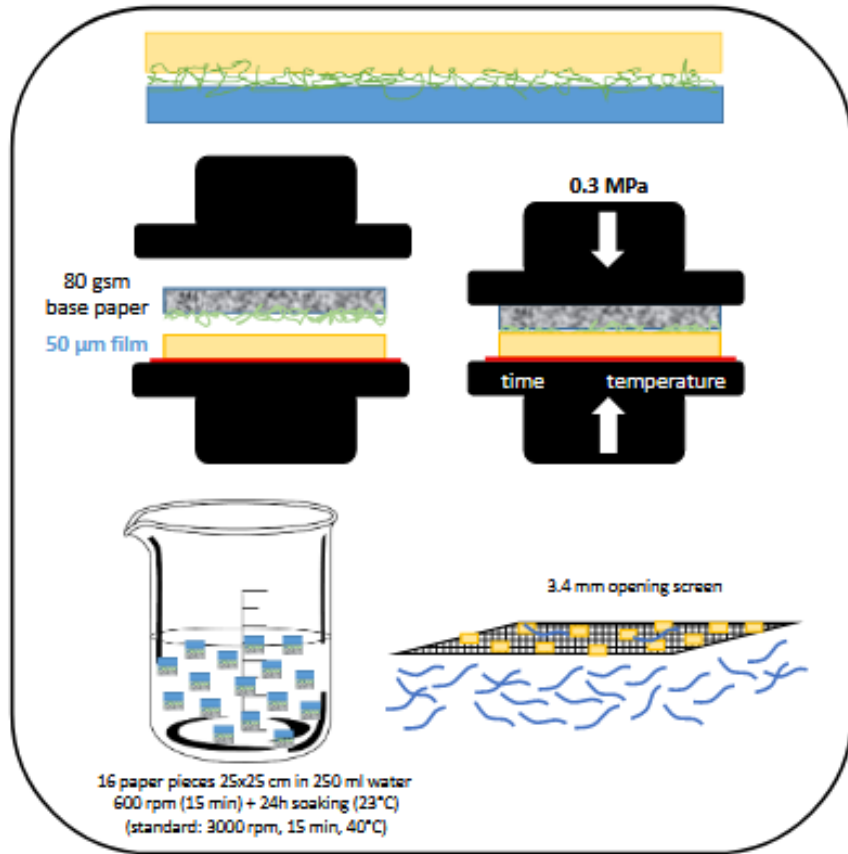
Recyclable materials



Recyclable materials

End-of-Life: Role of Nanocellulose in Paper Recycling

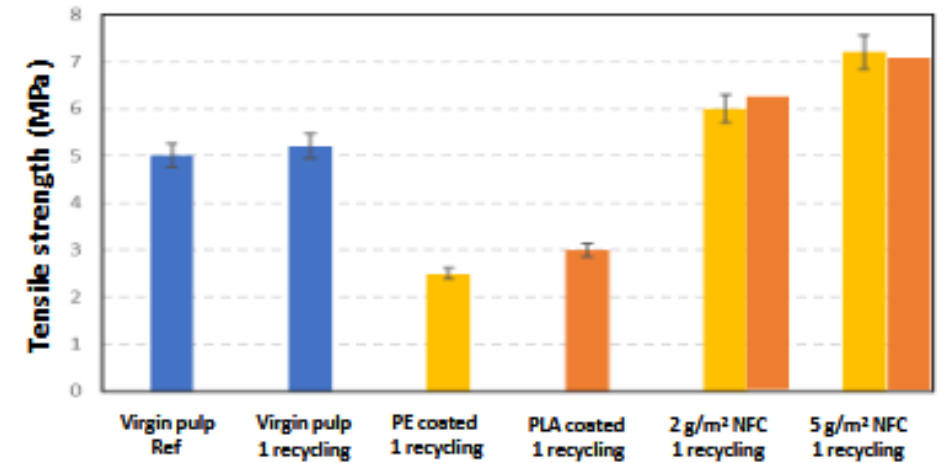
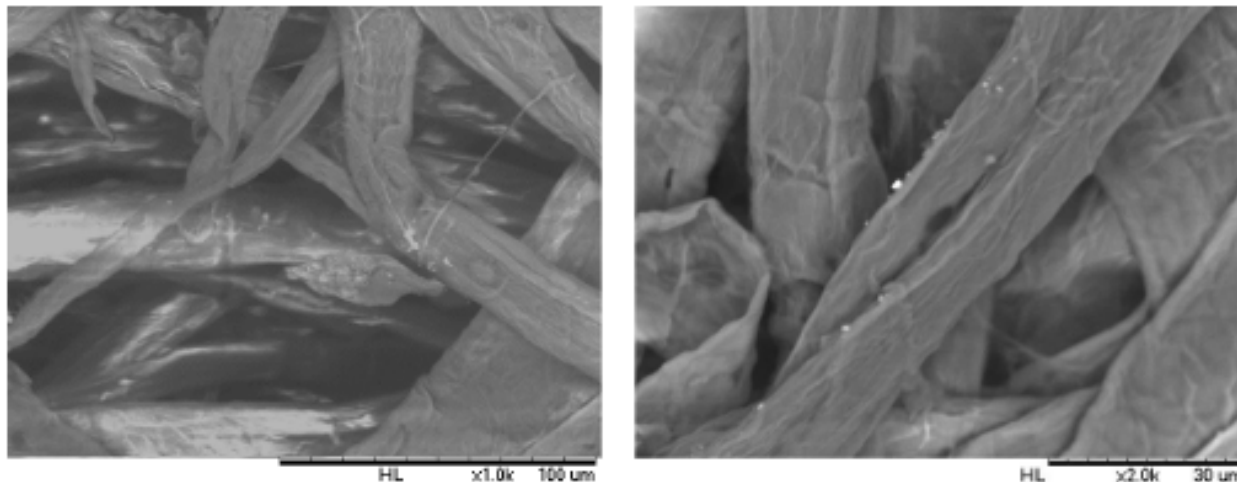
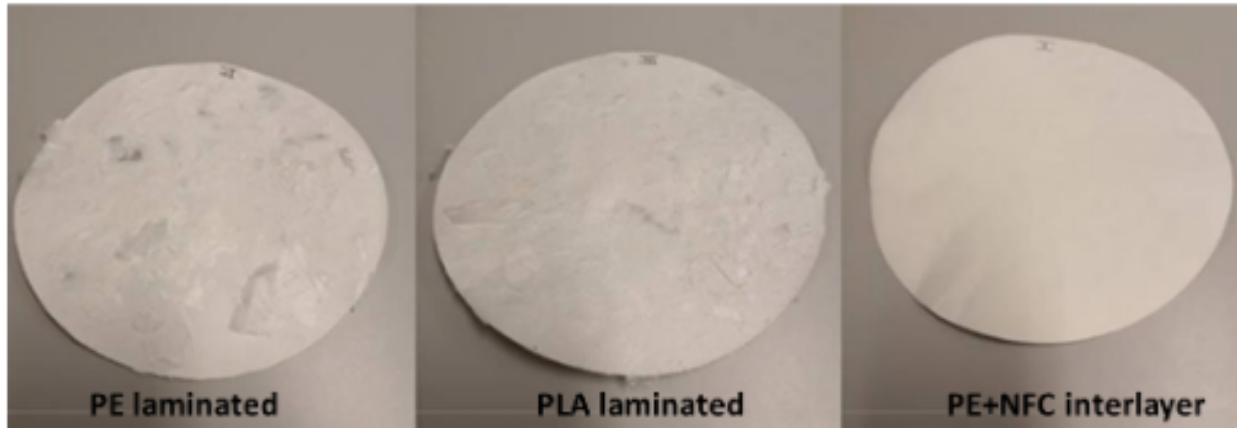
Preliminary testing on the lab-scale recyclability (fiber recovery) of experimental laminated paper coatings of PE/paper and PP/NFC/paper, which were disintegrated by mixing, soaking in water and screening.



- Fiber recovery = weight based calculated from weight change in PE film (with embedded fibers) after drying. Relative measurements different from actual recycling system.
- NFC “release layer” prevents penetration of PE in the paper structure. The release layer becomes flexible when wet and stiff when dried. Small amount of NFC remains in PE film, while rest recovered together with fiber fraction.

Recyclable materials

Visual and mechanical evaluation of handsheets with recycled pulp fibers



- Mechanical reinforcement effect of residual NFC fibers in recycled pulp comparable to reference testing with NFC as bulk reinforcement
- Further issues:
 - dewatering, accumulation of NFC, ...
 - reduced adhesive strength between PE-coating and NFC layer (eventually corona treatment, cationic starch additives/precoat)

Orientations



REDUCE



Social responsibility
Change of the
consumption habits

REUSE



Refill and Reuse

RECYCLE



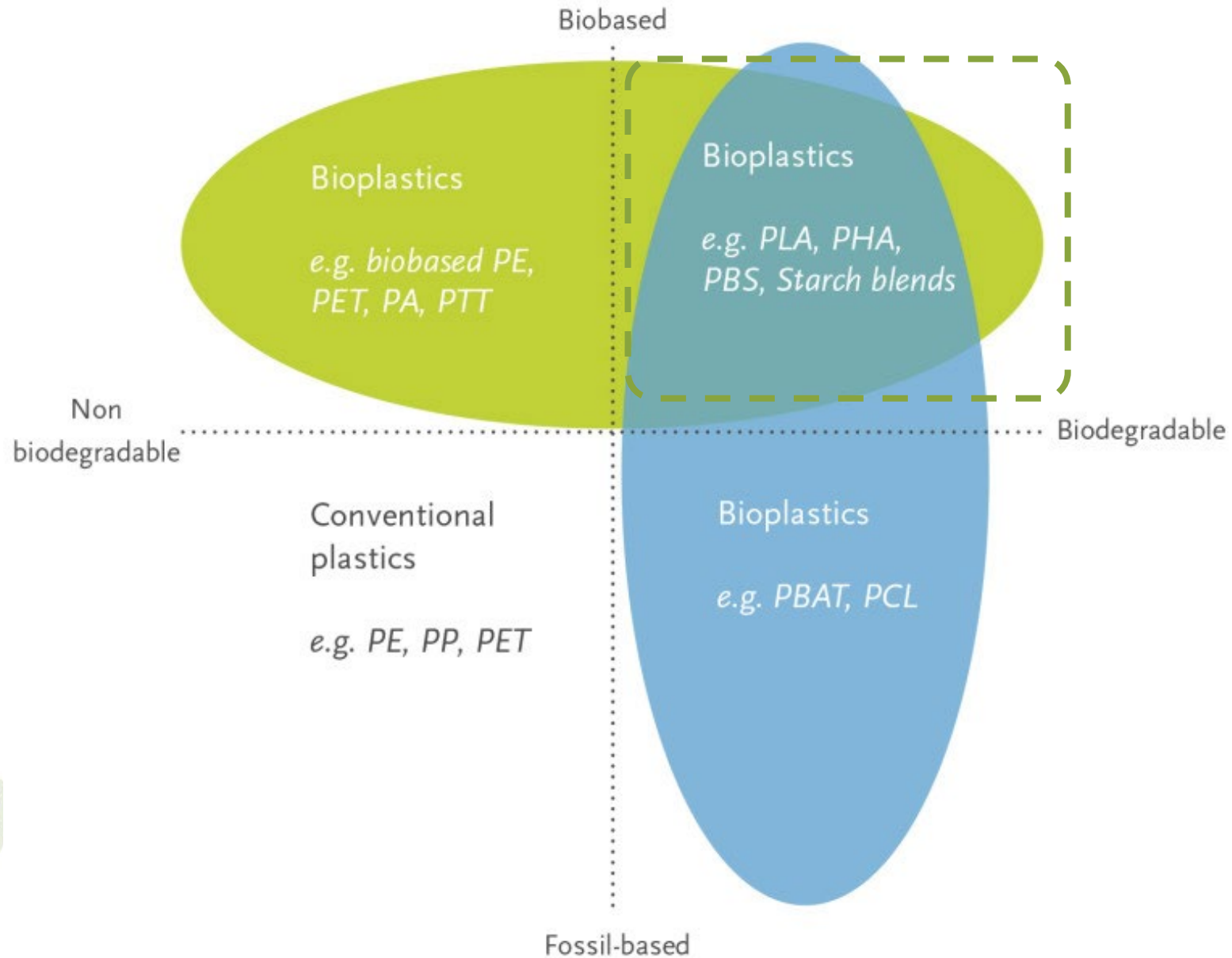
Recyclability for a better
feedstock management

