Heterogeneous chemical grafting of nanocelluloses by mechanochemistry: a potential for the packaging industry

Julia Pescheux-Sergienko, Loreleï Douard, Naceur Belgacem, Julien Bras

Univ. Grenoble Alpes, CNRS, Grenoble-INP, LGP2, F-38000 Grenoble, France

Research localization

UGA
Université Grenoble Alpes

lgp²

TAPPI NANO DIVISION

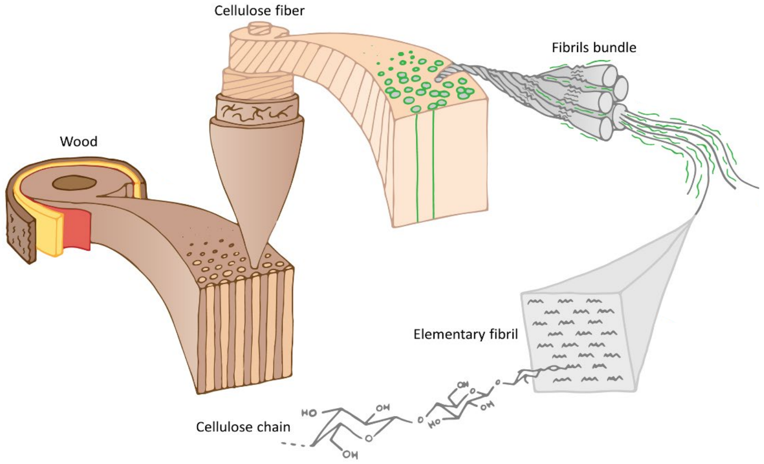
Project setting

Cellulose Valley BY FONDATION GRENOBLE INP — REINVENTING PACKAGING

→ Development of high performance and recyclable cellulose-based solutions for packaging industry

Cellulose as an alternative source

- Renewable
- Worldwide available
- Recycled
- Biodegradable



Legislation changes

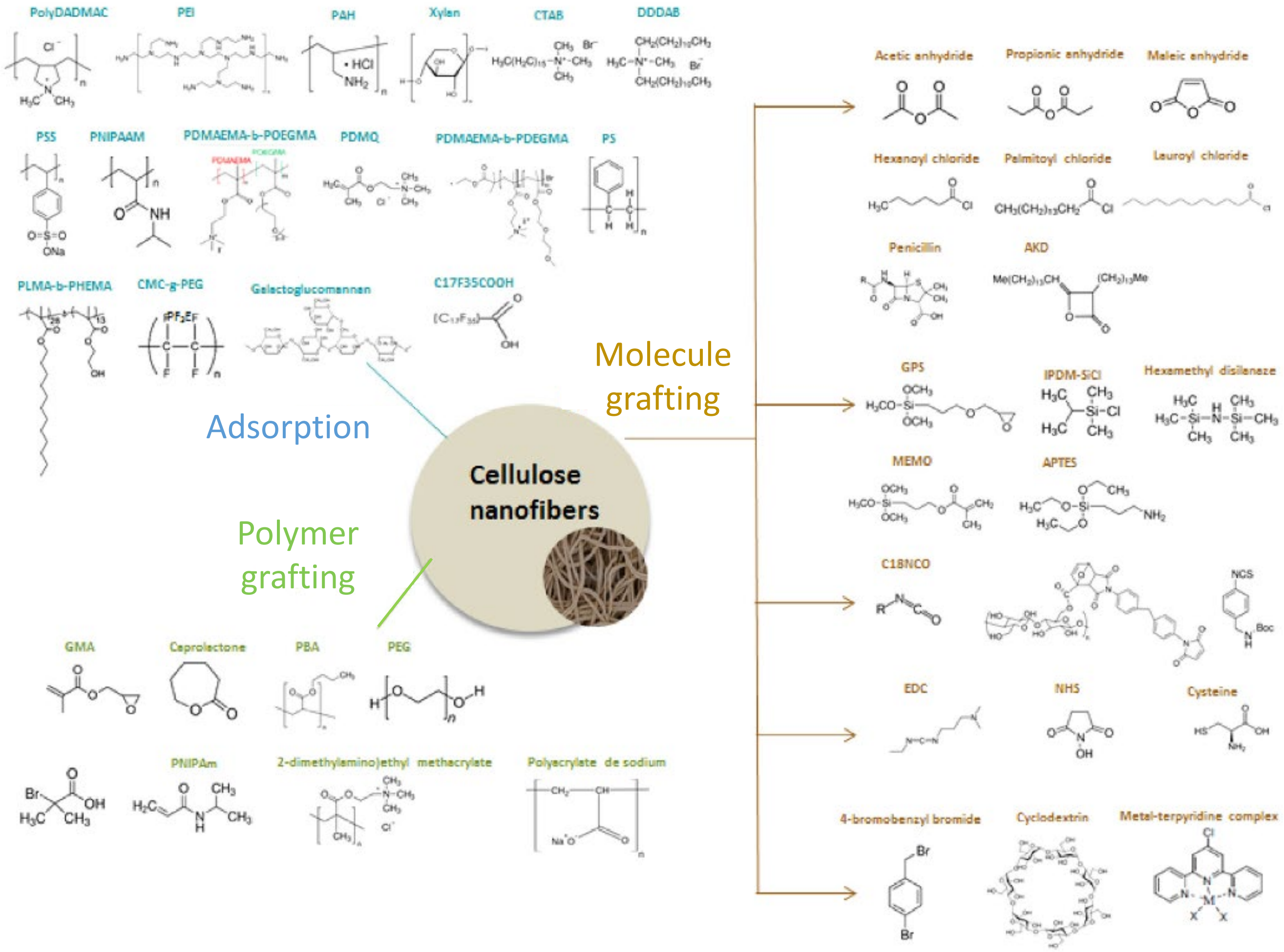
SUP SINGLE-USE PLASTICS DIRECTIVE

PhD subject

New cellulose engineering for high barrier specialty papers and 3D cellulosic materials

- Single Use Plastic Directive (UE) 2019/904. UE parlement directive of 5 June 2019.
- Gabriel Banvillet. Thesis at Universty Grenoble Alpes. 2021.

Cellulose modification



Overview of some of the classic cellulose nanofibrils (CNF) chemical modifications

Main disadvantages:

- Toxicity of solvents
- High reaction temperatures
- Long reaction times
- Washing steps

Mechanochemical derivatization

Rol et al. Recent advances in surface-modified cellulose nanofibrils. 2019.

Mechanochemistry history

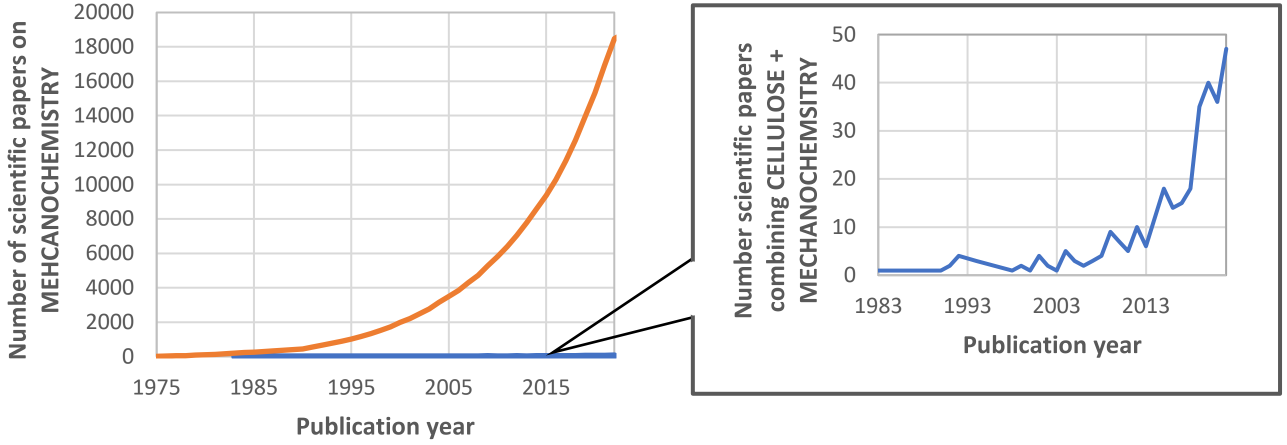
1890: Michael Faraday
First highlights the mechanical reaction by using a mortar and pestle

1892: Carey Lea
Pioneer of modern mechanochemistry

Demonstration of mechanical forces acting on activation energies

1980: First works of application of mechanochemistry to cellulosic products

2008: Identification of mechanichemistry by IUPAC as one of the emerging and pontential-worthy technologies

