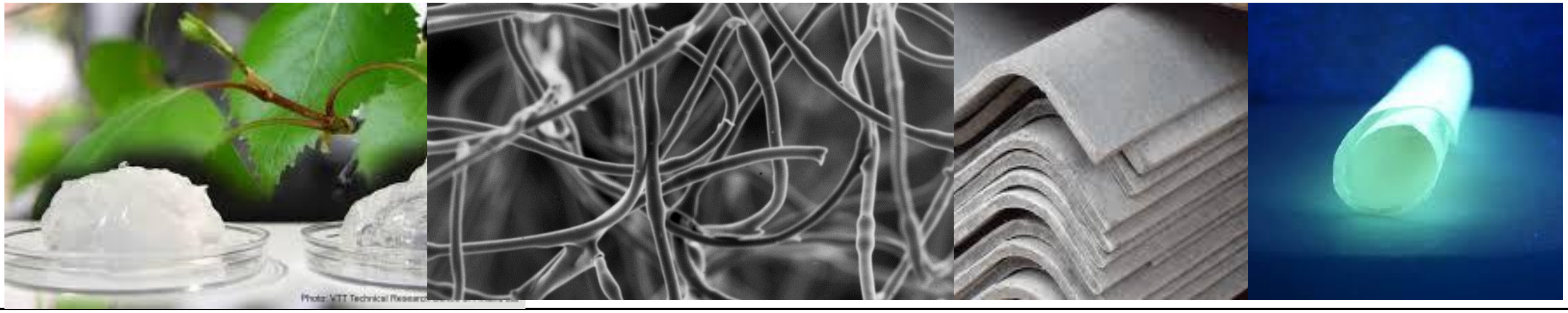
RESIDUAL LIGNOCELLULOSE AND OTHER AGROINDUSTRY BYPRODUCTS ADDING VALUE TO SMART CONSTRUCTION ELEMENTS

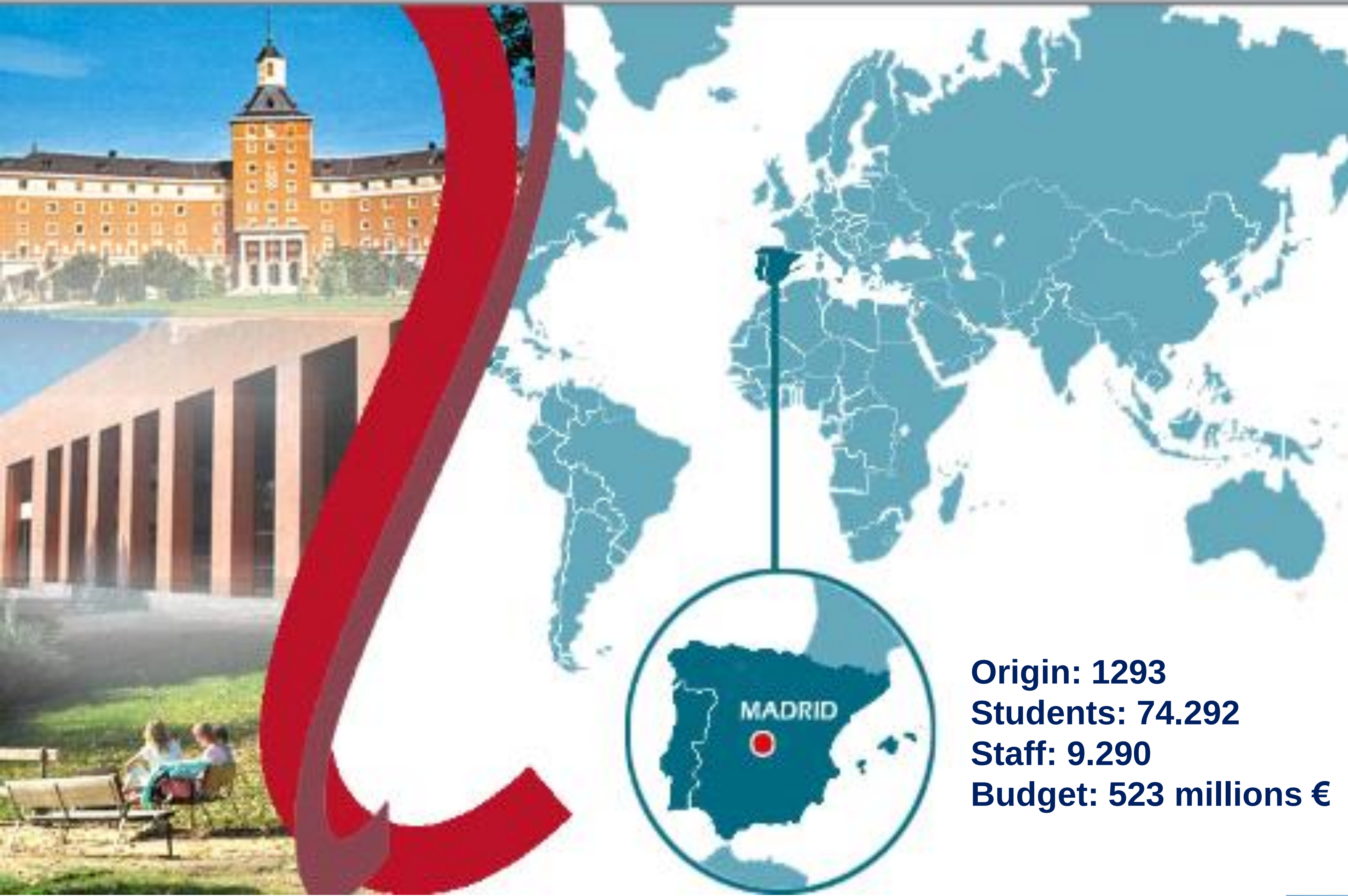
Proposal – Horizon 2020 call:

Integration of Energy Smart Materials in Non-residential Buildings

Cellulose and Paper Research Group
(University Complutense of Madrid/Spain/Carlos Negro)



University Complutense of Madrid



Origin: 1293
Students: 74.292
Staff: 9.290
Budget: 523 millions €

Department of Chemical Engineering and Materials
Research Group: Cellulose, Paper & Water

Its activities are conducted in two lines: Fundamental Research and the Applied Research, in order to enhance the technical and scientific expertise of the industry. The Fundamental Research is devoted to the acquisition of new knowledge and the fundamental understanding of the phenomena taking place during pulp and papermaking. On the other hand, the Applied Research is devoted to the application of these knowledge to solve the needs of the industry and suppliers.

Fundamental and Applied Research

- Acquisition of new Knowledge.
- Fundamental understanding of the phenomena taking place during industrial processes.
- Sustainable industrial production.
- Development and optimization of new industrial treatments.
- Application of the gained new knowledge to solve specific needs of industry and suppliers.

Fundamental and Applied Research

Sustainable Paper and Fibercement Production

- **Process optimization: wet-end chemistry, flocculation, drainage and retention processes.**
- **Product (paper/board/cement) properties improvement: mechanical, physical and optical properties.**
- **Lignocellulosic resources (virgin, recycled, agrowastes).**
- **Reuse and recyclability (final product and wastes generated in the processes).**

Fundamental and Applied Research

Sustainable Paper and Fibercement Production

Sustainable Water Management

- **Minimisation of water consumption (e.g. circuits closure, reclaimed water).**
- **Optimization of industrial wastewater treatments.**
- **New technologies developed and proved at lab and pilot scale.**
- **Advanced Oxidation Processes (AOPs).**

Fundamental and Applied Research

Sustainable Paper and Fibercement Production

Sustainable Water Management

Nanotechnology: Nanocellulose

Nanotechnology: Nanocellulose

- **Production of different NC (cellulose nanofibers, cellulose nanocrystals, hairy cellulose and bacterial cellulose) from different from different lignocellulosic raw materials.**
- **Characterization of NC (e.g. nanofibrillation yield, transmittance, carboxylic content, polymerization degree….).**
- **Surface modification of NC.**
- **Application and optimization of the use of NC to different industrial sectors: papermaking, water treatment, food industry and sustainable building materials.**