BIODEGRADABLE & BIODEGRADABLE

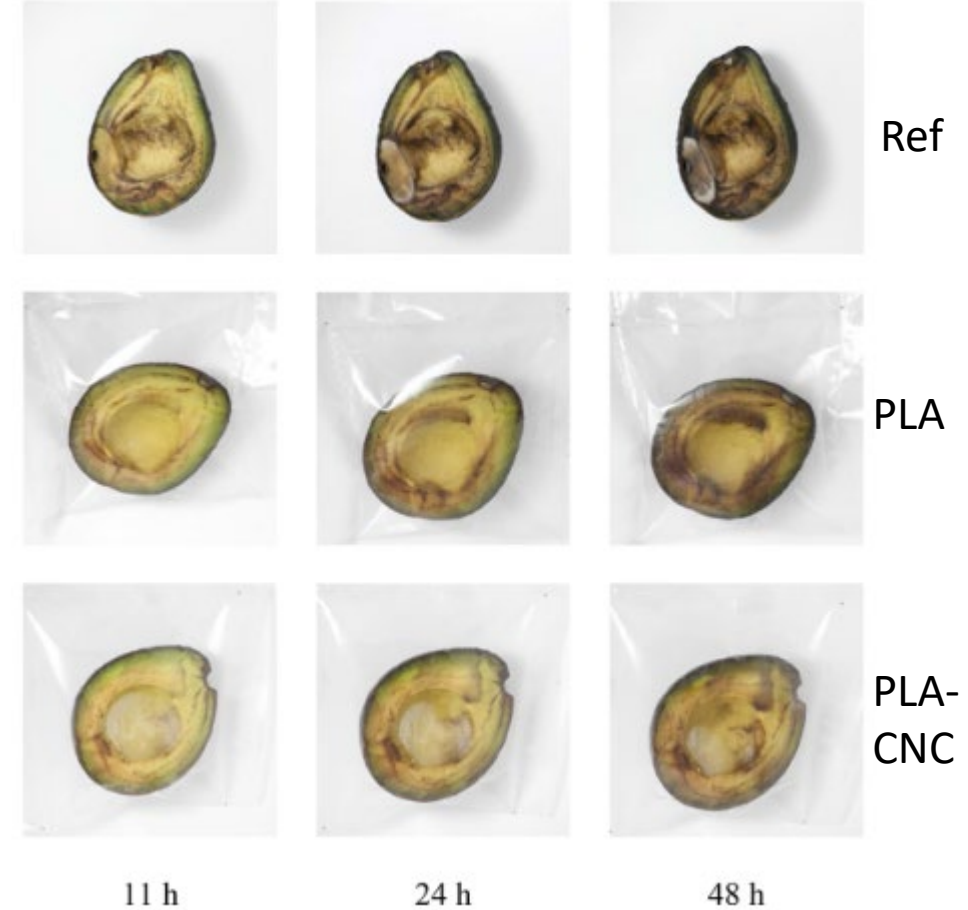
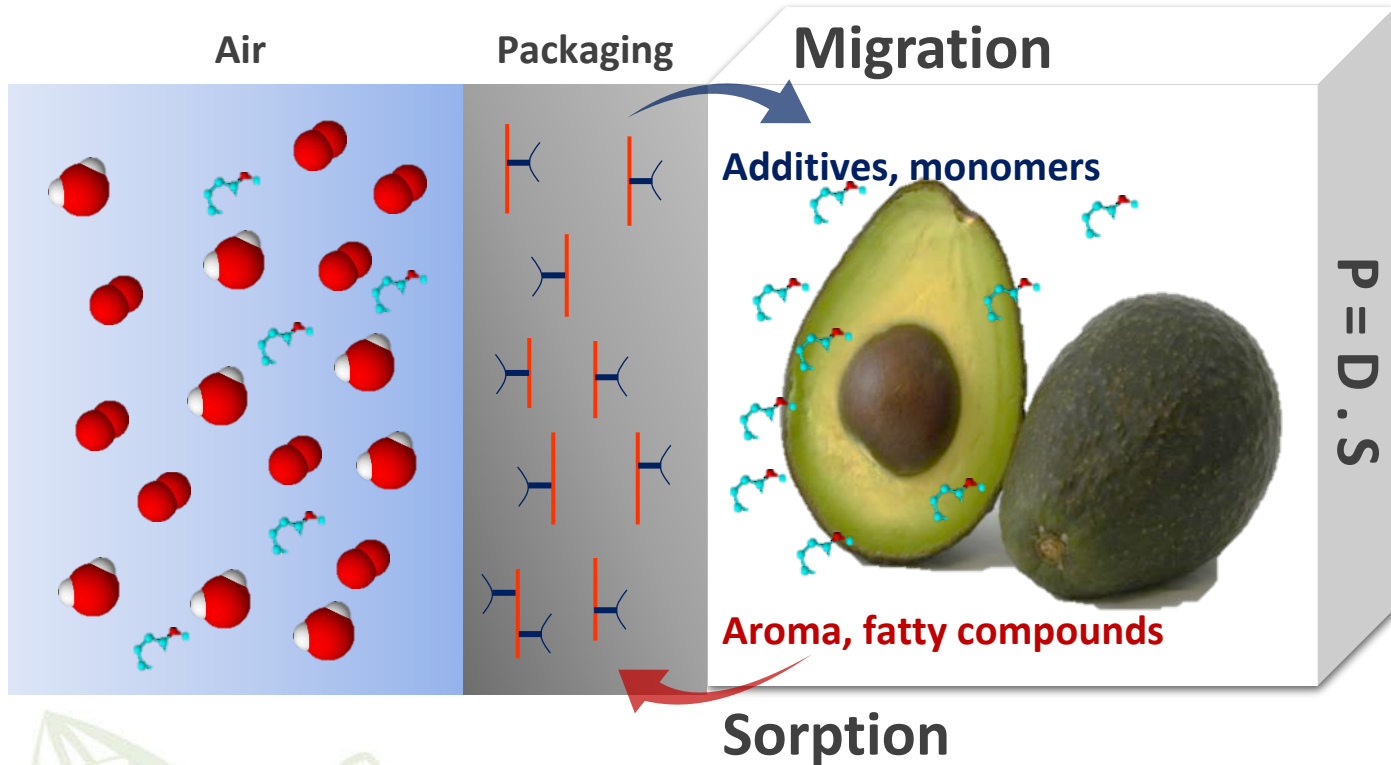


Biodegradability to limit the
impact of leakage in
nature

BioPlastics



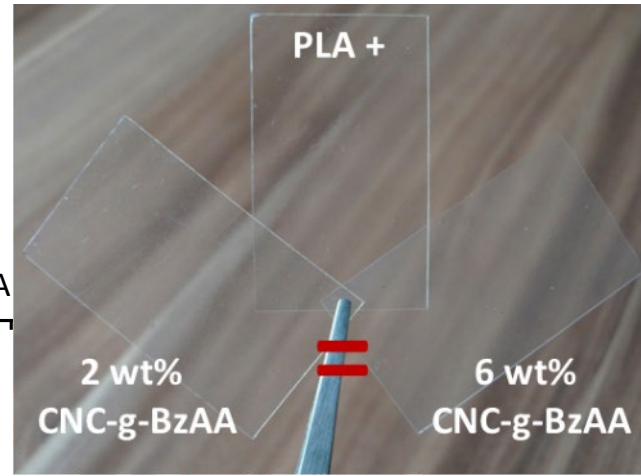
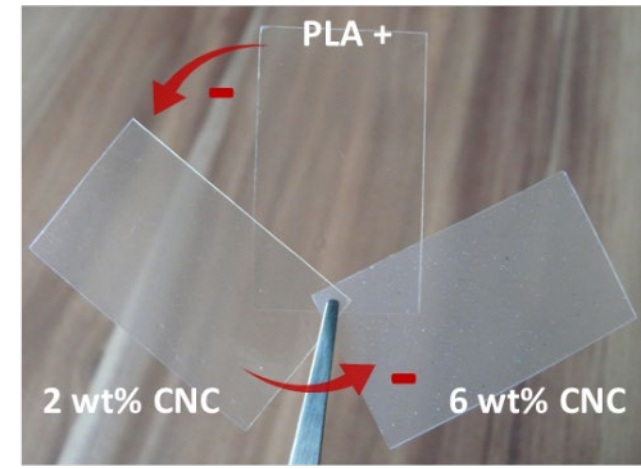
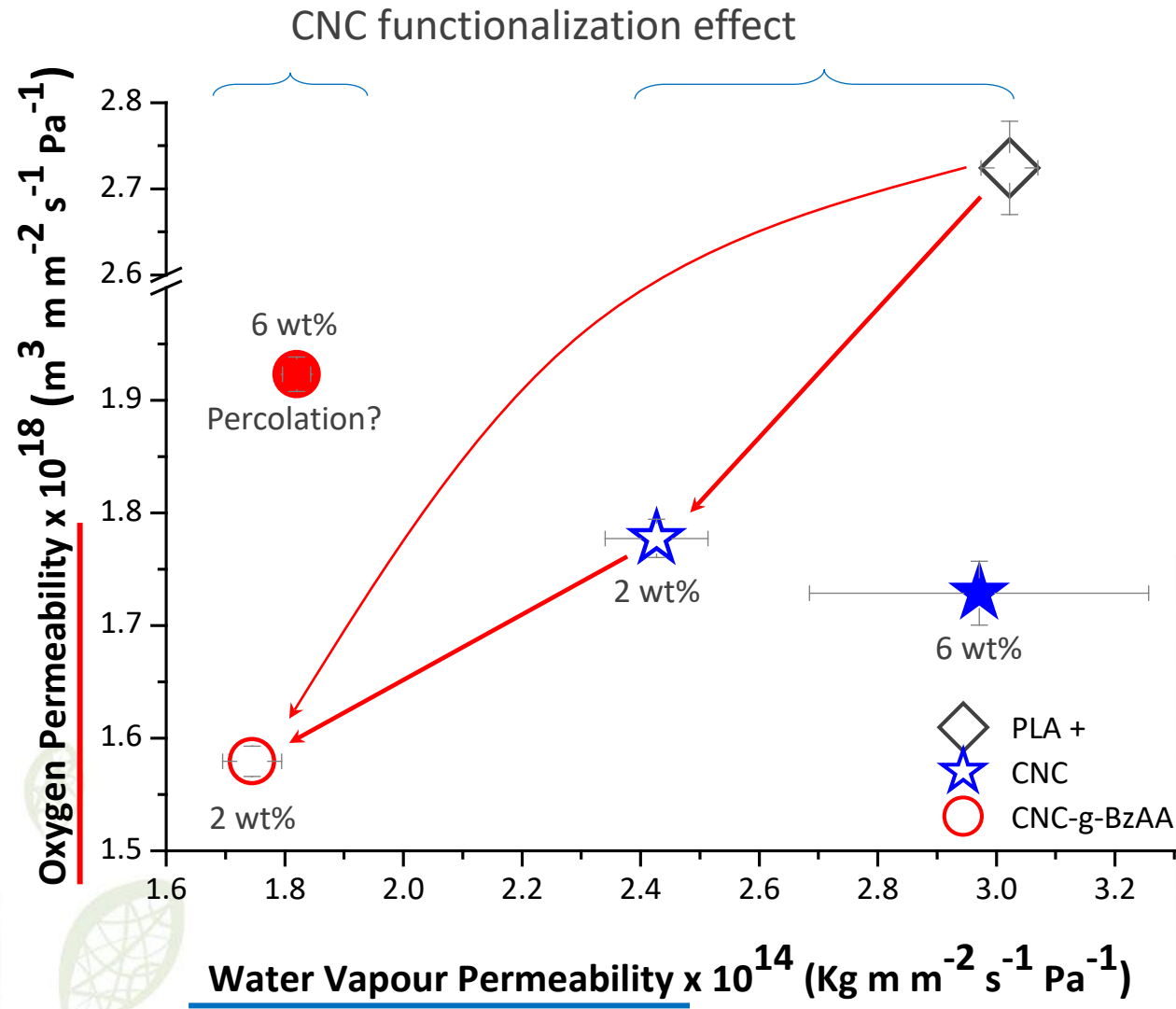
Barrier of biocomposites



Develop materials with **functional barriers** by the inclusion of **biobased nanoadsorbents (CNC)** in a polymer matrix

Wongthanaroj, et al, Sustainable and eco-friendly poly (Lactic acid)/cellulose nanocrystal nanocomposite films for the preservation of oxygen-sensitive food, Applied Food Research, Vol 2, 2022, 100222,

Barrier of biocomposites



Barrier of biocomposites



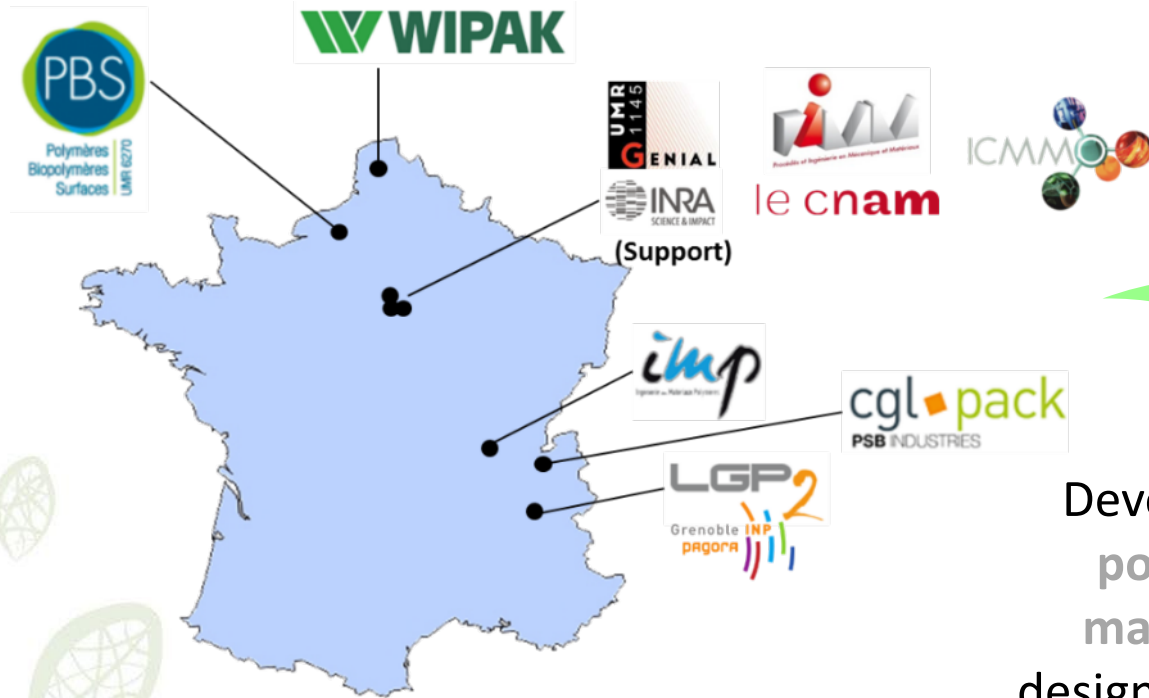
An ANR Project

GASP

Biobased High Gas and Vapor Barrier Polymers for Packaging

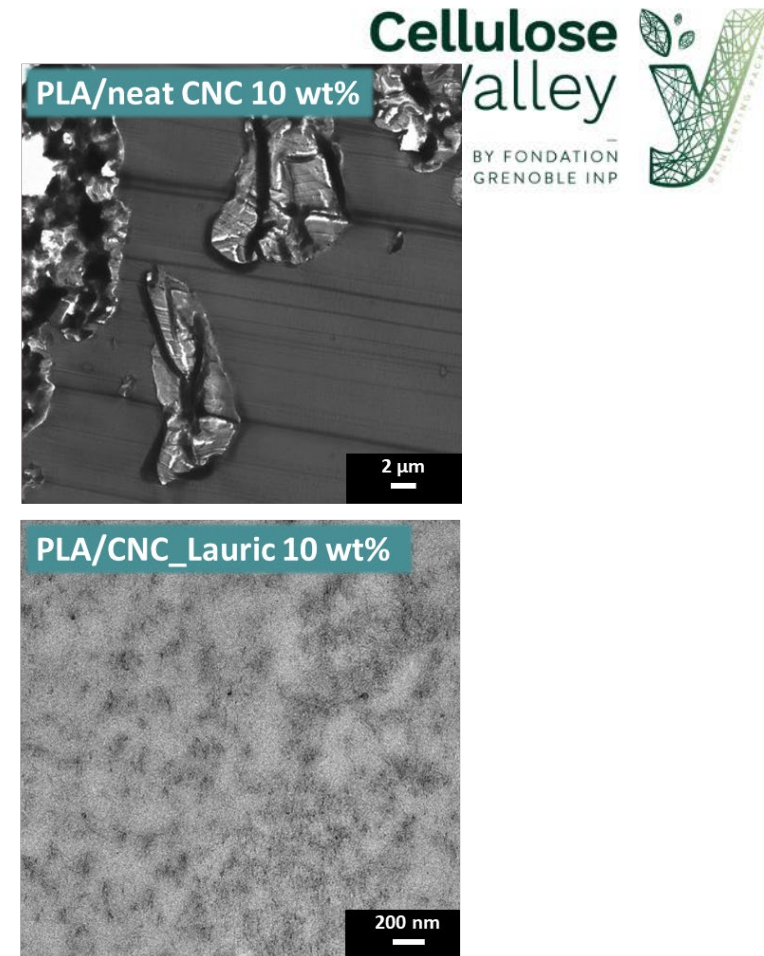
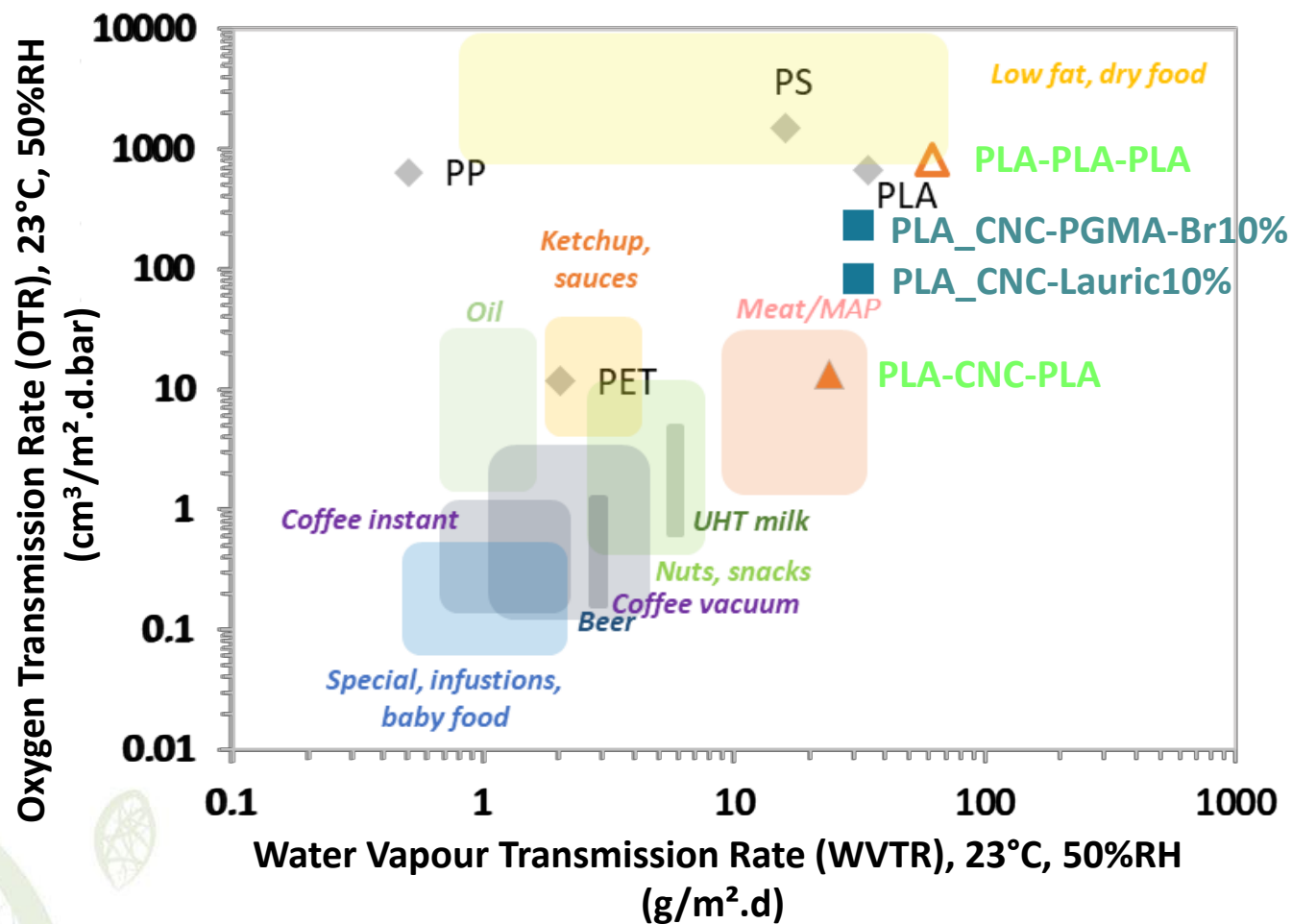
Total budget : 2 635 082 €