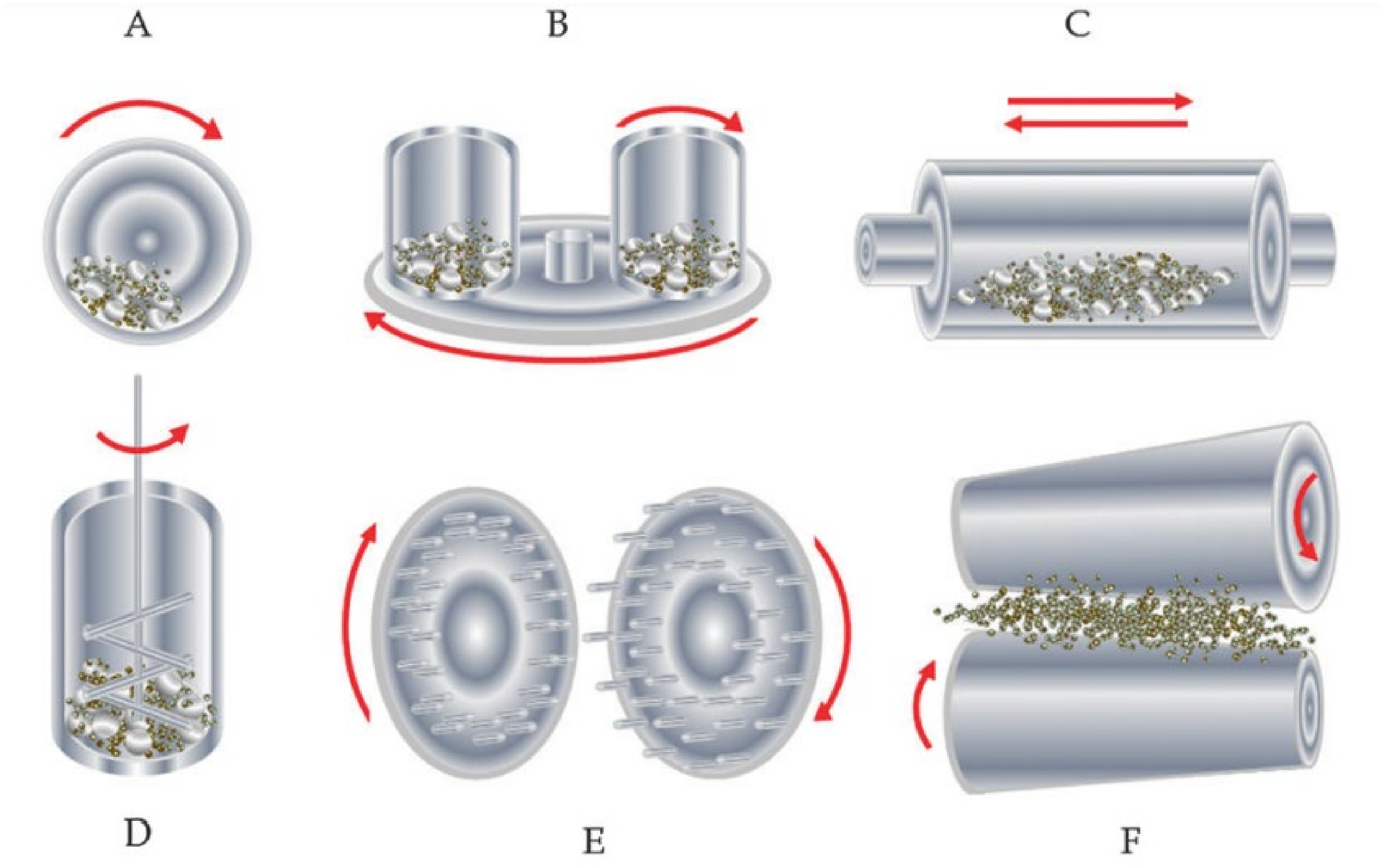


Bibliometrics of mechanochemistry and cellulose trough years (Web of Science. 22/03/2023)

Main advantages of mechanochemistry:

- Shorter reaction time
- Lower reaction temperatures
- Solvent free
- One-pot reaction
- Comparable yields
- Stereoselectivity

Devices used for mechanochemistry

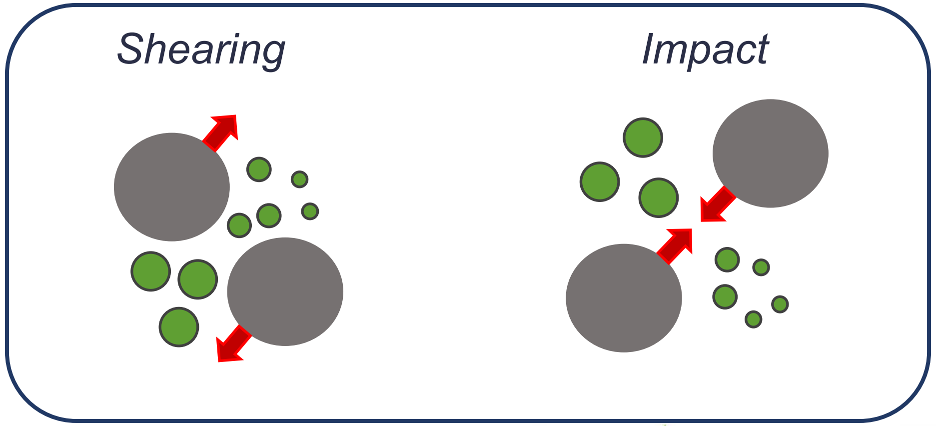


High-energy milling devices:

A: Drum mill B: Planetary mill C: Vibration mill

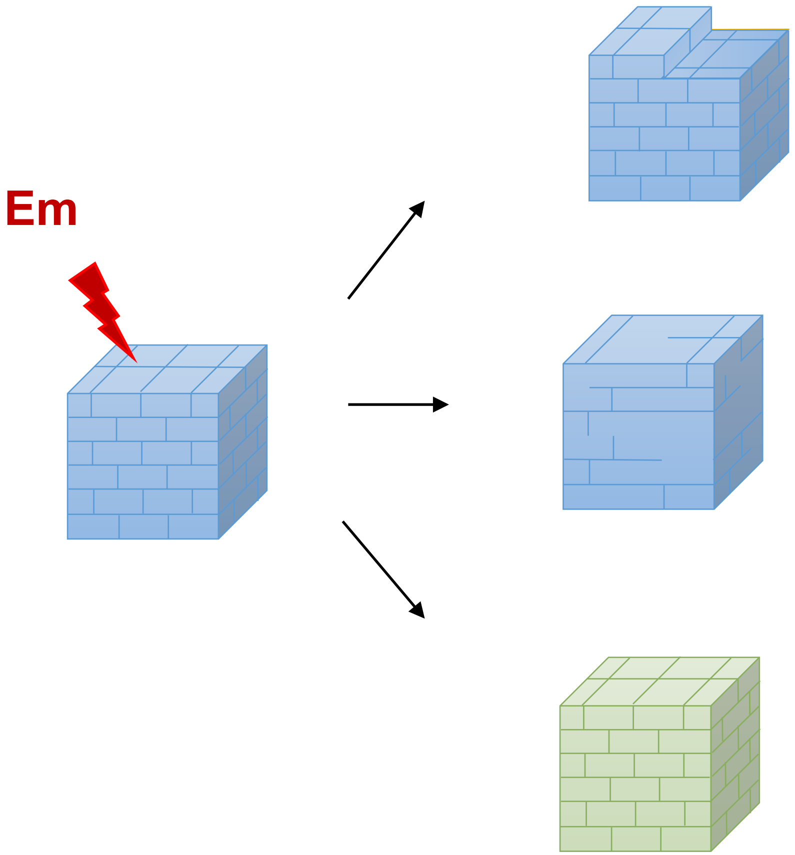
D: Attitor E: Pin mill F: Rolling mill

Involved mechanical forces:



Adapted from: P. Baláž *et al.* Hallmarks of mechanochemistry: from nanoparticles to technology. 2013.

Cellulose modification



❖ *Comminution*

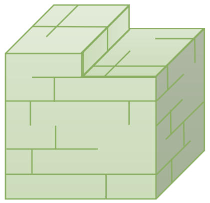
- *Morphological change*
- *Fragmentation*
- *Creation of new surface*

❖ *Structural change*

- *Amorphisation*
- *Polymorphic change*
- *Structural dehydration*

❖ *Chemical modification*

- *Decomposition*
- *Oxydo-reduction*
- *Complexe formation*
- *Depolymerisation*



Final product

Objectives

Reaction with cotton fibers

- Fibers modification
- Cellulose nanomaterials production?

Reaction with CNC

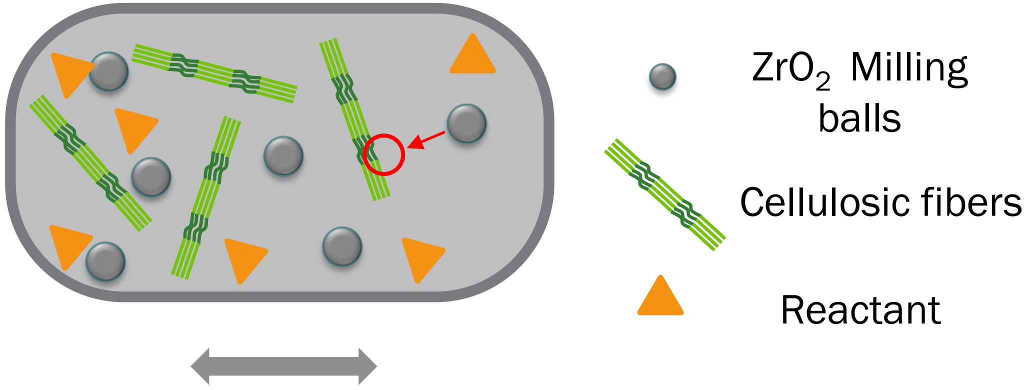
Objectives

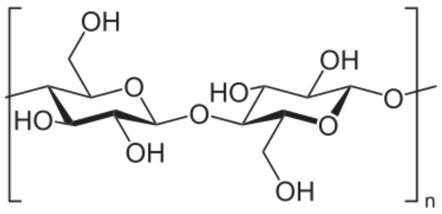
Reaction with cotton fibers

- Fibers modification
- Cellulose nanomaterials production?

Reaction with CNC

Set up of the reaction





Cellulose fibres (cotton, CC)

1/3 balls – 1/3 void - 1/3 reagents <u>0.5g</u> of cellulose

+

$O=C=N-(CH_2)_{17}CH_3$

Octadecyl Isocyanate (OI)

Operational parameters:

- Frequency of vibration: 30Hz
- Vibration time: from 5min to 3h
- Milling balls size : 5mm diameter
- Reaction conditions: Ambient air