EUROPEAN PROJECTS

FRAMEWORK PROGRAMME III 1990-1994

1. Control of flocculation of cellulose fibre and mineral solids in papermaking stocks

FRAMEWORK PROGRAMME IV 1994-1998

1. Study of professional training needs in the European pulp and paper industry
2. PIBARE
3. COLLOIDS
4. NEST

FRAMEWORK PROGRAMME V 1998-2002

FIFTH FRAMEWORK PROGRAMME

1. Formation avanceé et developpement professional en technologies papetetierés
2. REWAPULP
3. Microscopy as a tool in pulp and paper research and development
4. PITCH
5. RODET
6. SLIMEZYMES

FRAMEWORK PROGRAMME VI 2002-2006

SIXTH FRAMEWORK PROGRAMME

1. NODESZELOSS
2. ODOURCONTROL
3. SHAKER
4. MODELPACK

FRAMEWORK PROGRAMME VII 2007-2013

SEVENTH FRAMEWORK PROGRAMME

1. AQUAFIT4USE
2. CHEMWATER
3. FIBRE+
4. E4WATER

HORIZON 2020 2014-2020

1. Nano-CTB (proposal)

Cellulose, Paper & Water Research Group

UCM INGENIERÍA QUÍMICA

Carlos Negro

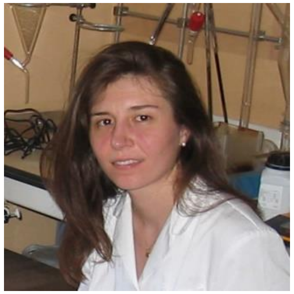
Ángeles Blanco

Concepción Monte

Helena Fuente

Rubén Miranda

Antonio Tijero



Daphne Hermosilla

Noemí Merayo

Ana Balea

Patricio López

Cristina Campano

Sara Gilarranz

José Luis Sánchez

Javier Tejera

Jiret Vargas

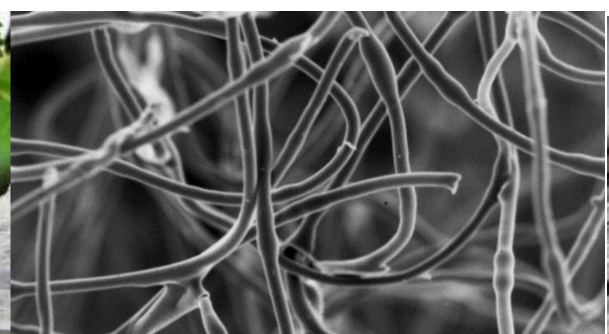
MICROCELLULOSE CTQ 2012-36868-C02-01)
NANOSOLPAPEL-REC (CTQ2013-48090-C2-1-R)
NANOPROSOST (CTQ2017-85654-C2-2-R).

GOBIERNO DE ESPAÑA
MINISTERIO DE ECONOMÍA, INDUSTRIA Y COMPETITIVIDAD

THE ROLE OF NANOCELLULOSE IN SUSTAINABLE FUTURE MATERIALS

C. Negro, C. Monte, H. Fuente, A. Balea, N. Merayo, C. Campano and A. Blanco. UCM, Madrid

cnegro@ucm.es



Incentives for Manufacturing Industry

- New source of raw material with wide, largely unexplored range of applications
  - New products

Nature-based

Huge applications

UCM INGENIERÍA QUÍMICA

NANO CELLULOSE

Why nano?