Duration : 48 months (2016-2021)



Development of 100% biobased polylactide nanocomposites materials including **CNCs** with designed barrier properties for food packaging applications

Barrier of biocomposites



1. M Le Gars, **Bras J**, H Salmi-Mani, M Ji, D Dragoë, H Faraj, S Domenek, N; Belgacem, P.Roger, Polymerization of glycidyl methacrylate from the surface of cellulose nanocrystals for the elaboration of PLA-based nanocomposites, Carbohydrate Polymers (2020) 234, 115899 2
2. M Le Gars, A Delvart, P Roger, MN Belgacem, **Bras J**, Amidation of TEMPO-oxidized cellulose nanocrystals using aromatic aminated molecules, Colloid and Polymer Science (2020), 1-15 2
3. M Le Gars, B Dhuiège, A Delvart, MN Belgacem, K Missoum, **Bras J**, High-Barrier and Antioxidant Poly (lactic acid)/Nanocellulose Multilayered Materials for Packaging, ACS omega (2020) 5 (36), 22816-22826
4. H Faraj, C Sollogoub, A Guinault, M Gervais, Bras J, H Salmi-Mani, P Roger, M Le Gars, S Domenek, A comparative study of the thermo-mechanical properties of polylactide/cellulose nanocrystal nanocomposites obtained by two surface compatibilization strategies, Materials Today Communications, (2021), 102907

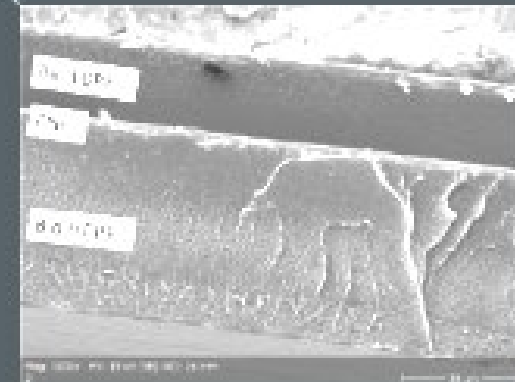
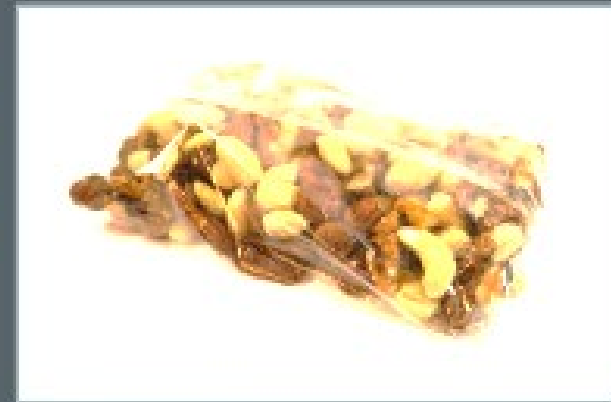
Bioplastic and multilayer approach



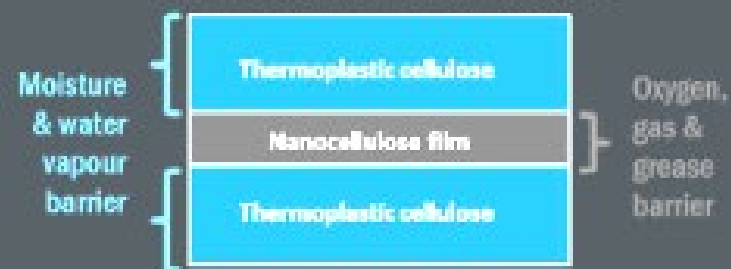
Bio-based stand-up pouch (SUP)



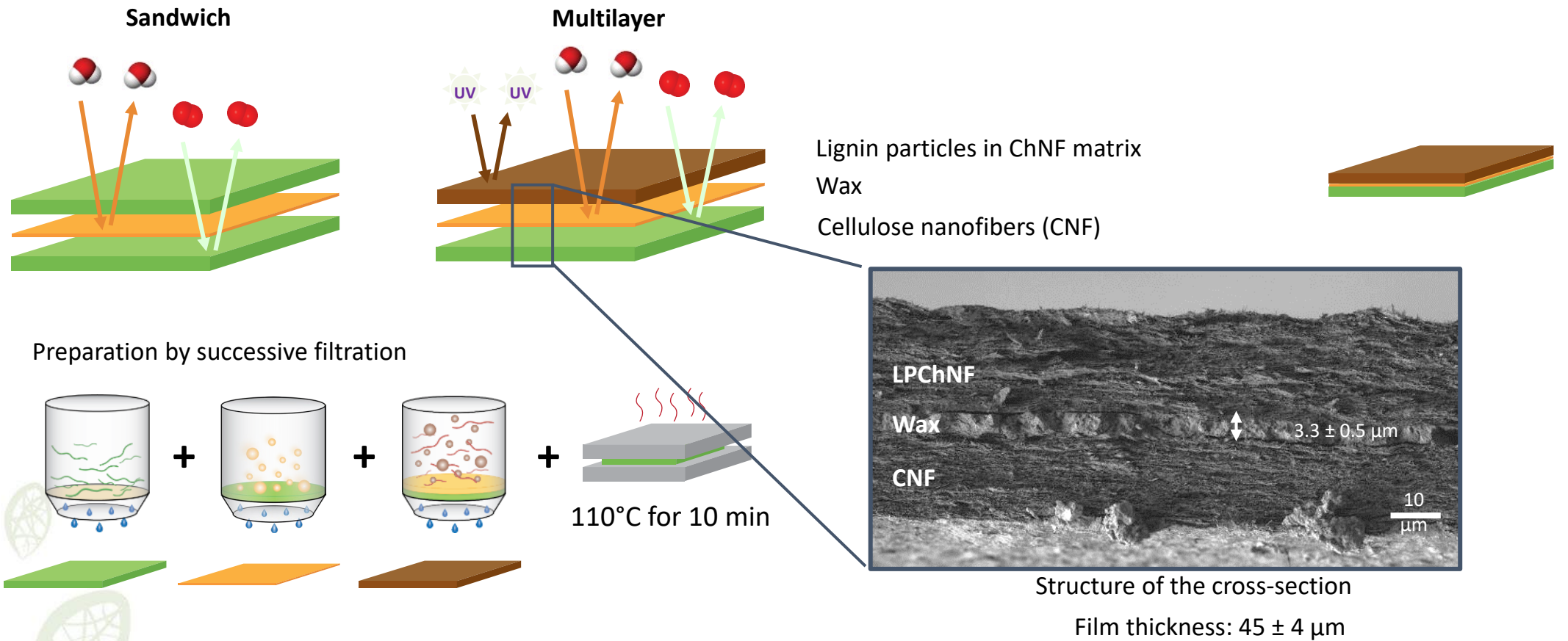
BIO-BASED BARRIER SOLUTION FOR SUSTAINABLE PACKAGING



3 LAYER BARRIER FILM STRUCTURE

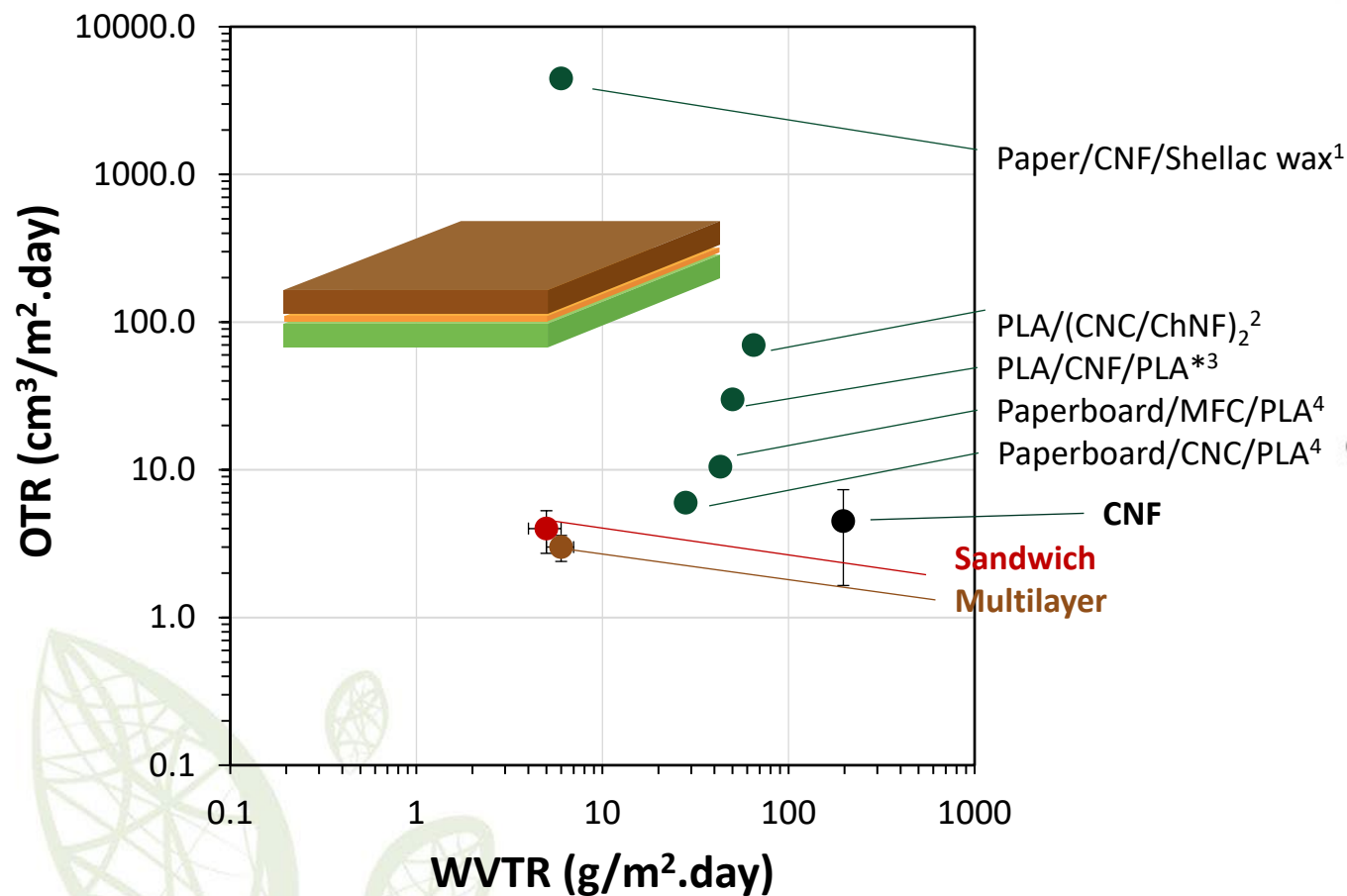


Bioplastic and multilayer approach

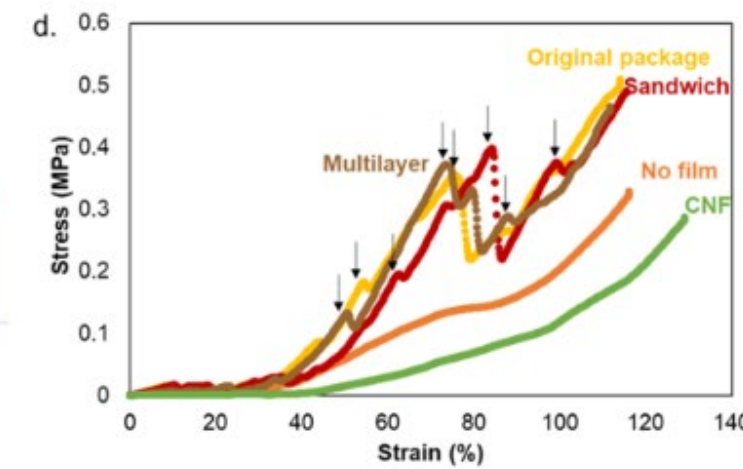
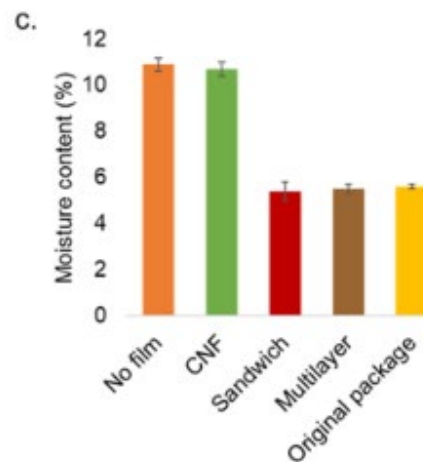
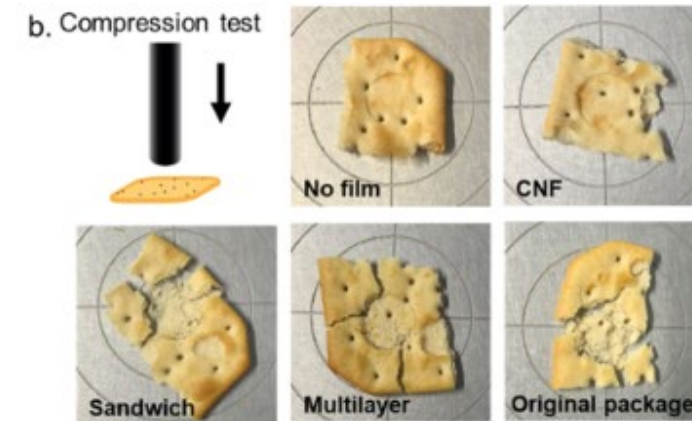
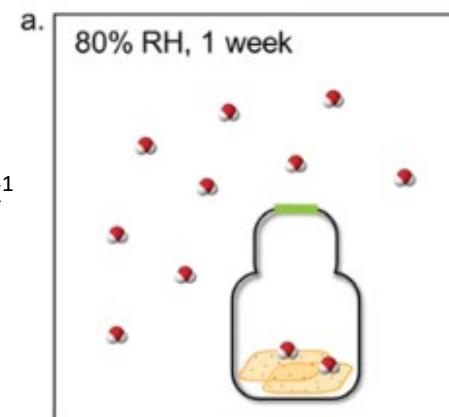