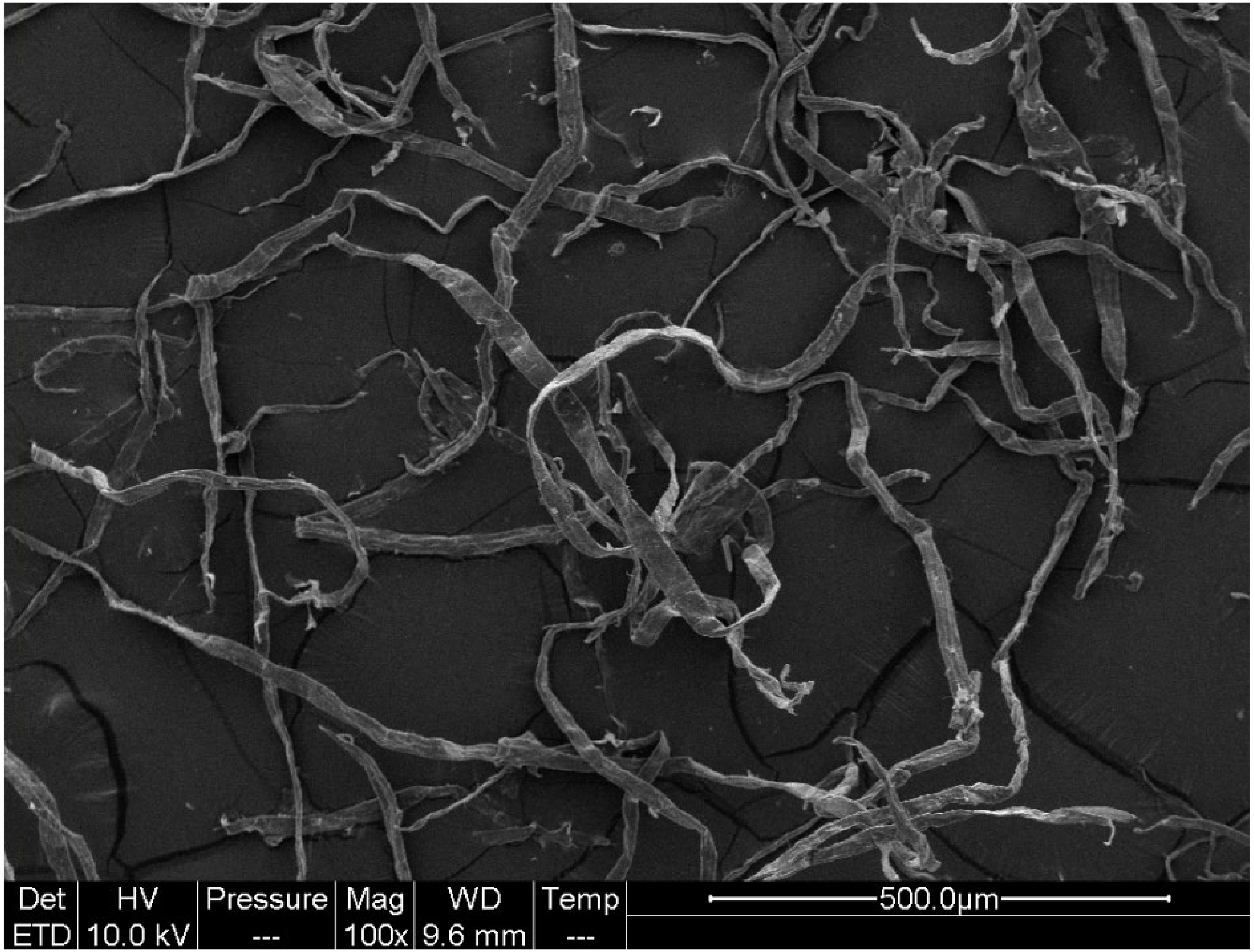
Objectives

Reaction with cotton fibers

- Fibers modification
- Cellulose nanomaterials production?

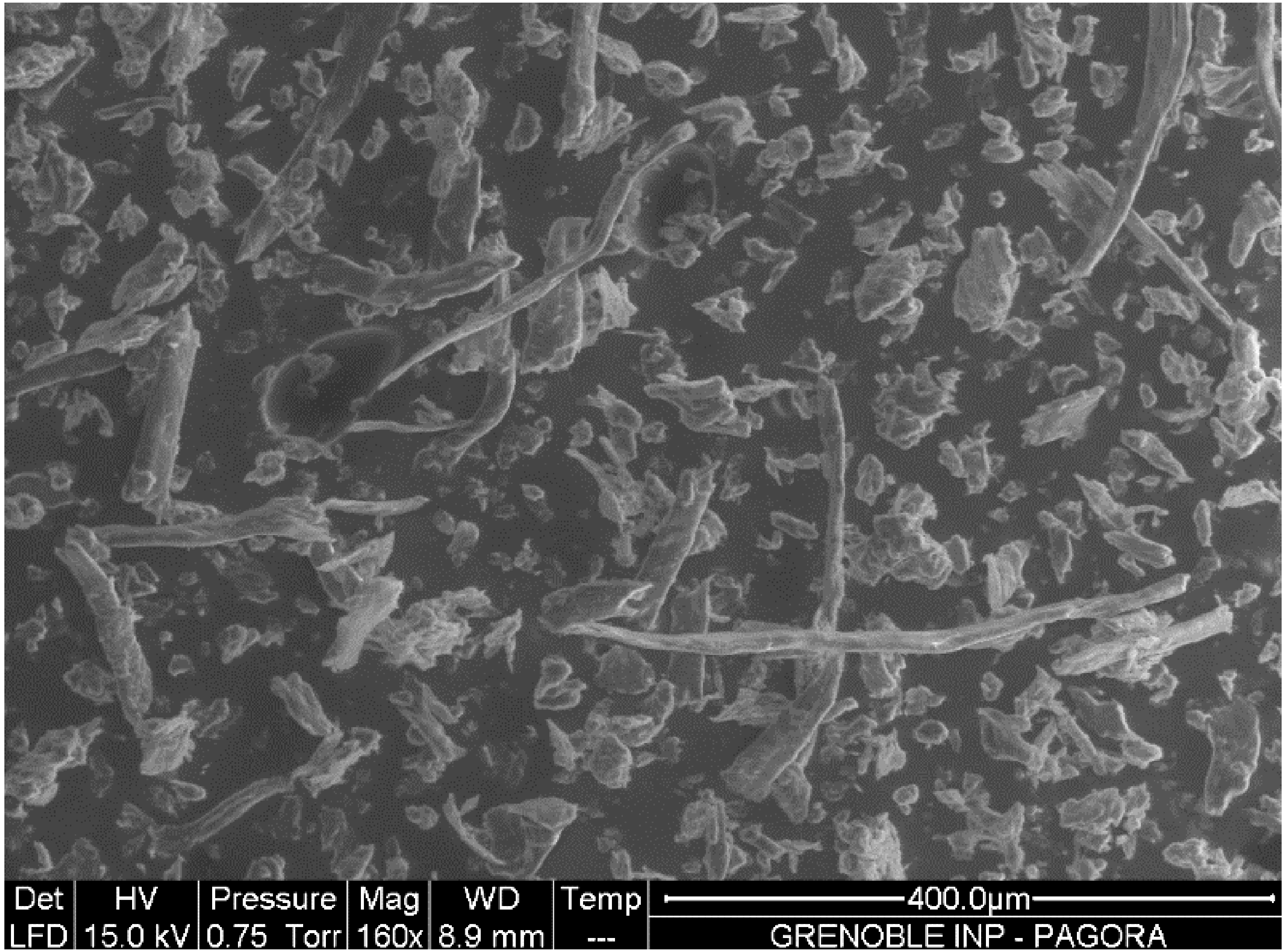
Reaction with CNC

Fibers morphology

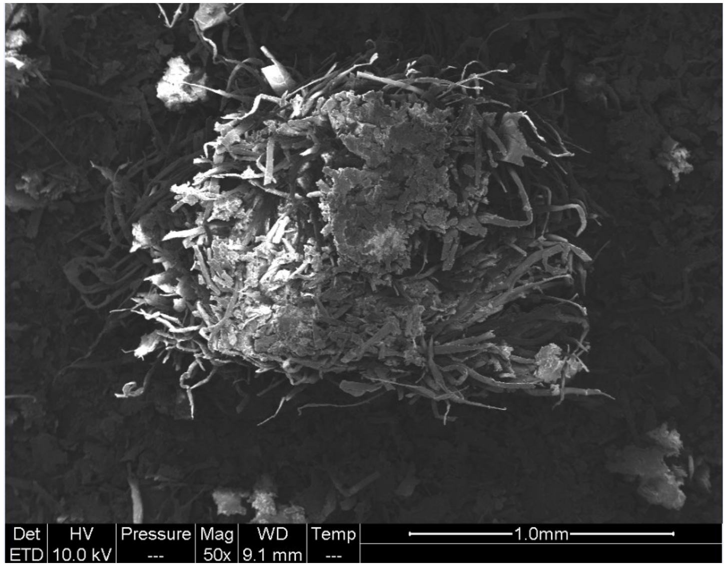


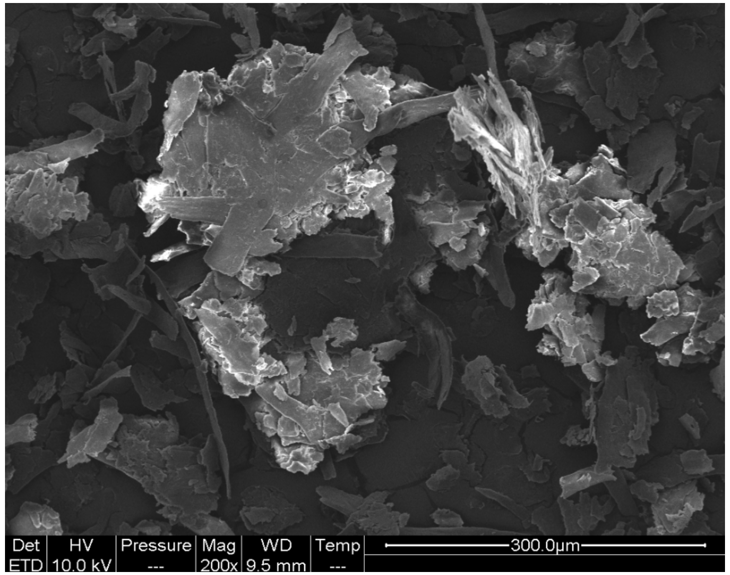
SEM images of cotton fibers. ***UNTREATED***