The size reduction enables new opportunities for the development of innovative nano systems and nanostructured materials

Particle of any shape with dimensions < than 100 nm

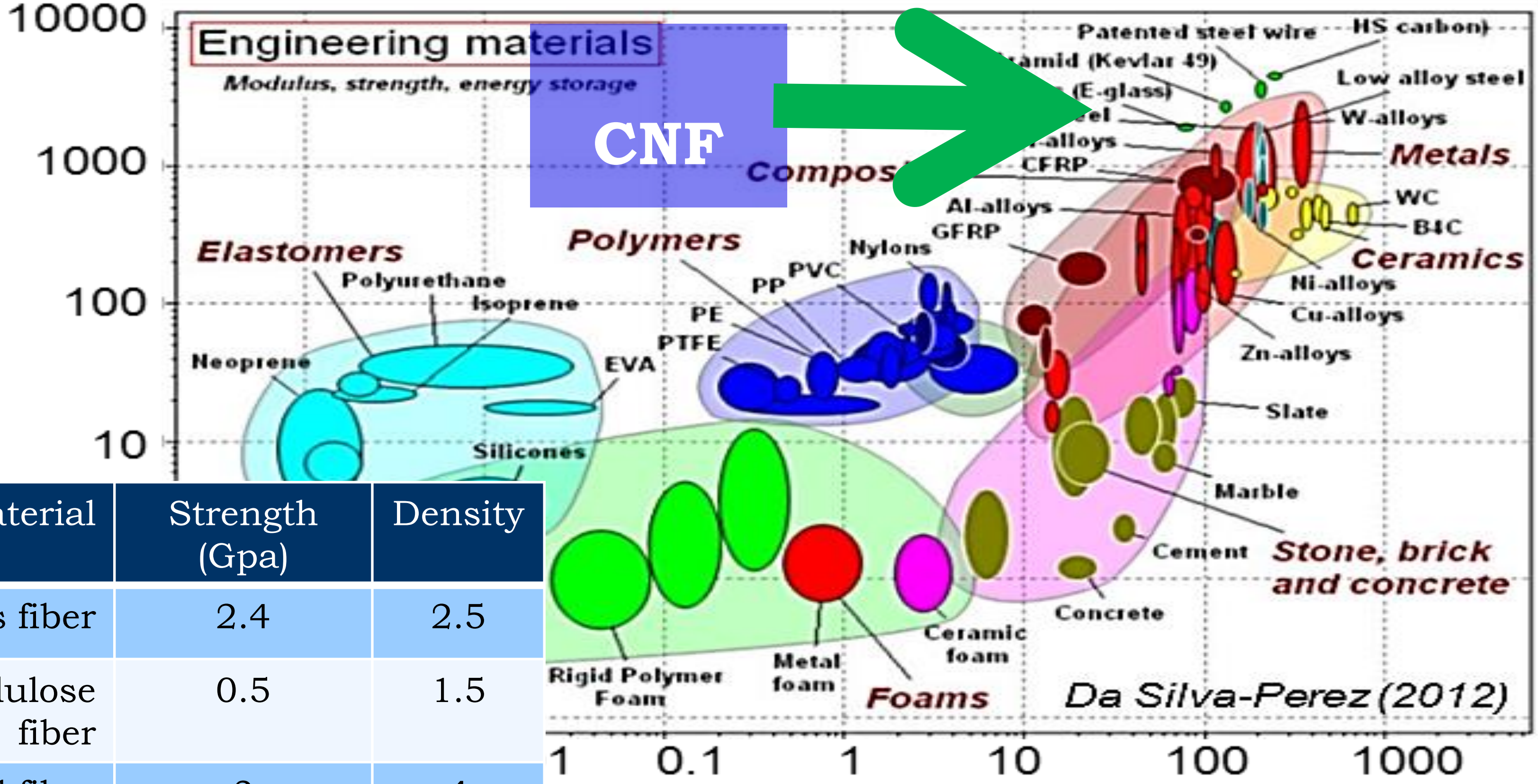
- Very strong
- Large specific area
- Highly reactive
- Less Defect
- Thermal stability
- Unique optical, electrical, magnetic properties

Why cellulose?