Bioplastic and multilayer approach

Comparison with biobased multilayers in literature
(23°C, 50% RH)

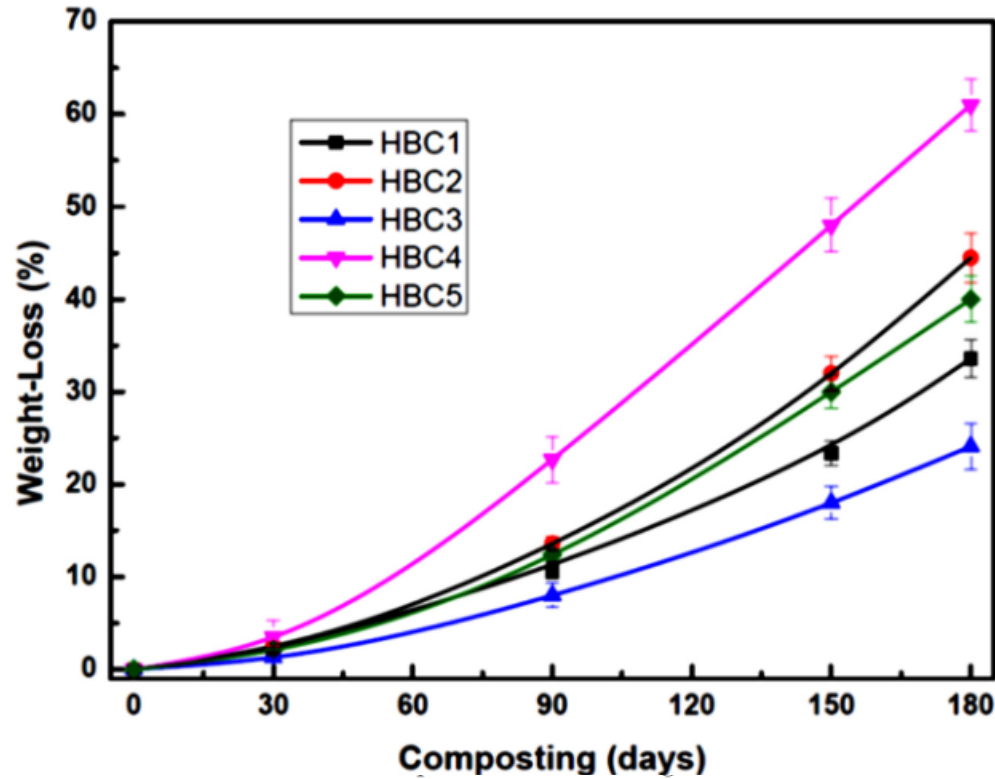


*OTR measured at 0% RH

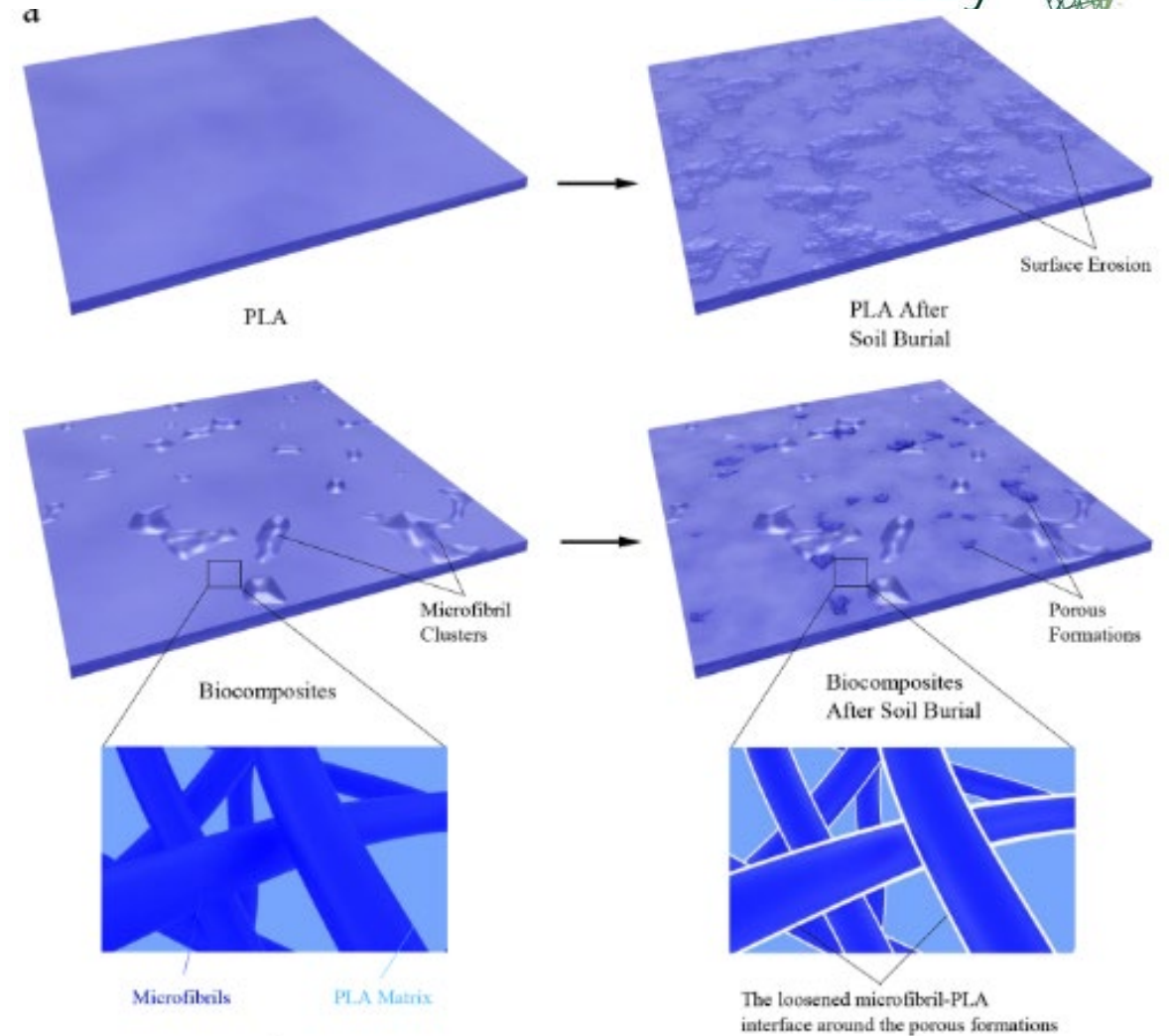


E Pasquier, BD Mattos, H Koivula, A Khakalo, MN Belgacem, OJ Rojas, J. Bras, ACS Appl. Mater. Interfaces 2022, 14, 26, 30236–30245

Impact on biodegradability



	PLA (wt.%)	MFC (wt.%)	CNC (wt.%)
HBC1	100	0	0
HBC2	80	20	0
HBC3	95	0	5
HBC4	75	20	5
HBC5 (central point)	87.5	10	2.5



Galera Manzano, L.M et al Effect of Cellulose and Cellulose Nanocrystal Contents on the Biodegradation, under Composting Conditions, of Hierarchical PLA Biocomposites. *Polymers* 2021, 13, 1855.

Yetiş, F., Liu, X., Sampson, W.W. et al. Biodegradation of Composites of Polylactic Acid and Microfibrillated Lignocellulose. *J Polym Environ* 31, 698–708 (2023).

Orientations



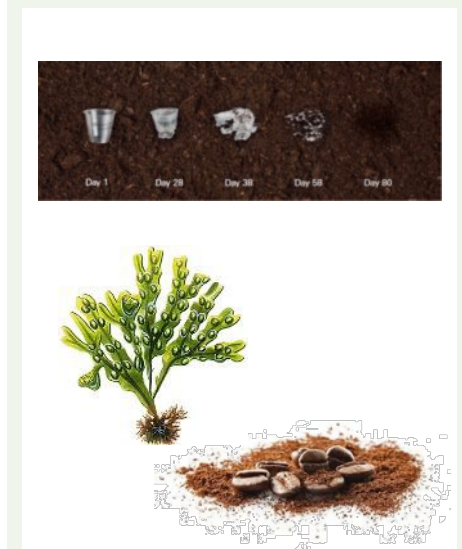
REDUCE

REUSE

RECYCLE

BIOBASED & BIODEGRADABLE

Fibre & Paper Based Materials



Social responsibility
Change of the consumption habits

Refill and Reuse

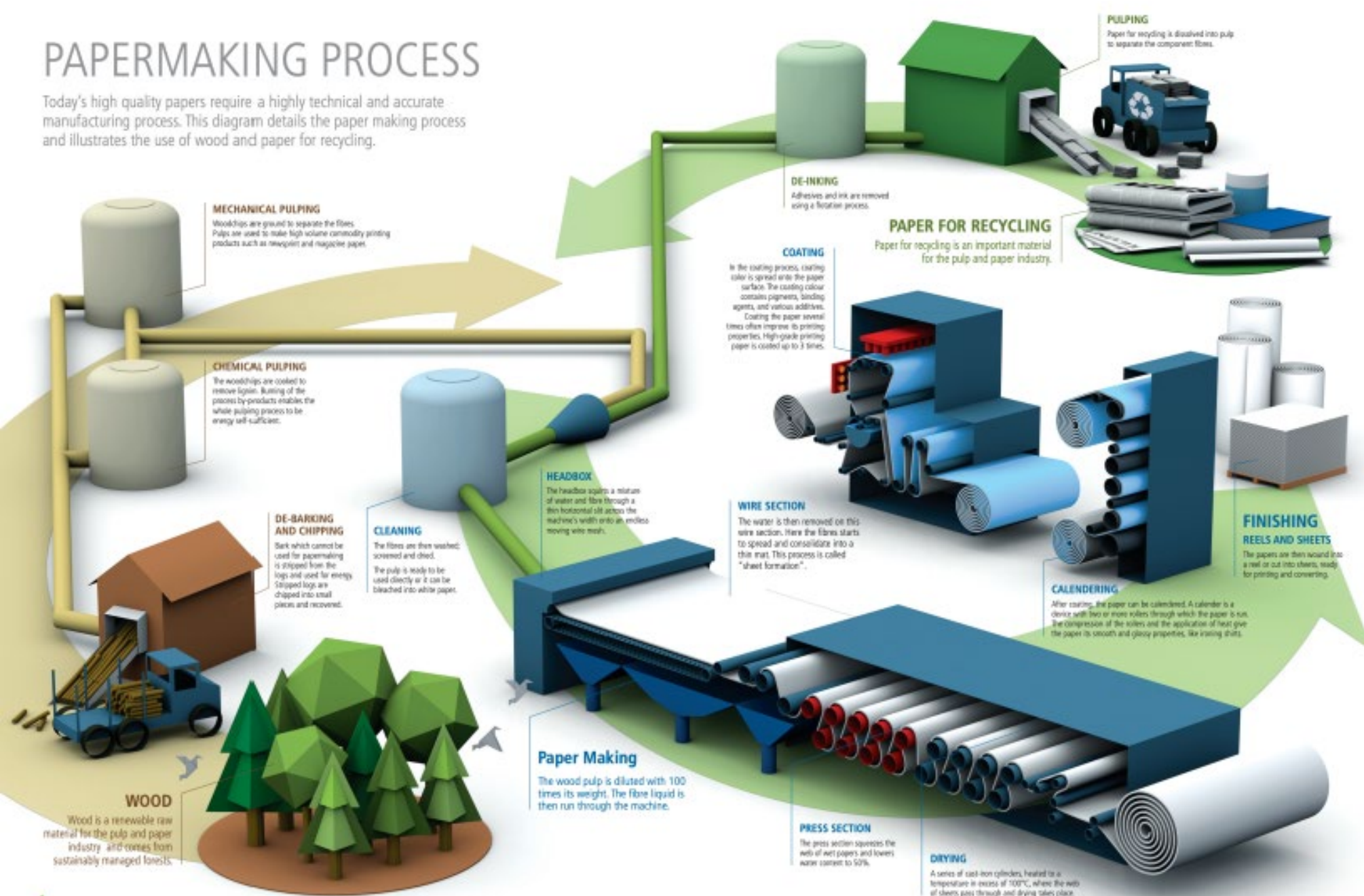
Recyclability for a better feedstock management

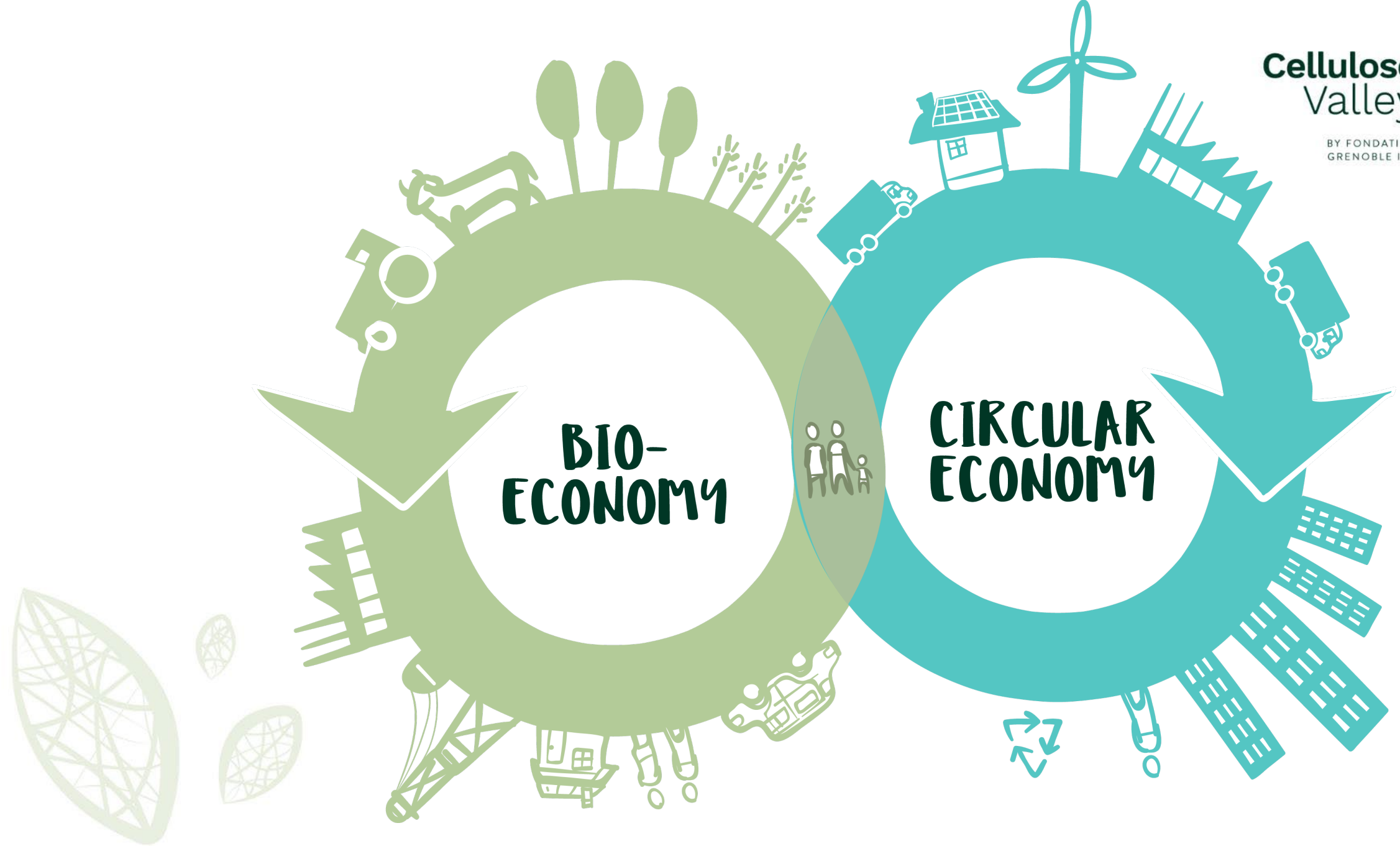
Biodegradability to limit the impact of leakage in nature

Biosourced & Renewable
Recyclable
Biodegradable

PAPERMAKING PROCESS

Today's high quality papers require a highly technical and accurate manufacturing process. This diagram details the paper making process and illustrates the use of wood and paper for recycling.