Fibers morphology

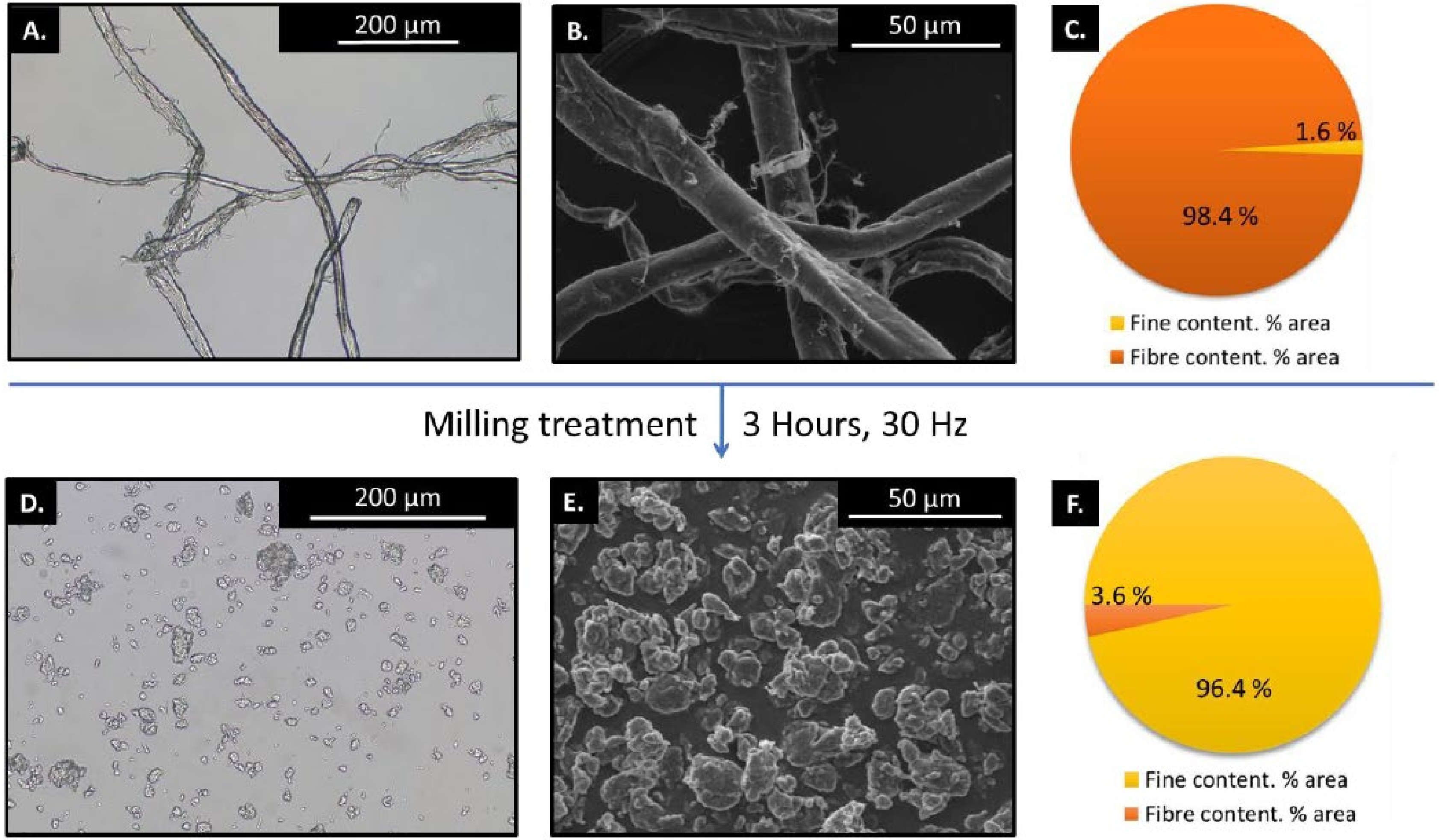


SEM images of cotton fibers ***TREATED*** *at 30Hz,* ***30min***





Fibers morphology

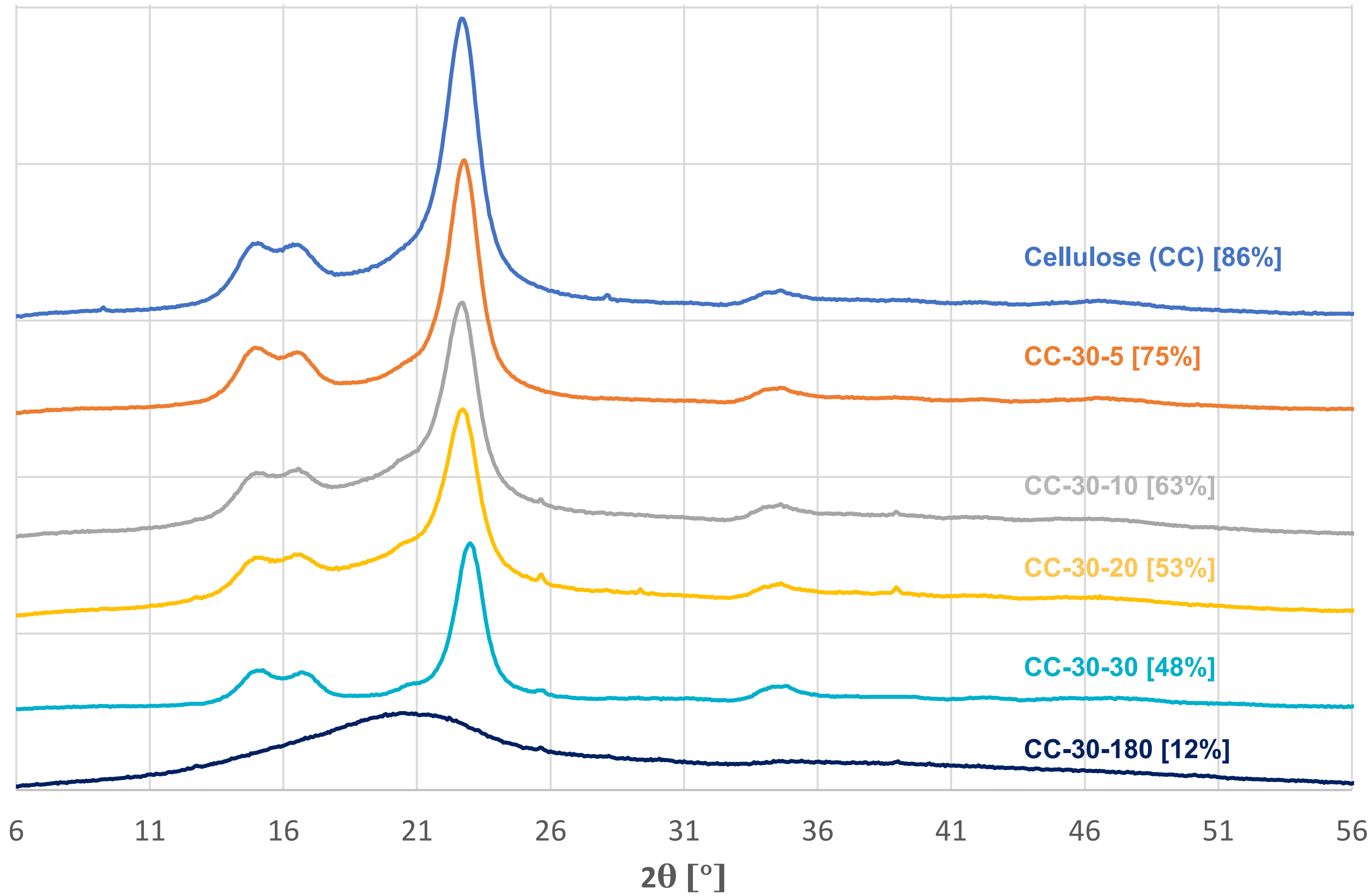


*SEM images of cotton fibers treated at 30Hz, **3hours**.*
Morfi analysis of fibrous dimensions

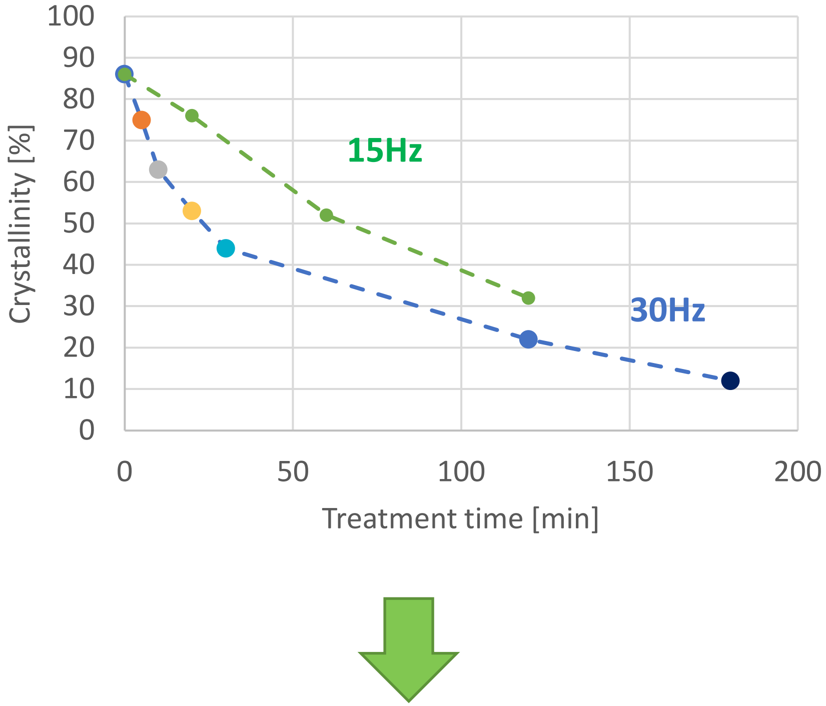
Cotton fibers, untreated
Length: 650µm +/- 50µm
Width : 25µm

At long times treatment the material tends to homogenize

Fibers crystallinity

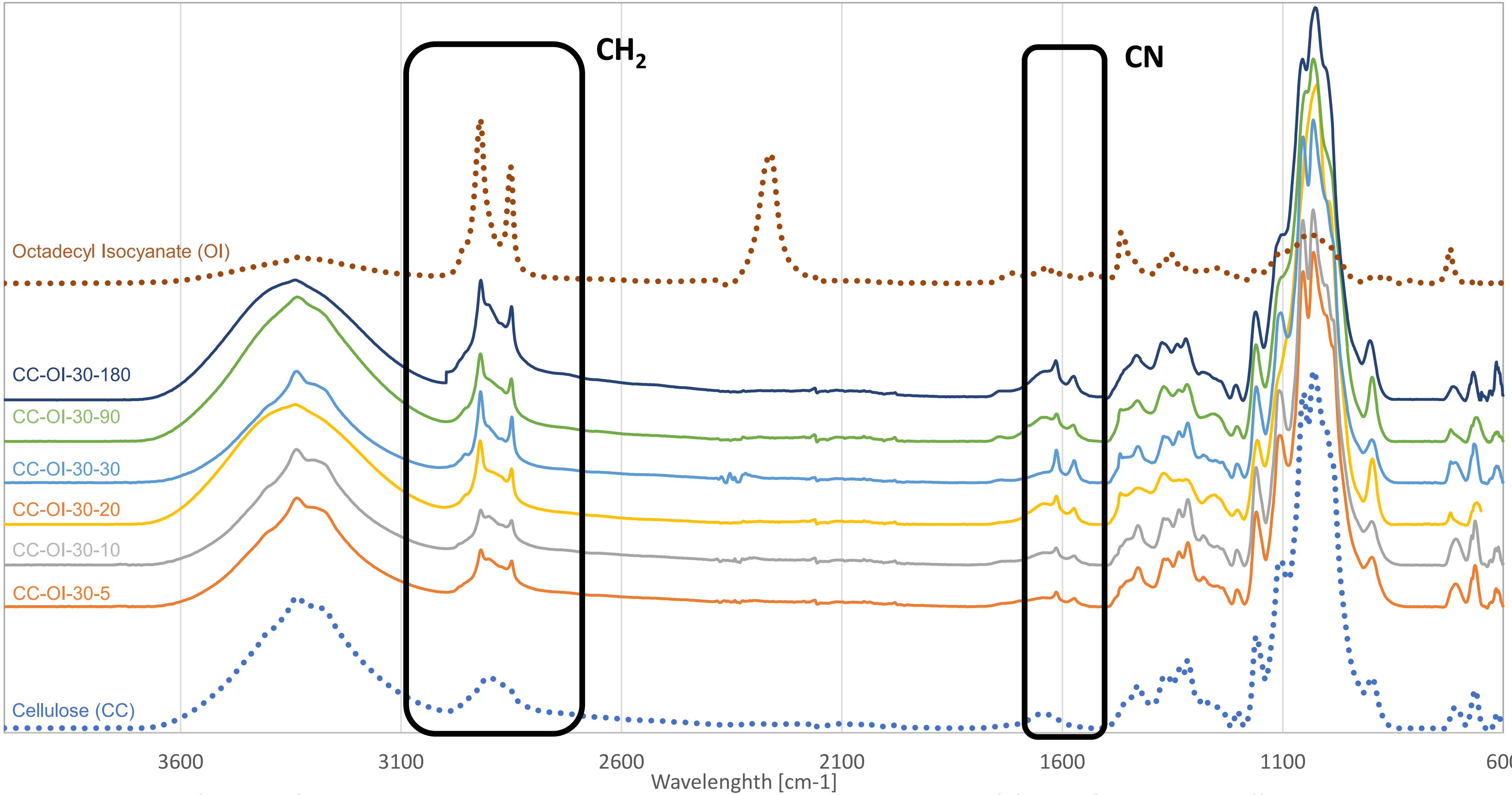


X-Ray Diffraction Crystallography Results after vibratory milling at 30Hz
Amorphous substration calculation method