Towards paperization

ACCESSORIES



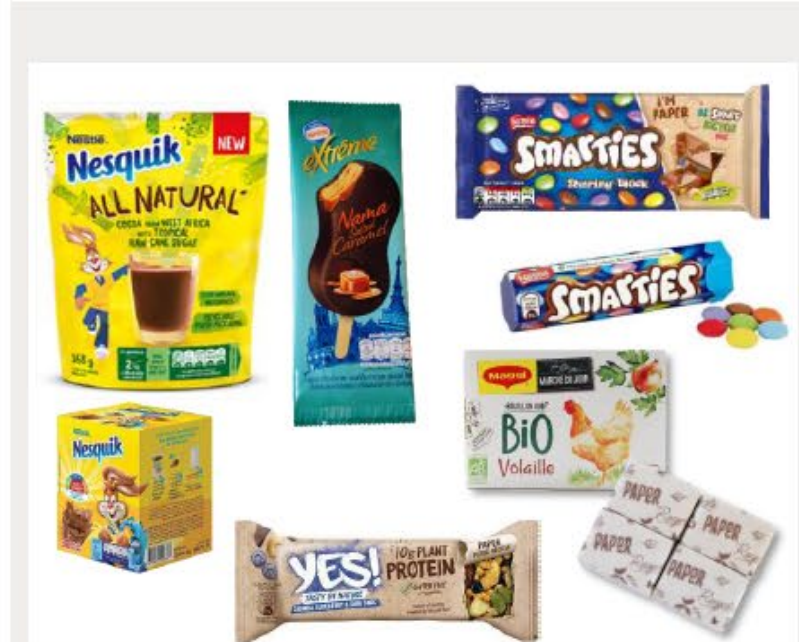
- Paper straws
- Paper cups

SECONDARY PACKAGING



- Re-groupment pouches
- Boxes or envelopes

PRIMARY PACKAGING

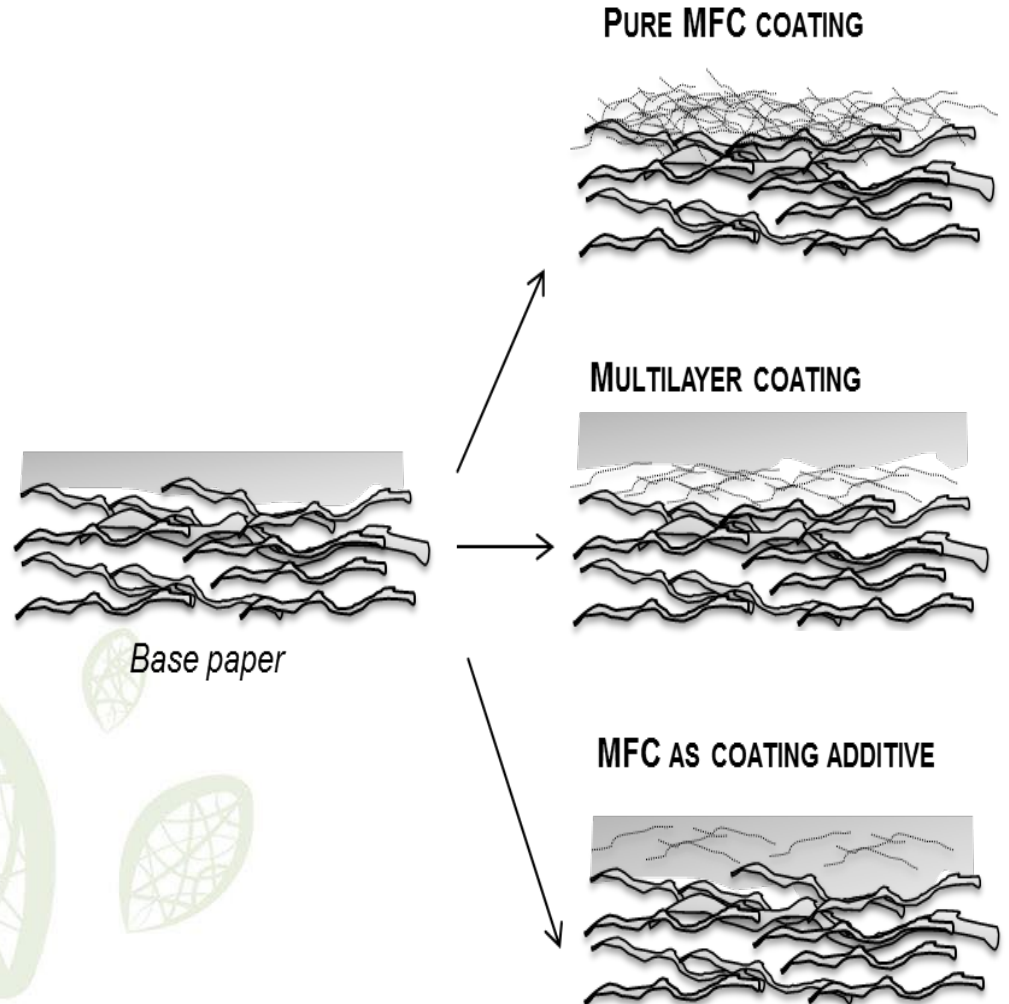


- Beverage powder pouches
- Chocolate flow-packs
- Ice cream wrappers
- Bouillon cube wrappers

Classic strategies

STRATEGIES

APPLICATIONS TARGETED



- **(I) BARRIER PROPERTIES**

Air, Oxygen, Grease, Water vapor, ...

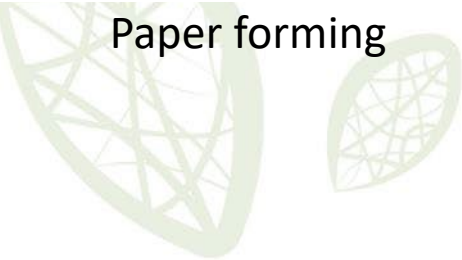
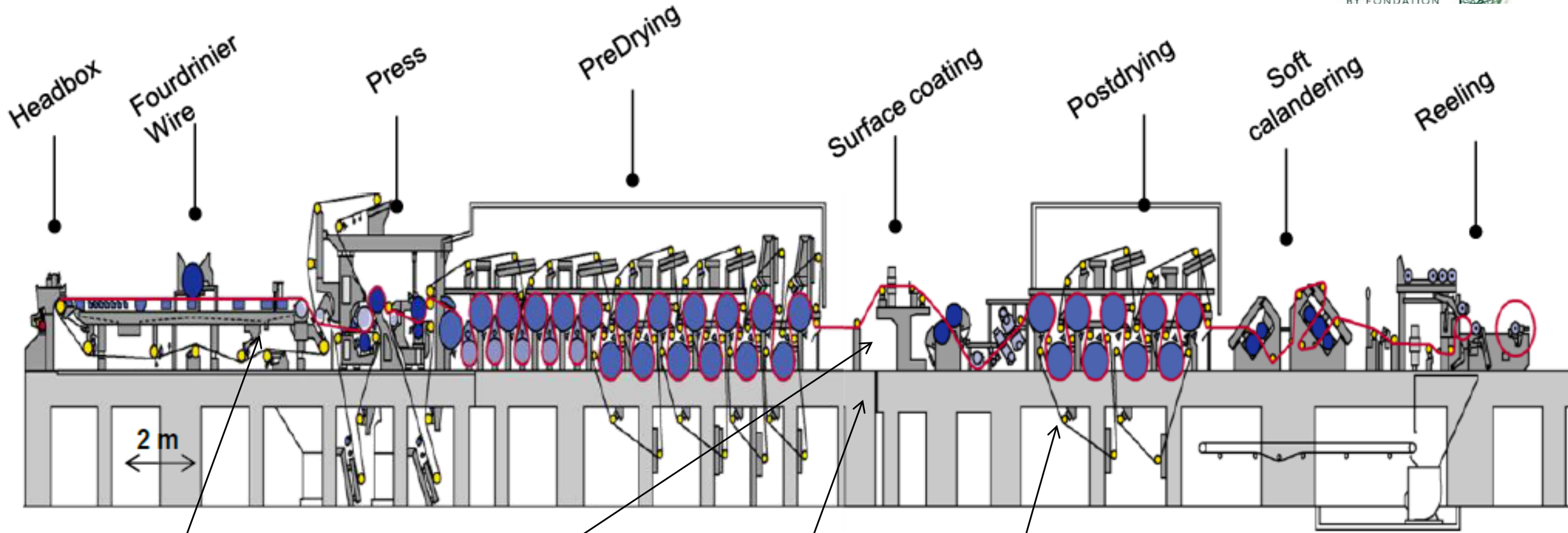
- **(II) PRINTING PROPERTIES**

Flexography, offset, inkjet

- **(III) FUNCTIONAL PROPERTIES**

Antimicrobial, hydrophobic paper, conductive paper

Classic strategies



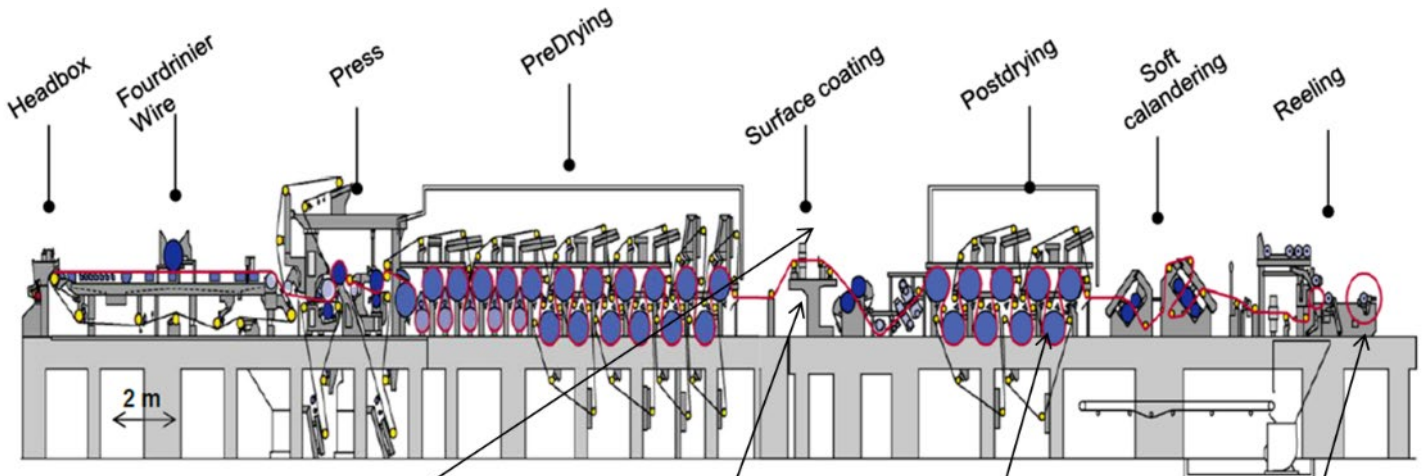
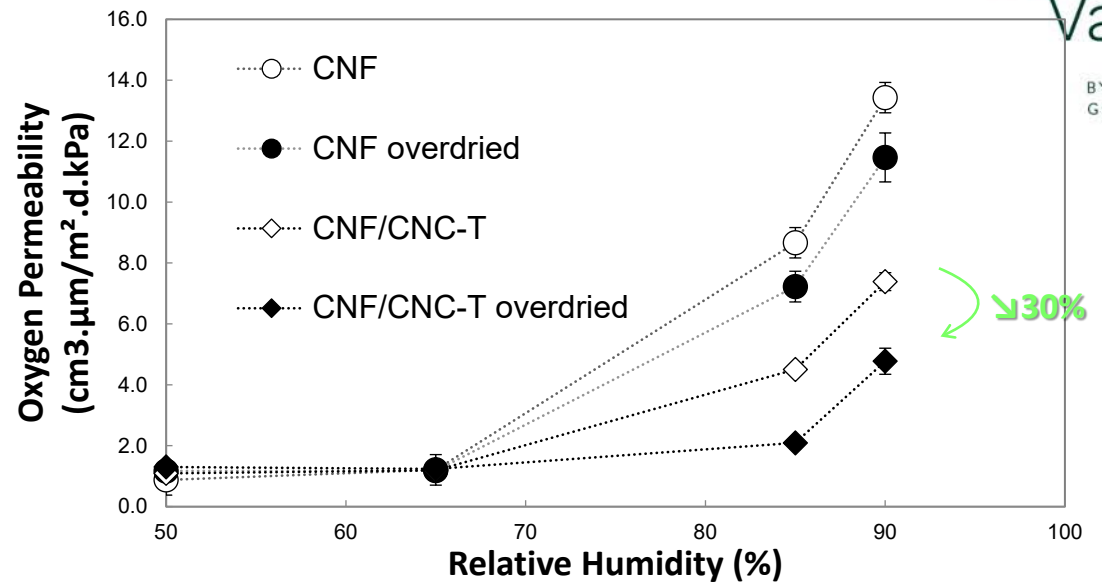
Coating Formula & rheology process

Coating process

Drying

Classic strategies

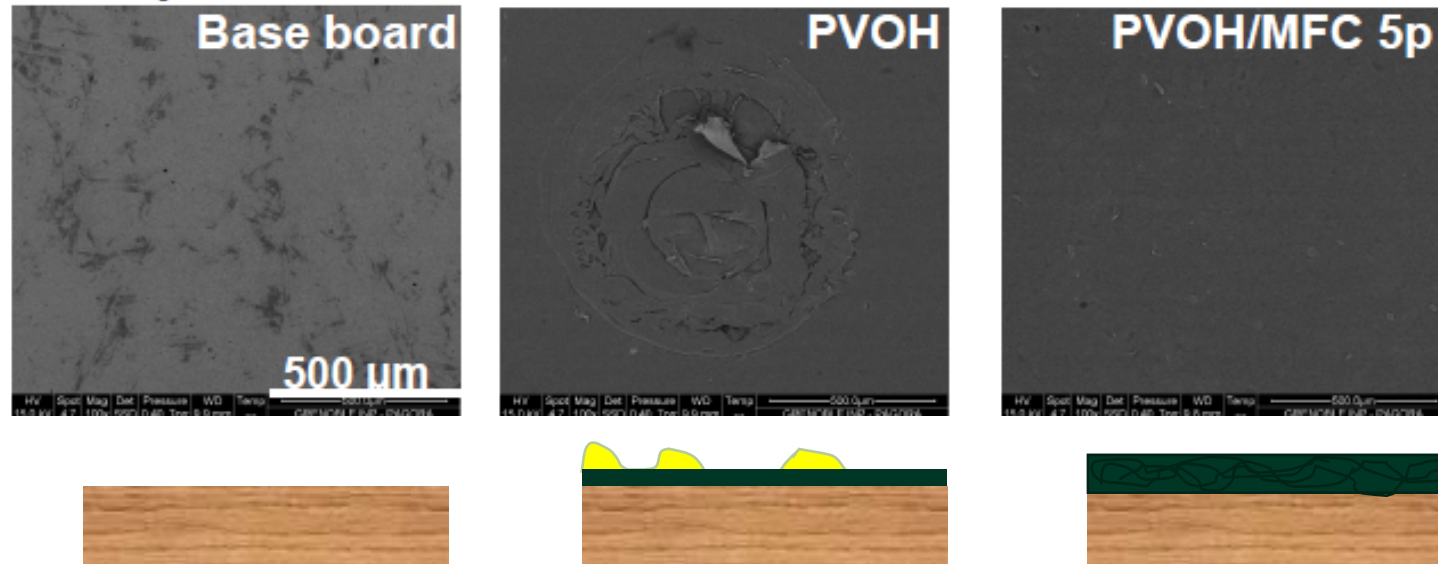
Bardet, Reverdy, Belgacem, Leirset, Syverud, Bras, J (2015)
Cellulose, 22(2), 1227-1241



Coating Formula & rheology process Coating process **Drying** Properties

Classic strategies

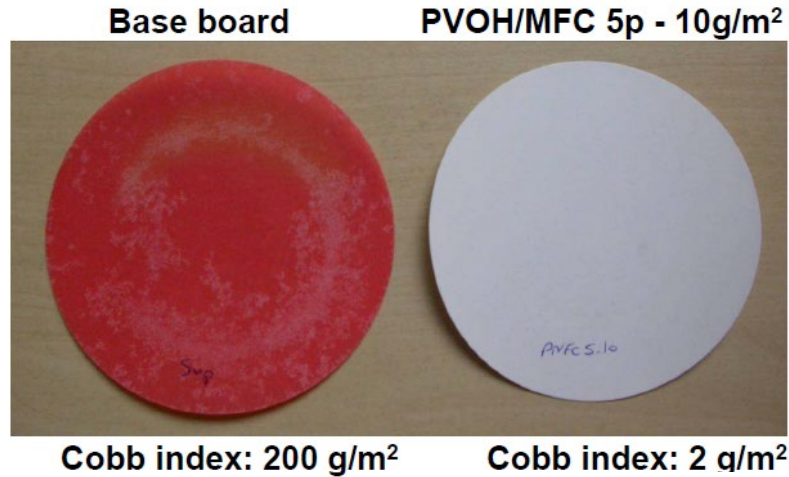
- **Drying behaviour**
 - Drying strategy very hard to monitor with PVOH:
 - ✓ Blistering
 - Improvement of the layer drying with PVOH/MFC
 - ✓ Blistering reduction
- **SEM pictures**



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

Classic strategies

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

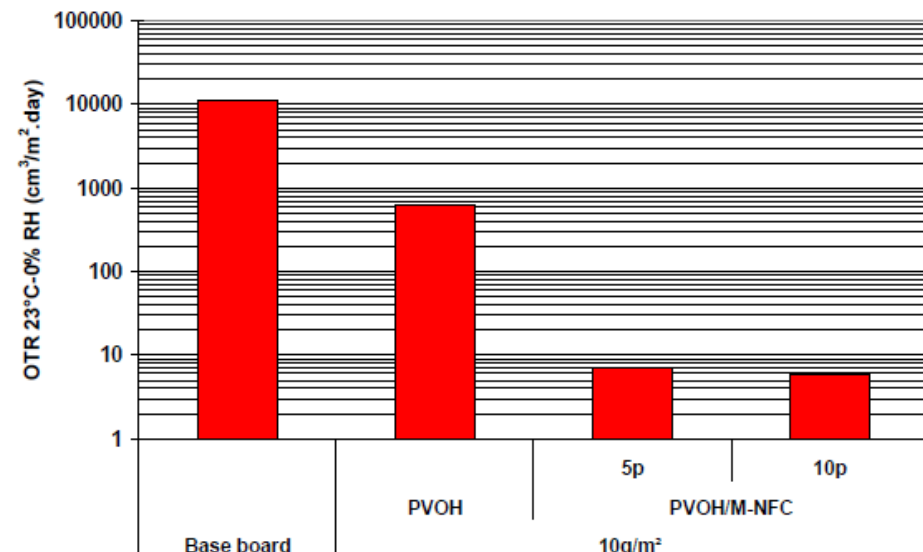


- Oxygen transmission rate 23°C-0% RH

From lab to industry:
Pakocell project (3 years projects 2015-2018)

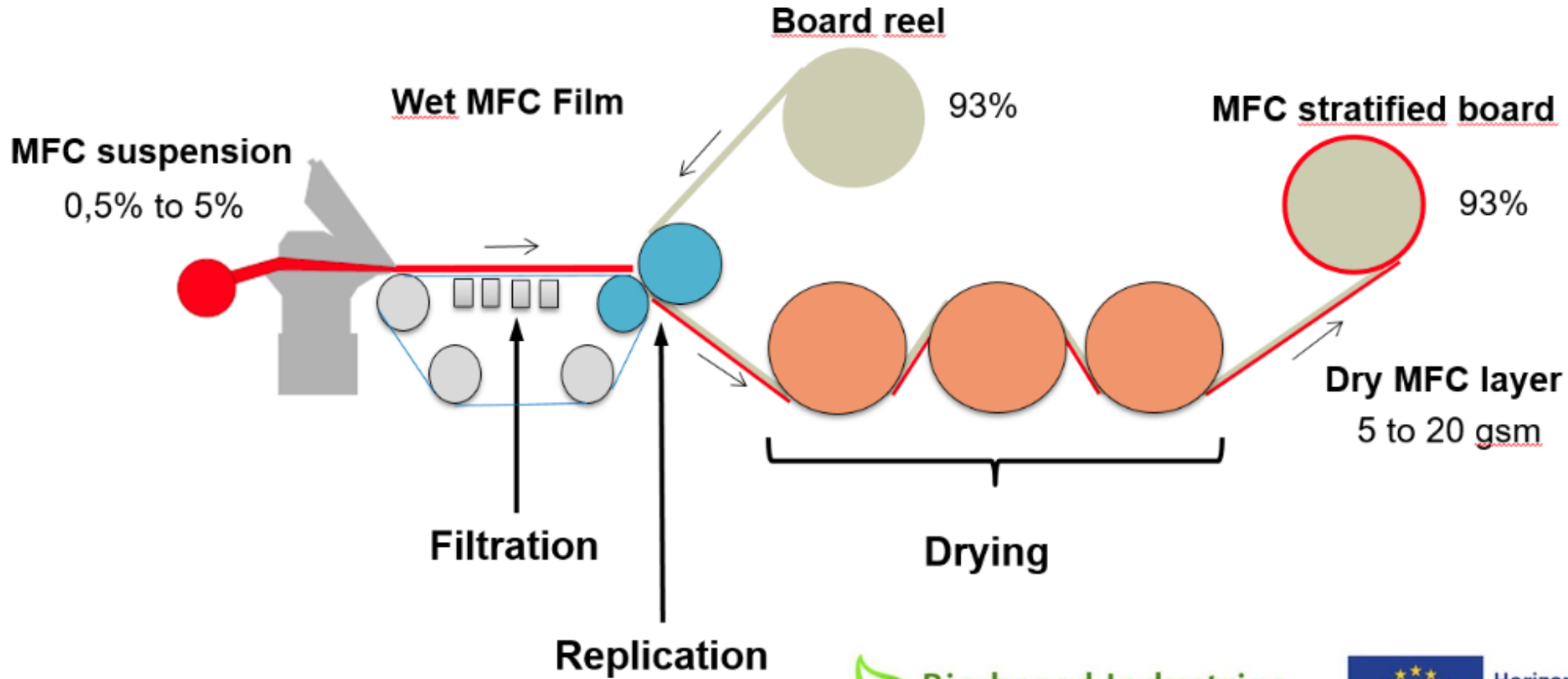


From lab to industry:
PaCow project (2 years projects 2021-2023)

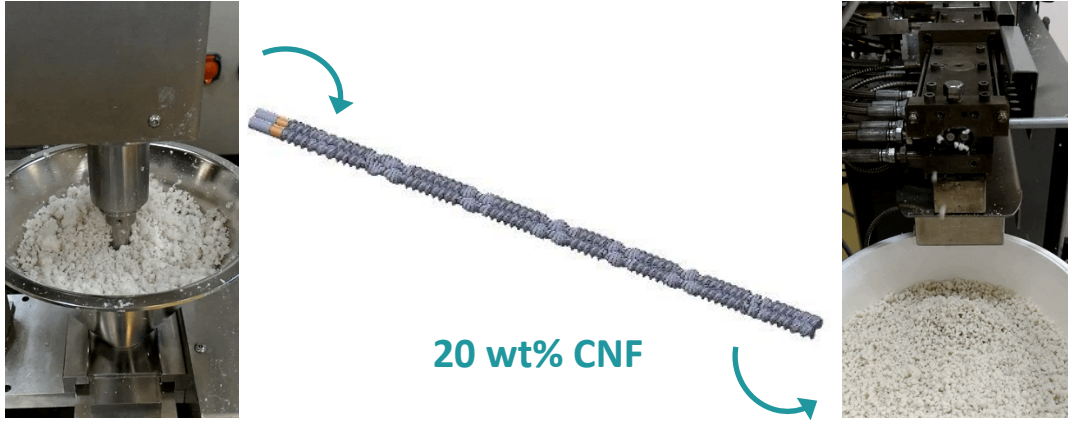


New strategies

Process developments to obtain 100% cellulosic packaging material, barrier, recyclable and compostable



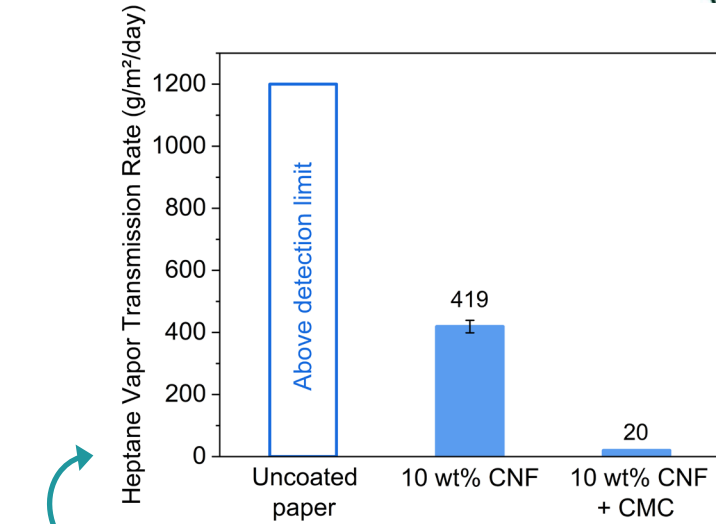
New strategies



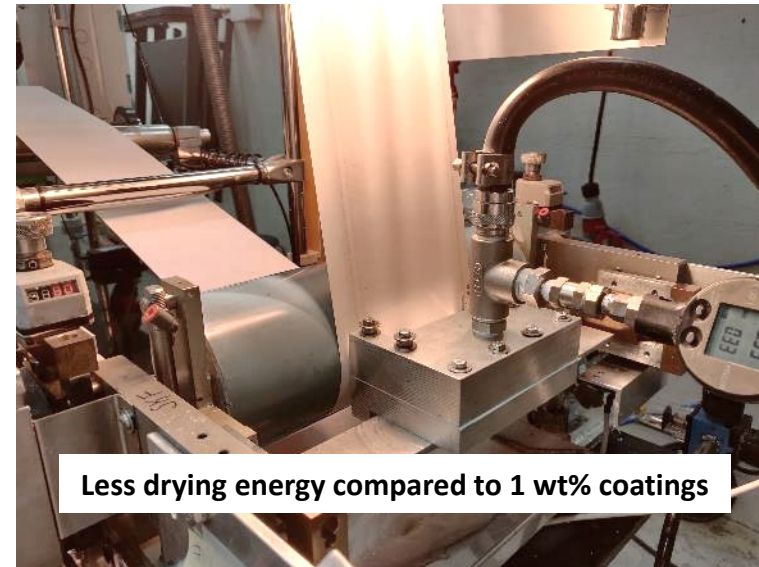
Roll-to-roll slot-die coater



Åbo Akademi
University
M. Toivaka,
R. Koppulu



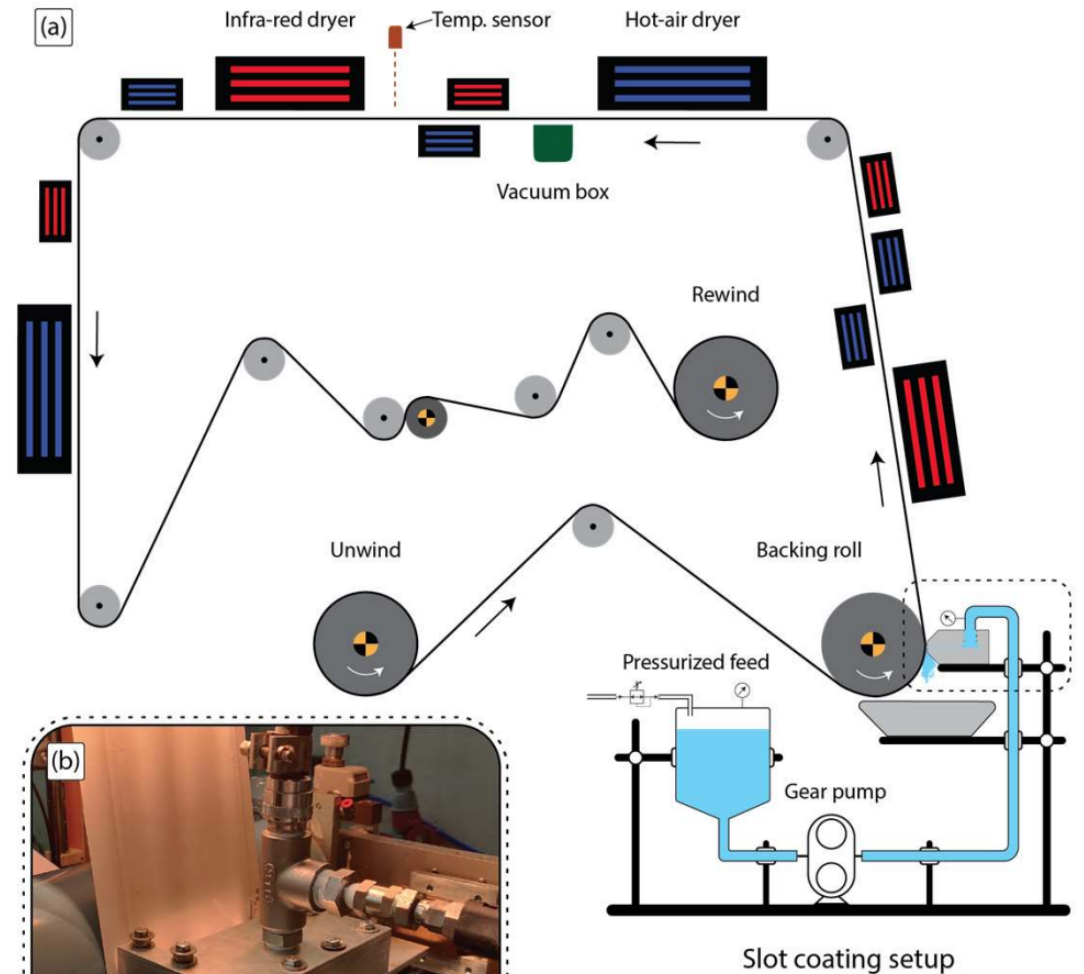
10 wt% CNF coating, with/without CMC



New strategies

Roll-to-roll coating

- Mini-pilot scale custom built setup based on RK Koater
- 300 mm max. web width, 50 m/min max. line speed
- Custom fitting of slot die (length: 50 mm, coating width: 100 mm, slot gap: 1000 μm)
- Adjustable gap between substrate and slot-lip for coat weight control
- ECNF coating:
 - Base substrate - Pigment coated paperboard (205 g/m², 270 μm)
 - Solids content – 12.5%
 - Three suspensions - ECNF, E5C, E5P (10% glycerol added as plasticizer to all suspensions)
 - Coating width – 100 mm
 - Wet thickness – 200 μm
 - Line speed – 4 min/min