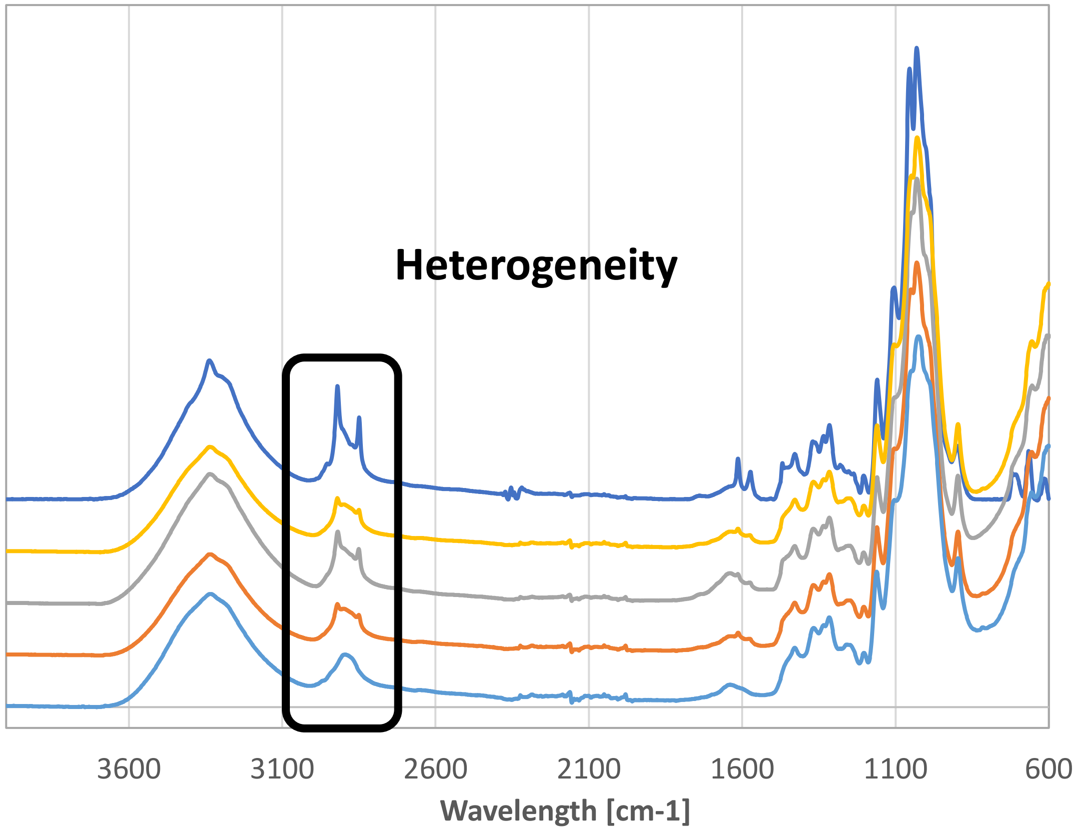
The amorphization is inevitable at long term

FTIR analysis

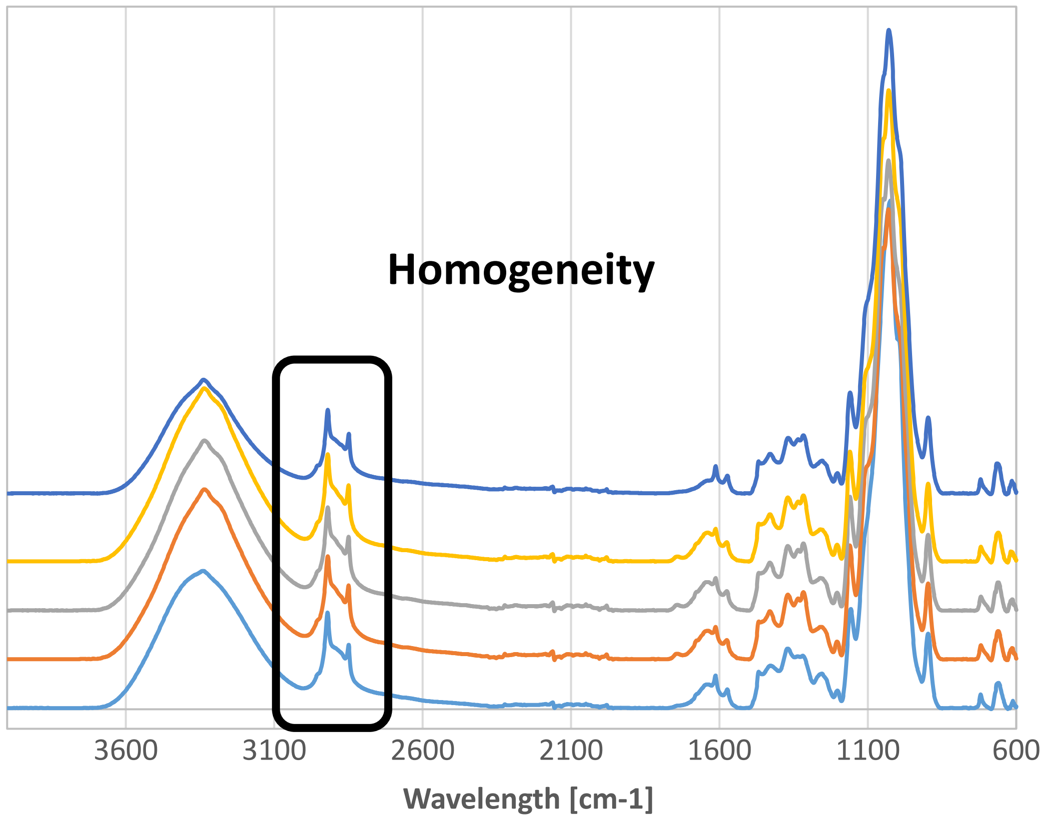


Infra-Red Spectroscopy analysis mechanochemical reaction between CC and OI at 30Hz. different reaction times.

Heterogeneity



*Infra-Red Spectroscopy analysis of mechanochemical reaction between CC and OI at 30Hz, **30min**.*



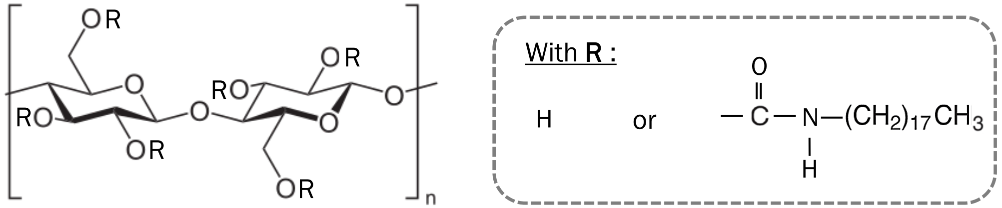
*Infra-Red Spectroscopy analysis of mechanochemical reaction between CC and OI at 30Hz, **3hours.***