Barrier properties

Suspension	Coating thickness (μm)	Coat weight* (g/m^2)	HVTR ($\text{g}/\text{m}^2\cdot\text{day}$)	KIT	Grease penetration** (hrs.)
ECNF	13.9 ± 3.1	21.5 ± 4.7	504 ± 71	5	< 0.2
+ 5% CMC	15.5 ± 1.7	24.0 ± 2.6	Below detection limit	12	1 - 31
+5% NaPA	19.2 ± 1.6	29.8 ± 2.4	440 ± 52	5	< 0.8
* calculated using SEM cross-section thickness and density of 1.55 g/cc, assuming fully dense nanocellulose layer					
**Three parallel samples. Failure time is given as range (min – max)					

- CMC has better barrier properties compared to NaPA addition or pure ECNF, which suffer from coating defects

HVTR (Heptane vapor transmission rate) measured according to Miettinen P., et al., 27th PTS Coating Symposium, 16-18, (2015)

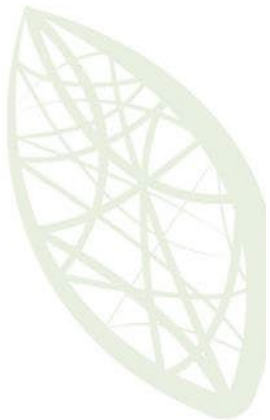
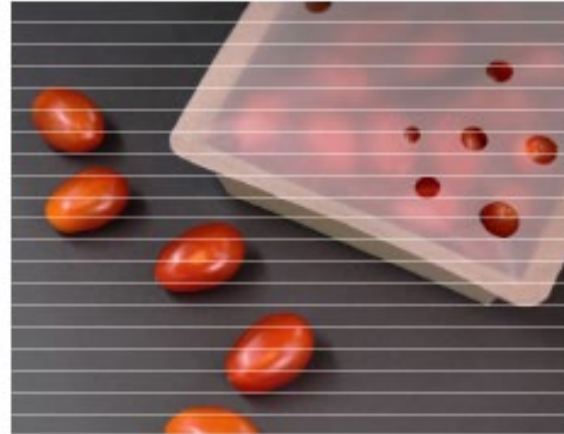
KIT value measured according to TAPPI T559 cm-12

Grease penetration measured according to ASTM F119-82

New strategies

HiCMF demo packages

Well suited for e.g. pouches,
windows and lids.



New strategies

Use atomic Layer deposition with nanocellulose



Revolutionary with only a few nanometers of ceramic ...

Our technology makes it possible to provide a coating of any cellulosic materials (paper, cardboard, moulded fiber).

We are able to process any 2D/3D shape, either stacks, rolls, trays.

www.cilkoa.com

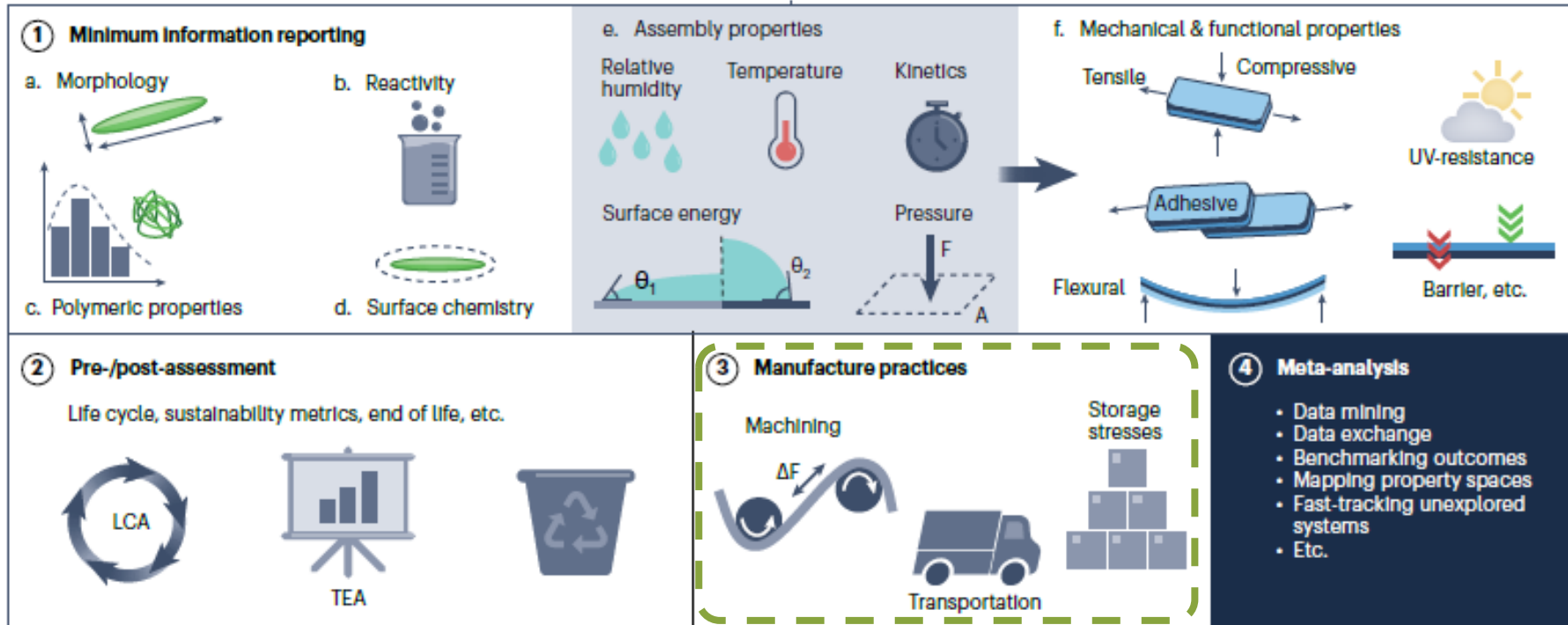
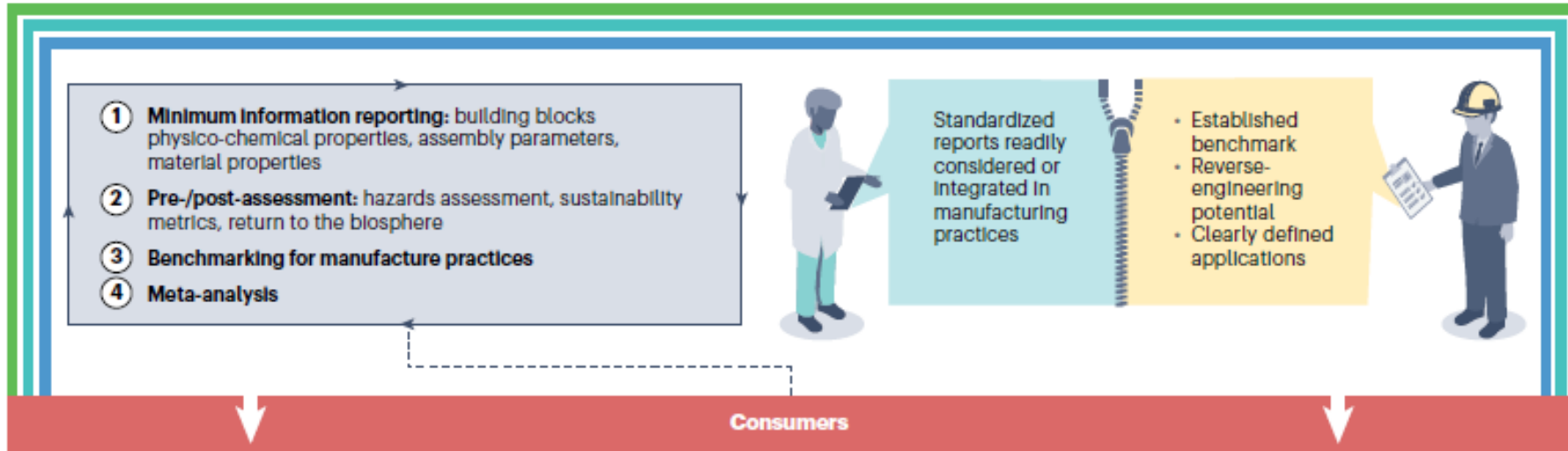
Barrier properties in action

Apple preserved from oxydation

Paper protected from water

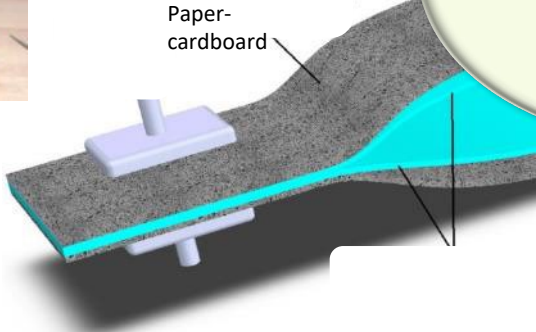
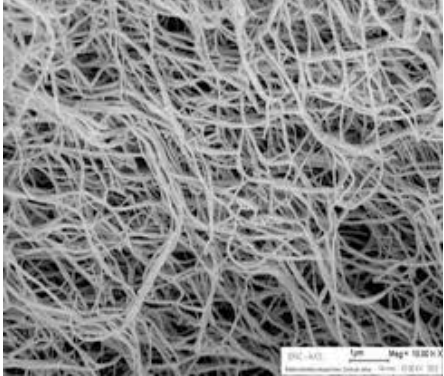
Moisture absorber staying dry





Ultra Sound sealing

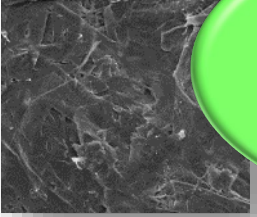
Nanocellulose design for ultrasounds welding



Ultrasounds welding process optimization



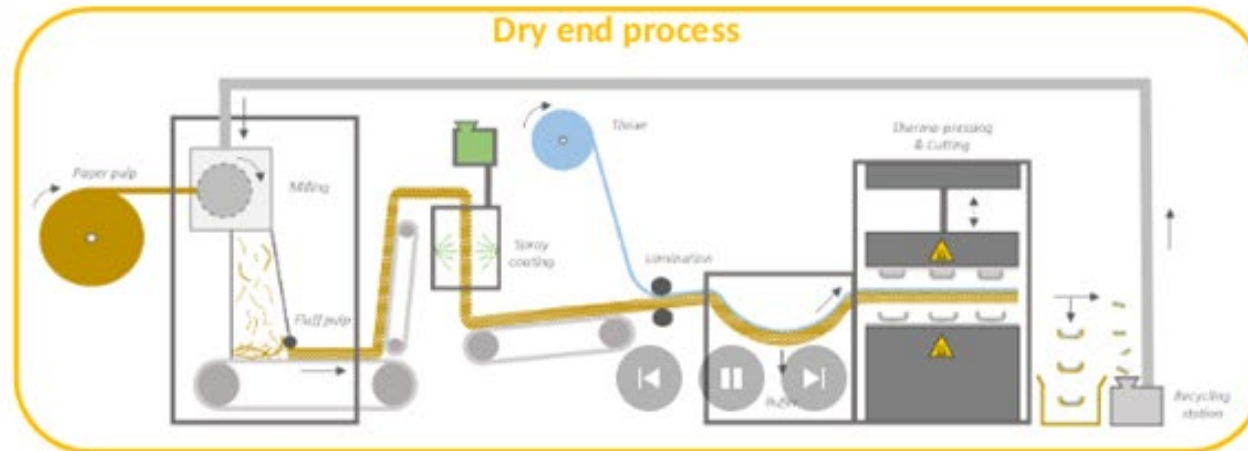
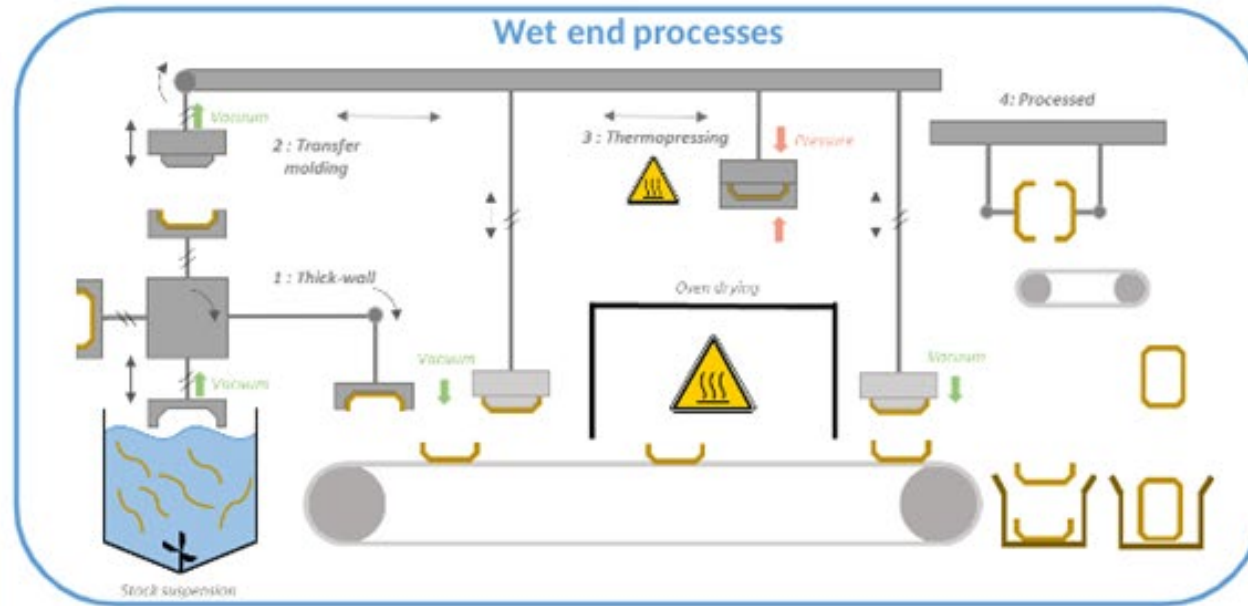
Adhesion understanding



Claire Monot, Jérémie Viguié, Quentin Charlier, Julien Bras, David Guérin, et al.. Ultrasonic welding of folding boxboards. *Bioresources*, 2021, 16 (3), pp.5766-5779.