At a certain time, the reproducibility of the results is achieved

Elemental analysis

$$DS = \frac{6*M(C) - C\%*Magu}{C\%*Moi - 19*M(C)}$$

Degree of Substitution formula

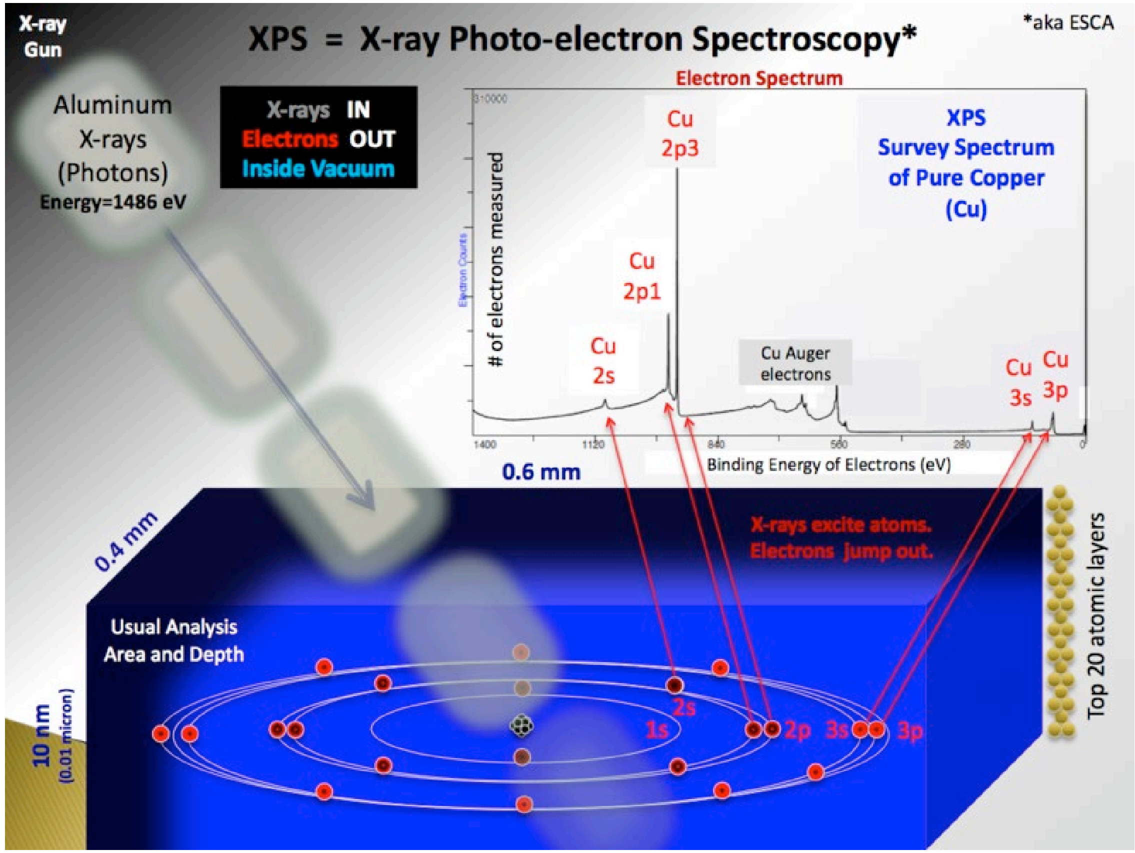


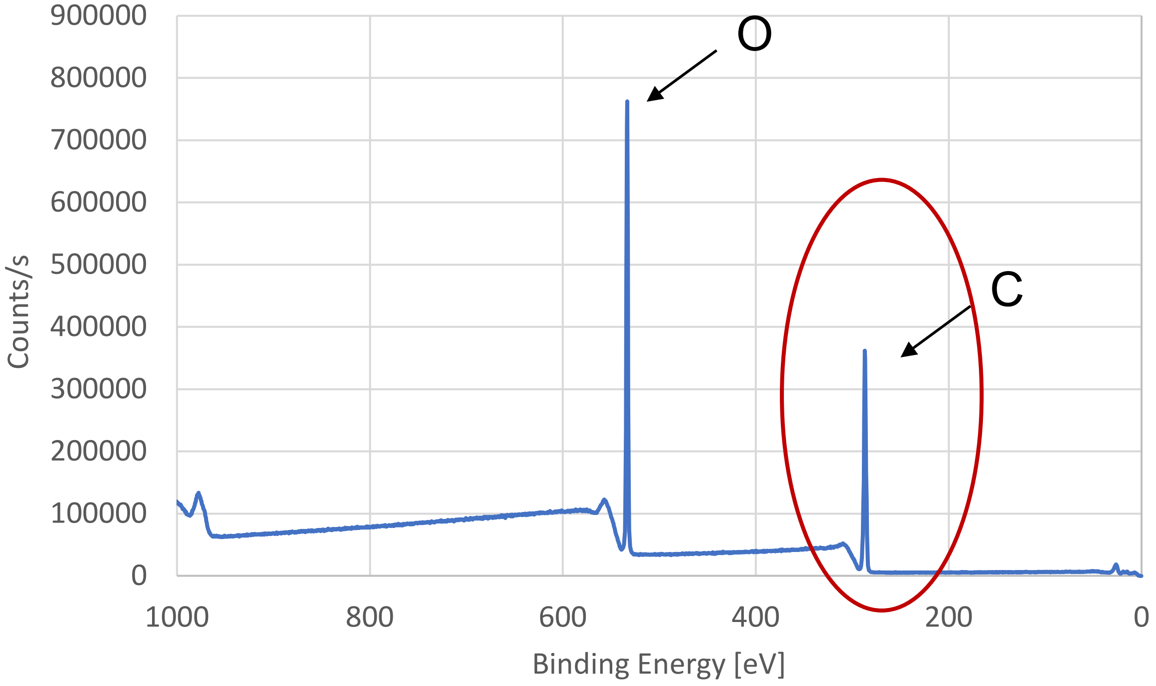
	H%	N%	O%	C%	C% corrected	DS
Cellulose (CC)	6.14	-	49.14	42.47	44.45	
CC-OI-30Hz-**10min**	6.35	< 0.05	49.05	43.36	45.38	**0.02**
CC-OI-30Hz-**20min**	6.56	< 0.05	48.49	44.49	46.56	**0.04**
CC-OI-30Hz-**30min**	6.79	< 0.05	46.95	45.05	47.15	**0.05**

Elemental analysis results for mechanochemically treated cellulose with OI.

The input of energy is allowing the grafting

X-Ray photoelectron spectroscopy





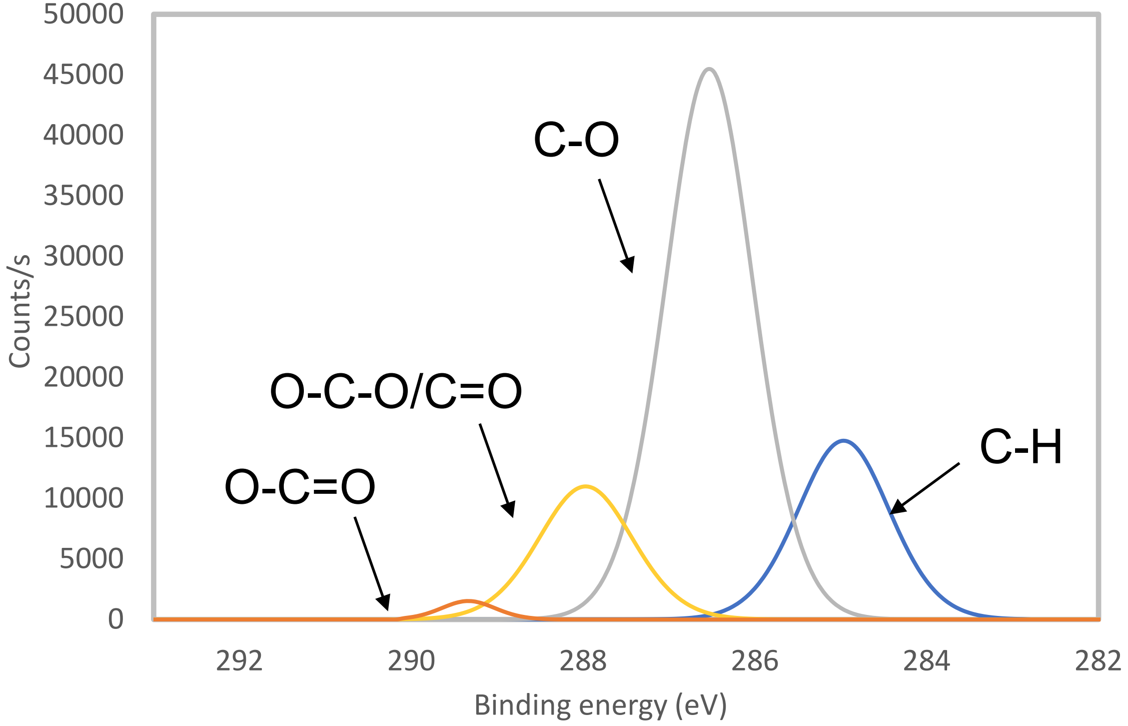
*X-Ray Photoelectron Spectroscopy analysis of cotton fibers treated in vibratory mill at 30Hz for **30min.***

C1 C-H	C2 C-O	C3 O-C-O/C=O	C4 O-C=O	C5 C-N
285.1 eV	286.6 eV	287.8 eV	289.2 eV	286.0 eV

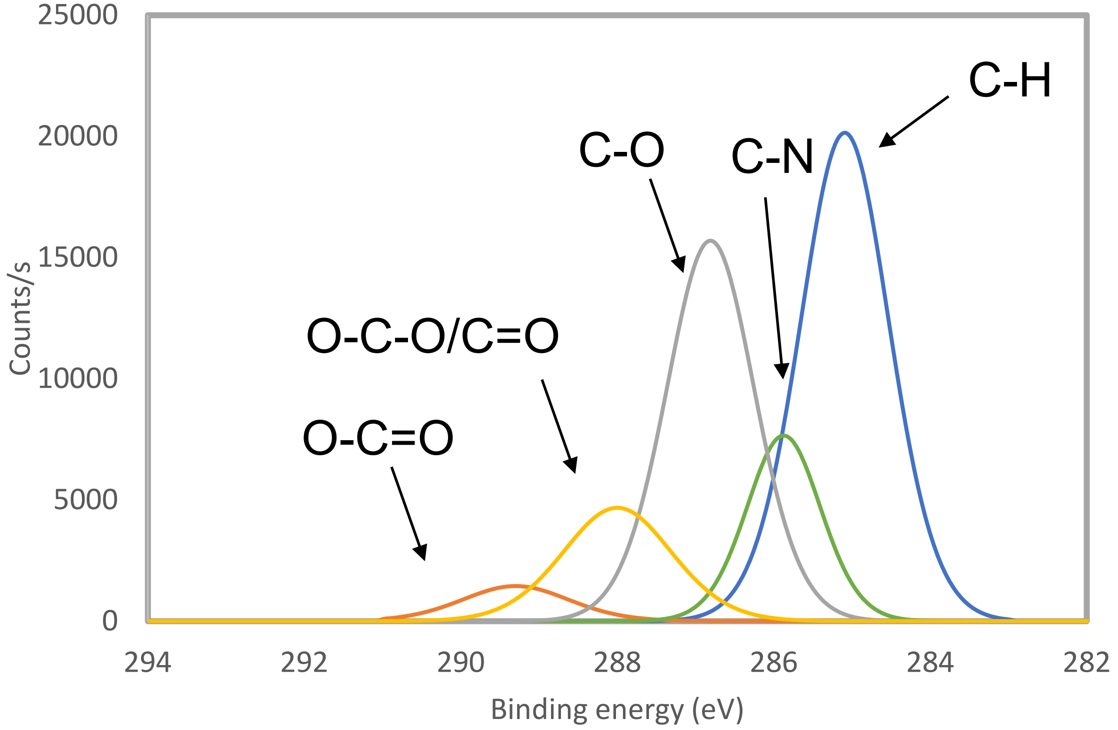
Binding energy of the decomposed C signal from XPS

Identification of the contribution of the bonds in which the element is present

X-Ray photoelectron spectroscopy



*X-Ray Photoelectron Spectroscopy analysis of cotton fibers treated in vibratory mill at 30Hz for **30min, C decomposition**.*



*X-Ray Photoelectron Spectroscopy analysis of cotton fibers treated **with octadecyl isocyanate** in vibratory mill at 30Hz for **30min**.*

$$DSS = \frac{M_{AGU} * C(N)}{(100 - M(N)) - (Moi * C(N))}$$

Degree of substitution on the surface

DS: 0.05
DSS: 0.36

The grafting is mainly happening on the surface

Gousse et al. Stable suspensions of partially silylated cellulose whiskers dispersed in organic solvents. 2002

Objectives

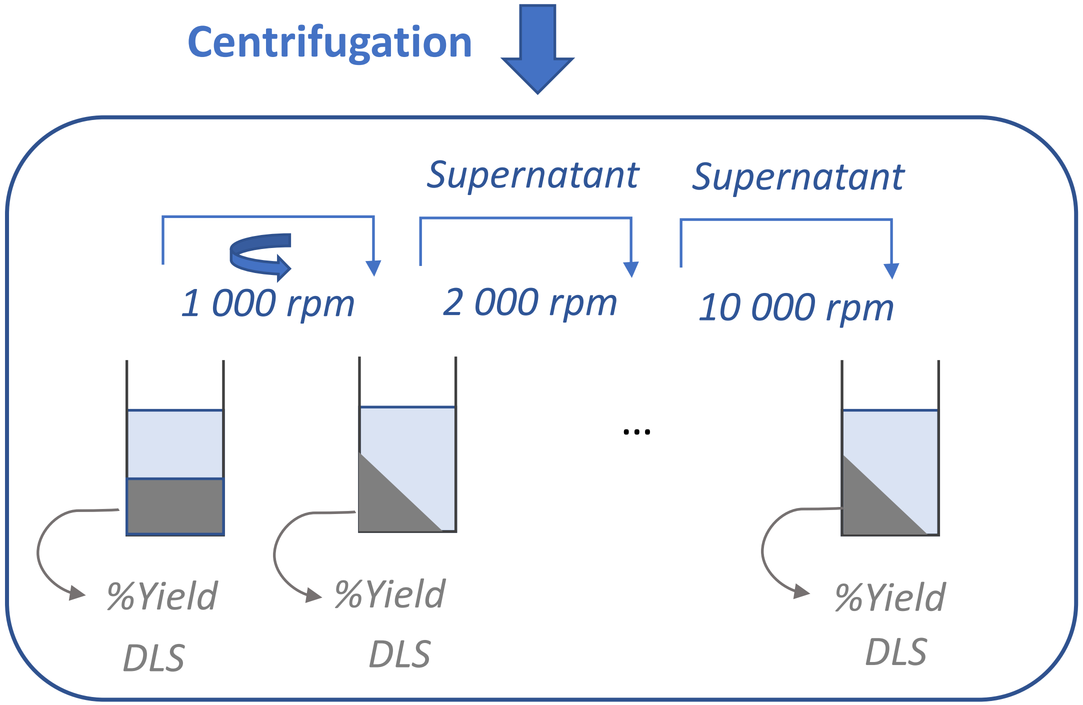
Reaction with cotton fibers

- Fibers modification
- Cellulose nanomaterials production?

Reaction with CNC

Is there CN production?

Reaction
cellulose fibres
at 30Hz, 30min



Separation by successive centrifugation process

RPM	Mass proportion	Size [nm] / PI
1 000	99,08 %	NA
2 000	0,60 %	6123 / 0,8
4 000	0,16 %	7028 / 1
6 000	0,12 %	6530 / 1
8 000	0,04 %	4720 / 1
10 000	0,004 %	3366 / 1
Supernatant after 10 000	0 %	NA

Crossing of gravimetric and DLS measurements for centrifuges material

- The nanosized is conceivable
- Proof from AFM and TEM

J. Desmaisons. Thesis at Universty Grenoble Alpes. 2018.

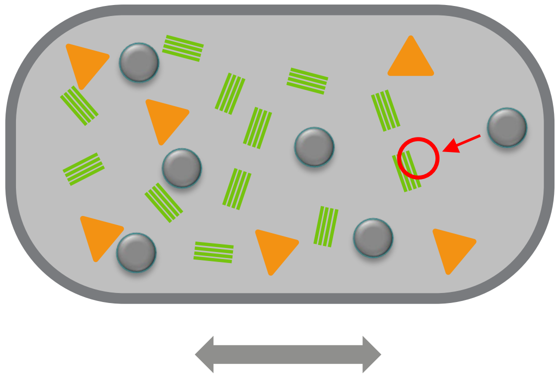
Objectives

Reaction with cotton fibers

- Fibers modification
- Cellulose nanomaterials production?

Reaction with CNC

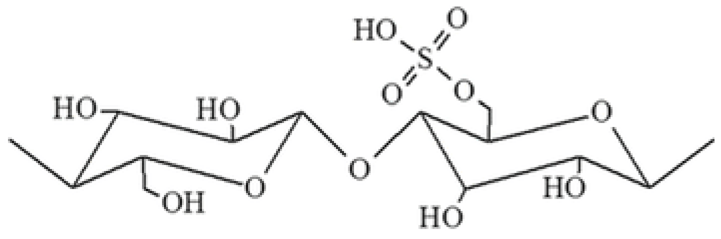
Set up of the reaction



ZrO_2 Milling balls

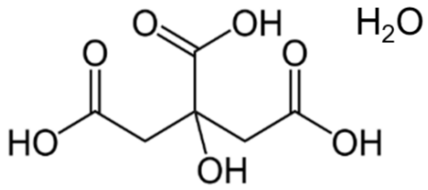
CNC

Reactant



Cellulose Nano Crystals (CNC, celluforce)

+



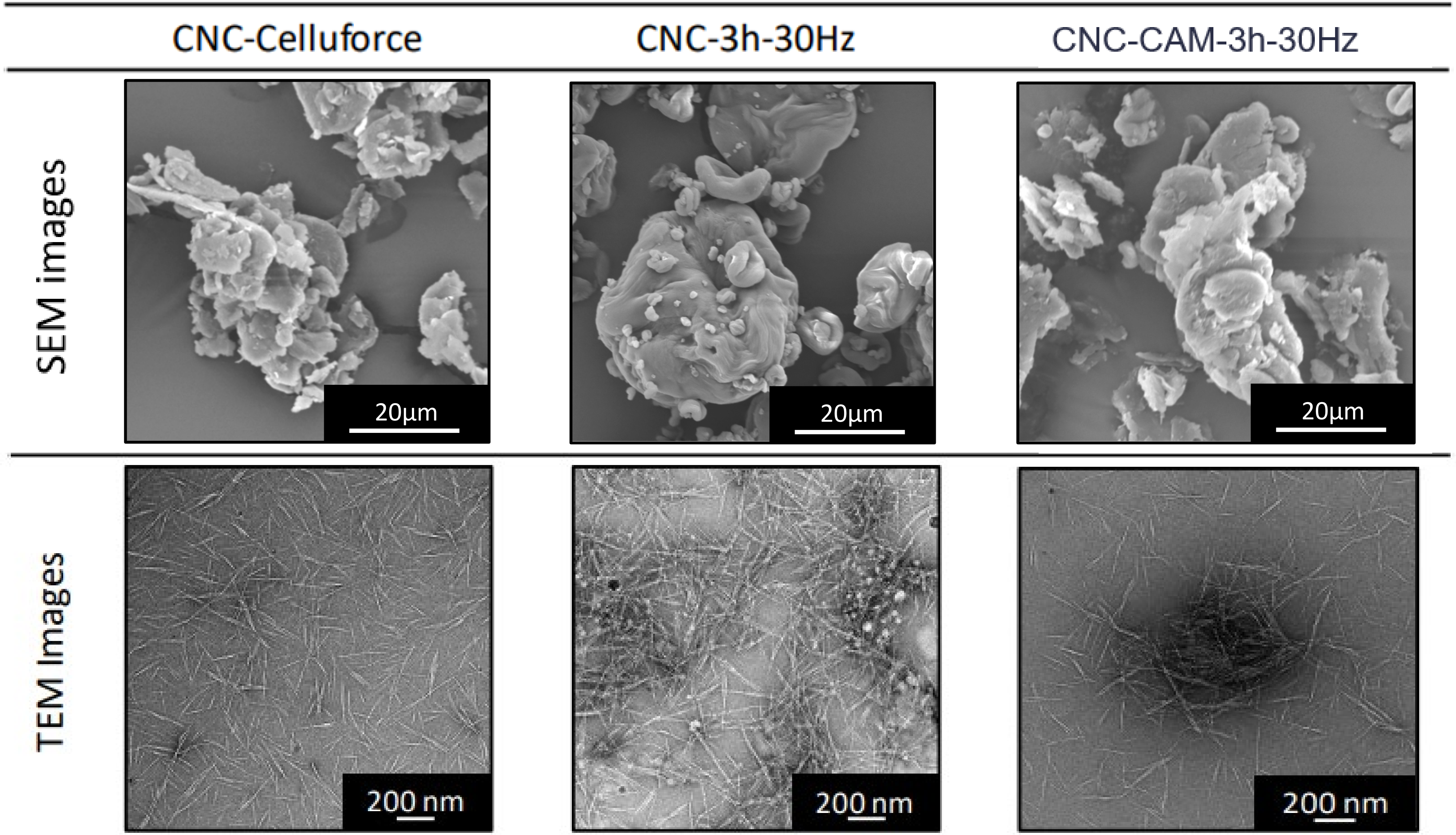
Citric Acid Monohydrate (CAM)

1/3 balls – 1/3 void - 1/3 reagents <u>1g</u> of CNC

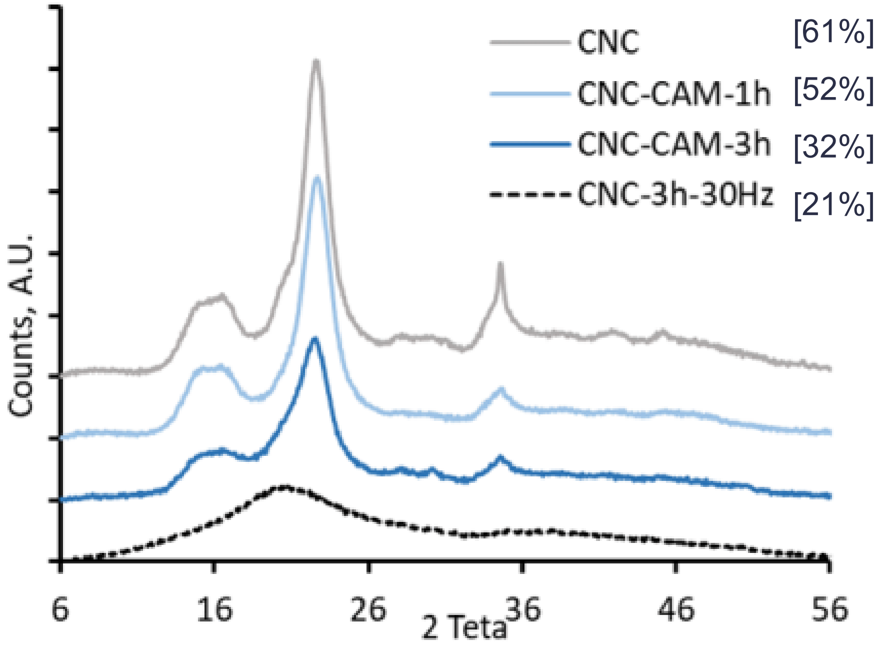
Operational parameters:

- Frequency of vibration: 30Hz
- Vibration time: from 5min to 3h
- Milling balls size : 5mm diameter
- Reaction conditions: Ambient air