Bras et al, WO2017207941 (A1) - FIXING METHOD

New 3D cellulose Materials



Orientations



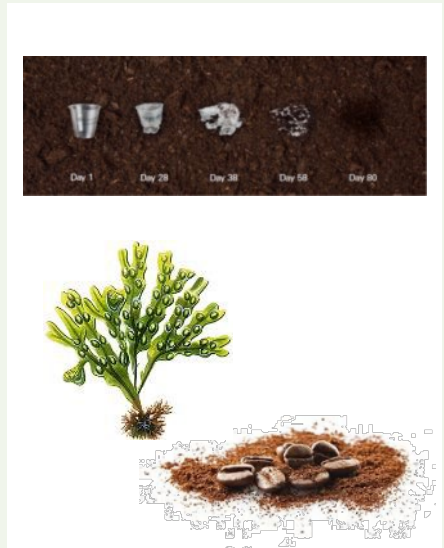
REDUCE

REUSE

RECYCLE

BIOBASED & BIODEGRADABLE

Fibre & Paper Based Materials



Social responsibility
Change of the
consumption habits

Refill and Reuse

Recyclability for a better
feedstock management

Biodegradability to limit the
impact of leakage in
nature

Biosourced & Renewable
Recyclable
Biodegradable

Nanocellulose: Is it really a good solution for Sustainable Packaging?



YES

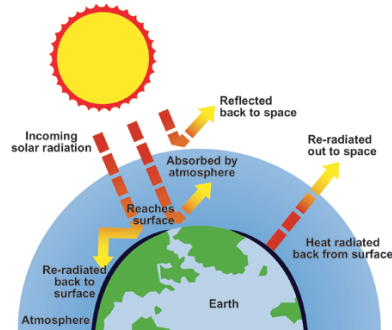
MOST OF THE TIME

But still some questions and
challenges to overcome



Cellulose Valley

Society expectation



SINGLE-USE PLASTICS
D I R E C T I V E

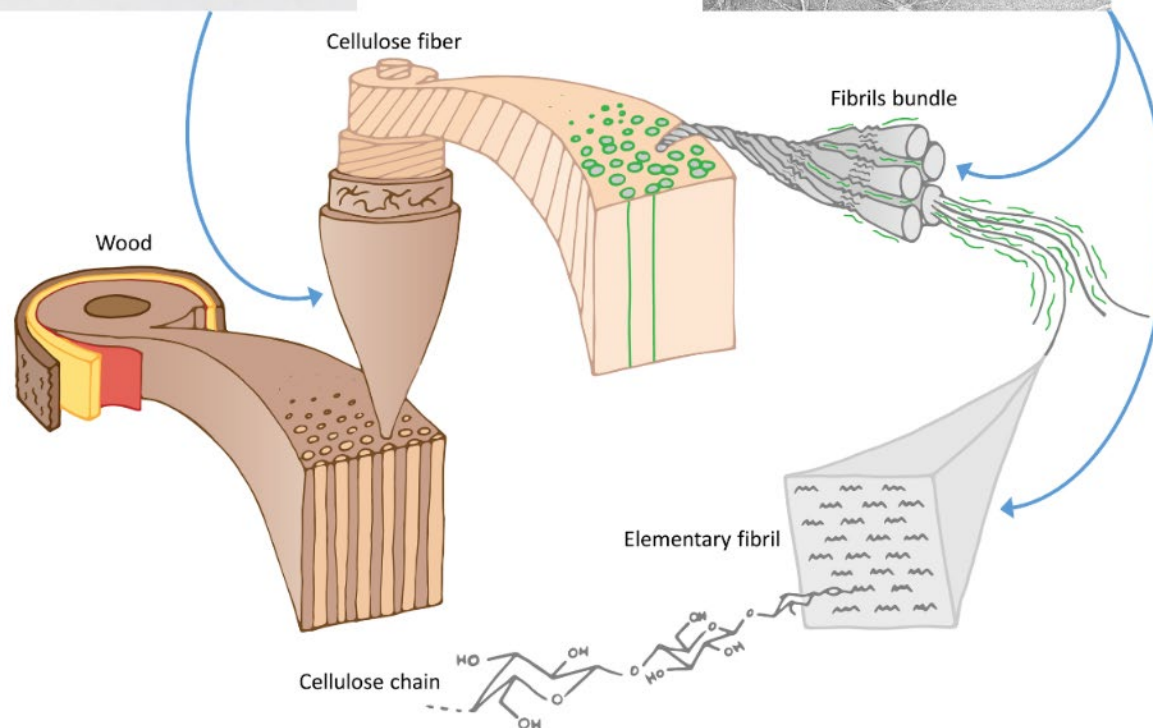
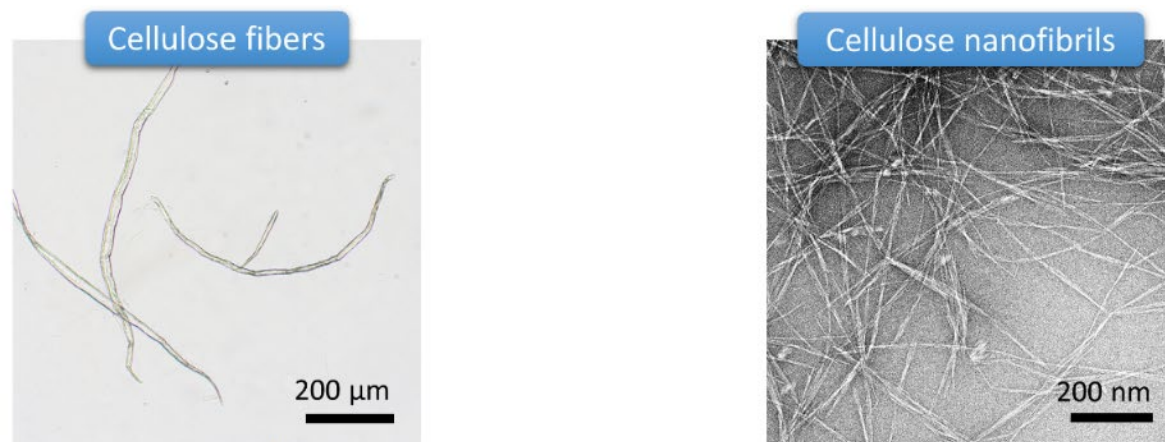
CHAIR CELLULOSE VALLEY



New Cellulose Solutions



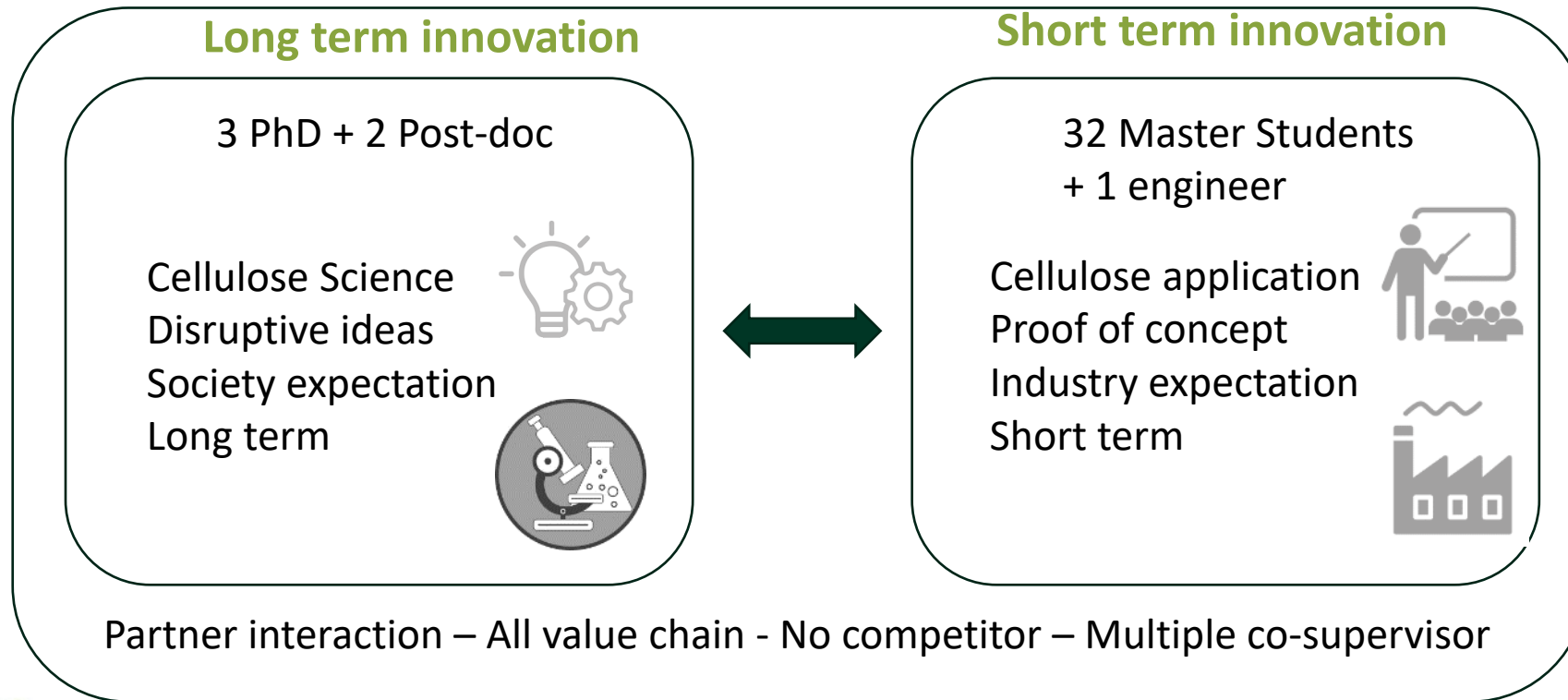
Cellulose Valley Science



KEYWORDS

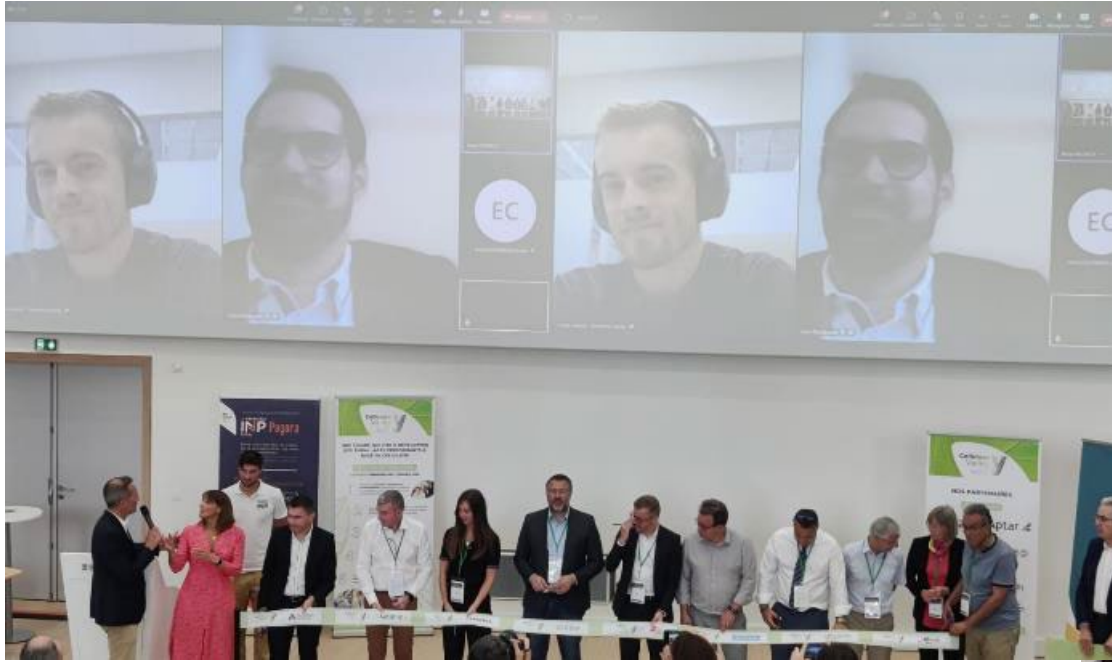
- Microfibrillated cellulose,
- Cellulose gel & regenerated cellulose
- Cellulose functionalization & derivatives
- Final cellulose materials: papers et cartons, molded cellulose, cellulose foam, cellulose biocomposites
- Transparent cellulose
- Water, grease and oil barrier properties
- Oxygen and water vapor barrier properties
- Cellulosic materials sealability & abrasiveness
- New process for cellulose surface coating & fonctionnalization
- New process for 3D forming of cellulose & extendible paper
- Other biobased materials, compatible with cellulose & inert in food contact
- Recyclability in cellulose stream
- Ecoconception & low carbon emission evaluation
- Packaging new approach, new consumer uses, viable alternatives (e.g. Reuse)

Cellulose Valley (2022-2026)



- **Multi-disciplinary:** Materials – Process - Chemistry
- **Multi-rythm:** Short term innovation vs long term innovation
- **Multi-expertise:** Several collaborators – co-supervisors
- **Multi-partners:** 8 companies in different fields –all value chain
- **Multi-scale:** from nano to micro and macro

Work is in Progress



CELLULOSE SCIENCE

Cellulose Science Webinar 2022

Join us online
on December 6, 2022
from 1:30 to 5:30 pm

Cellulose Valley | lgp² | INP Pagora UGA | Fondation Grenoble INP



all4pack

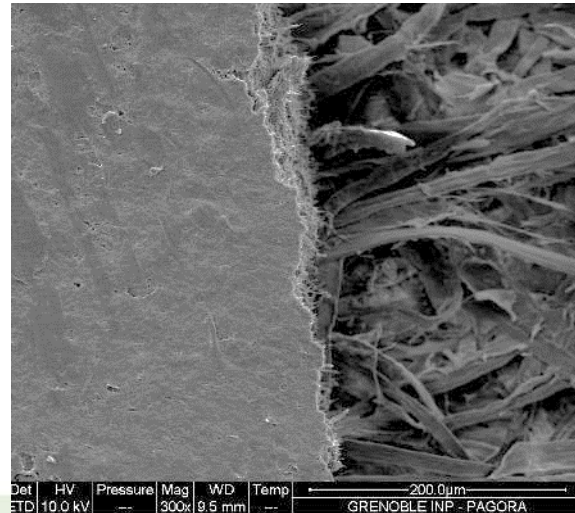
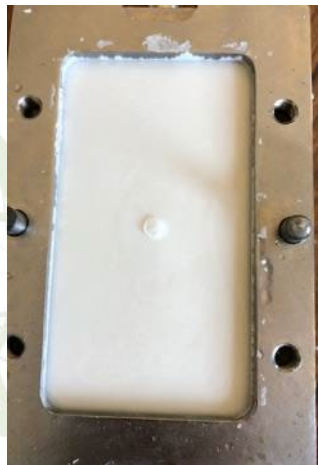
EMBALLAGE PARIS

CONFÉRENCES

A group of people standing in front of a blue and yellow background with the text "all4pack EMBALLAGE PARIS CONFÉRENCES".

Perspectives

2D Materials



3D Materials



THANK YOU FOR YOUR ATTENTION

Multiscale Biobased Materials Department
June 2023



It is people that matters
Trust into the new generation

2 post-doc position available, contact me
Julien.bras@grenoble-inp.fr