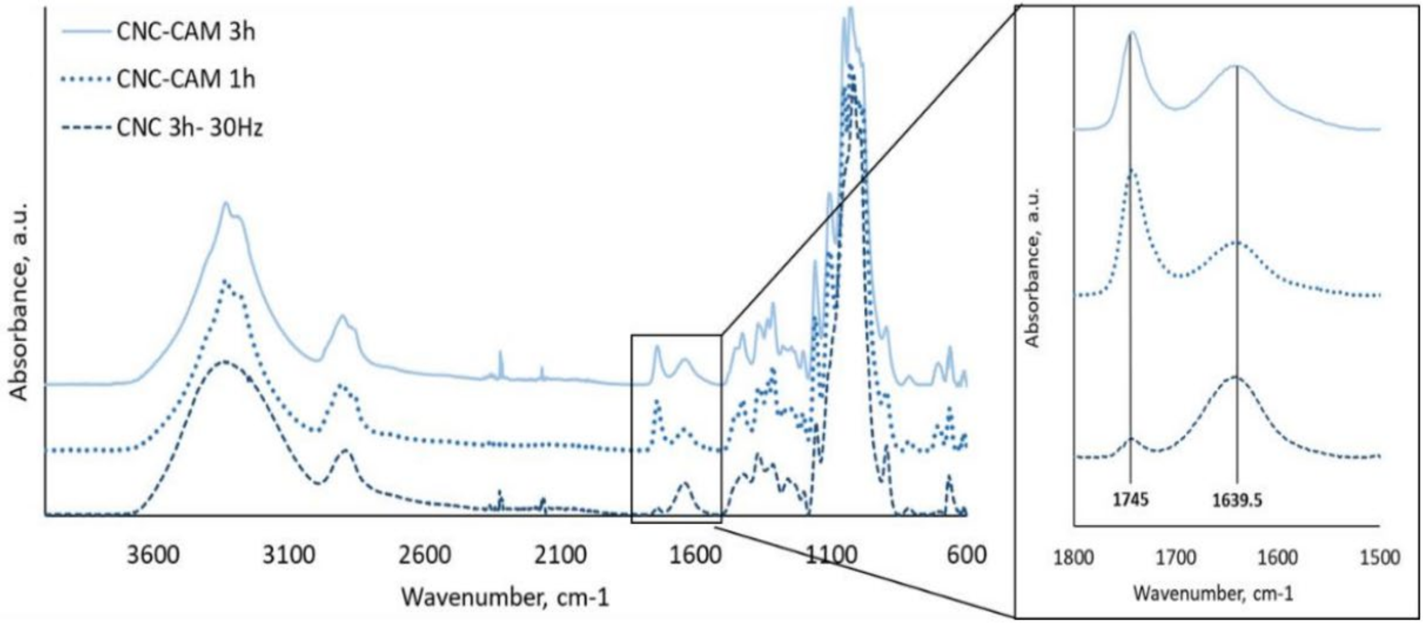
CNC modification



CNC modification



XRD analysis of CNC modified with CAM at 30Hz

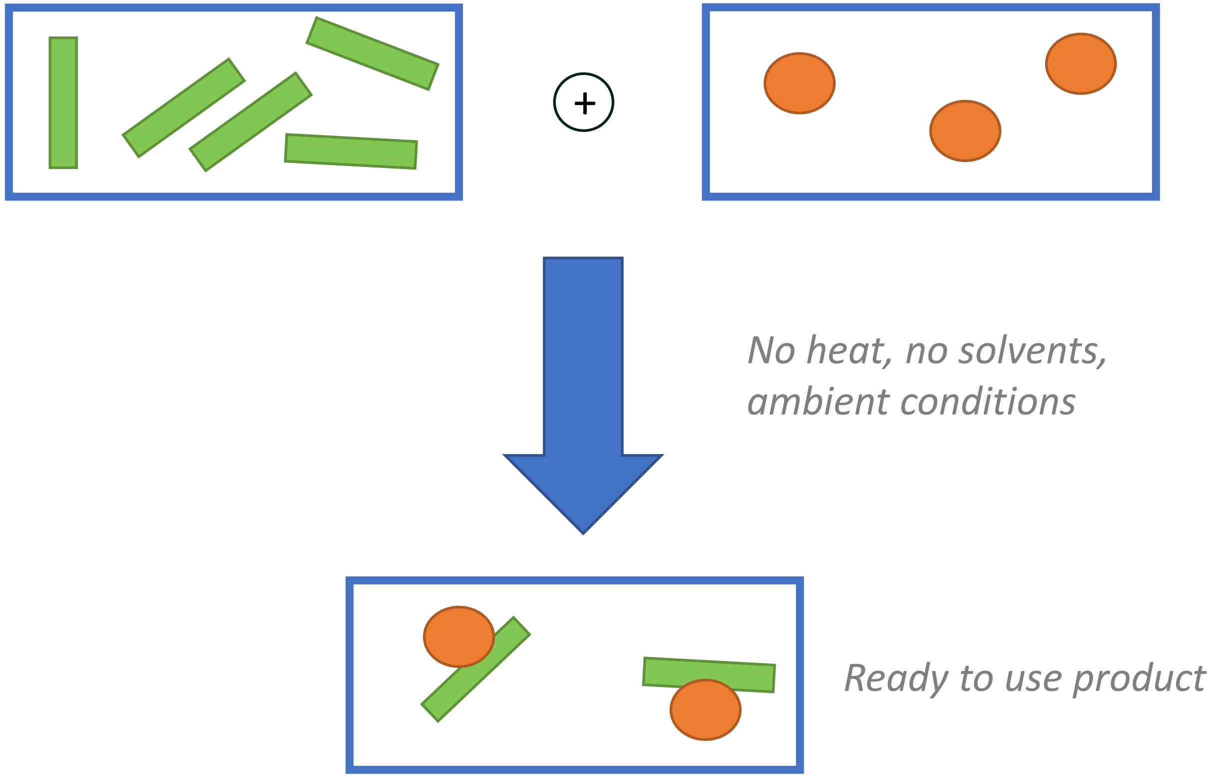


Infra-Red Spectroscopy analysis of CNC modified with CAM at 30Hz

The amorphization is showered with the addition of the reactant

The grafting is proved by direct and indirect methods

The industrial potential



Expected reaction path

Main envisioned advantages:

- Time and chemical savings
  - No solvents involved
  - Washing steps abolition
- Cellulose derivatized only on the surface
  - Suitable for surface functionalization
  - Lowered "denaturalization"
- Realization of "impossible reactions"

Conclusions

Conclusions

- Communition and derivatization of the cellulose are simultaneously taking place
- The reaction in chosen conditions is submitted to stochastic behavior
- The observed hydrophobical behavior is promising

Perspectives

- Better comprehension of the operational parameters
- The hydrophobicity needs to be tested through an applicative method

Acknowledgments

Supervisors: Dr. Julien BRAS and Dr. Naceur BELGACEM
Co-author: Dr. Loreleï DOUARD

Funding and support:
- University Grenoble Alpes. Grenoble INP. LGP2
- Cellulose Valley Project
  - Fondation Grenoble INP
  - Industrial partners

Help for analysis and services:
- Sandrine ADACH
- Thierry ENCINAS
- Bertine KHELIFI
- Sonia MOLINA-BOISSEAU

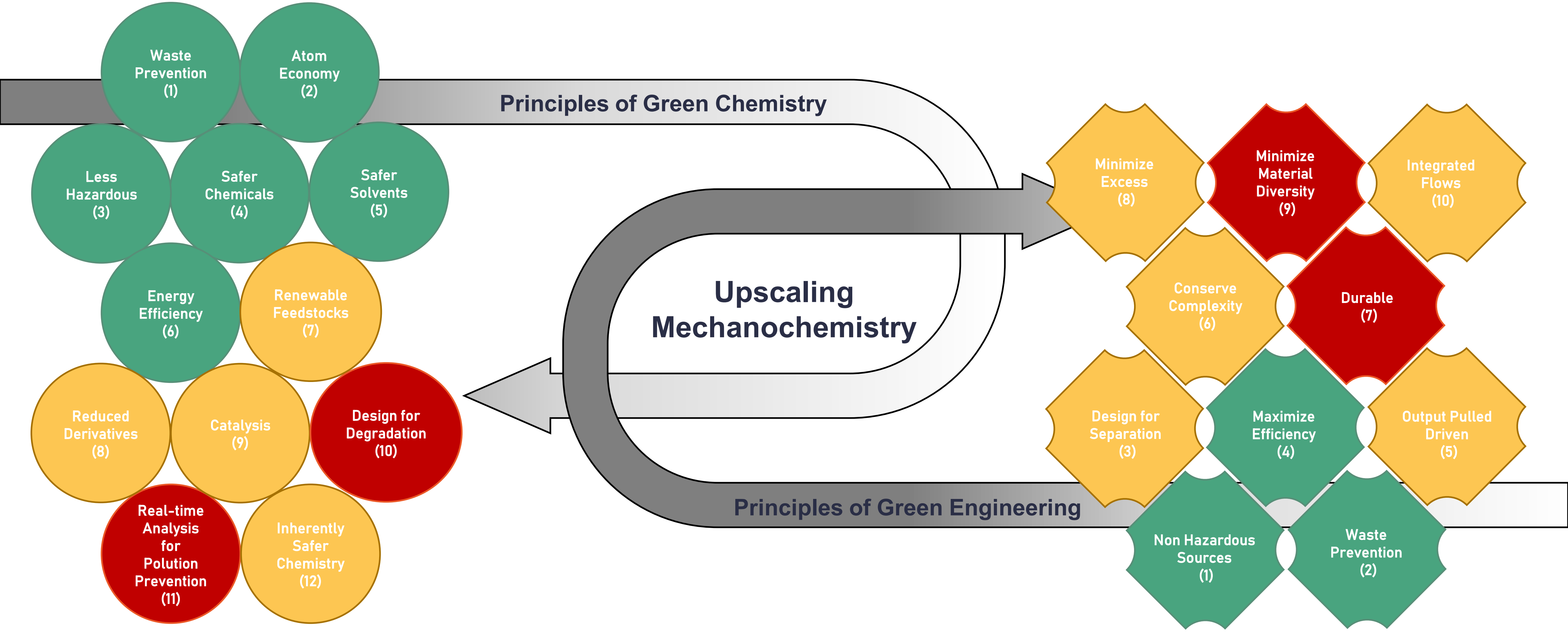
TAPPI NANO DIVISION

Thank you all for your attention!

Do you have any questions?

Julia.Pescheux-Sergienko@Grenoble-INP.fr

Upscaling mechanochemistry: a challenge



Adapted from: E. Colacino. V. Isoni. D. Crawford. and F. García. 'Upscaling Mechanochemistry: Challenges and Opportunities for Sustainable Industry'. *Trends in Chemistry*. May 2021.