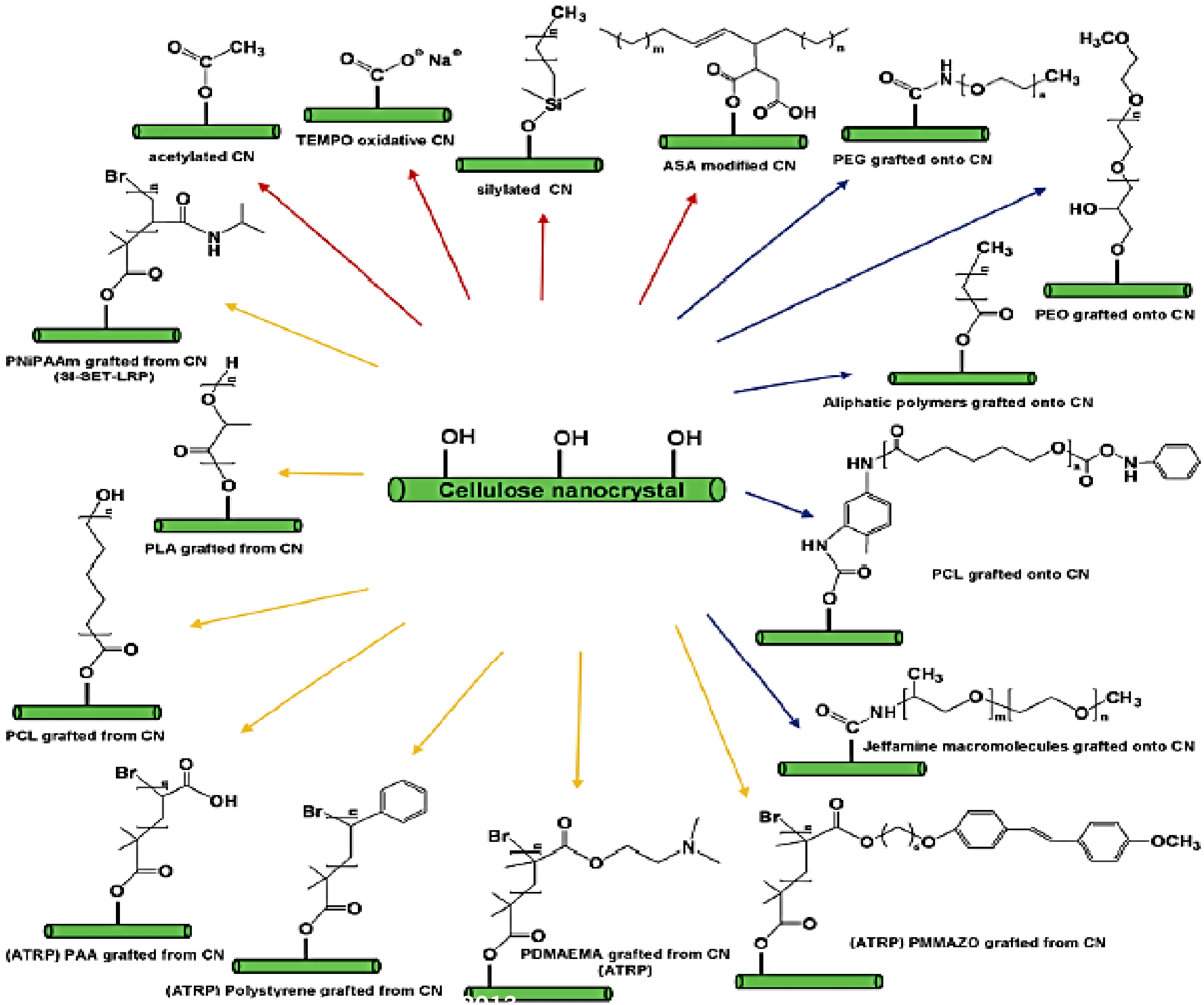
A sustainable material: high availability, natural & renewable, economic, non-toxic, biocompatibility and biodegradability

- High strength & modulus
- Flexible
- Lightweight material
- Electrically charged
- Chemically reactive
- Dimension stability
- Water absorption
- Barrier properties
- High aspect ratio
- Transparent and translucent
- Builds network structures

At the nano-scale, the material has fewer defects, and it is therefore stronger



Material	Strength (Gpa)	Density
Glass fiber	2.4	2.5
Cellulose fiber	0.5	1.5
Steel fiber	3	4
CNC	10	1.5
CNF	9-10	1.5


Cellulose nanocrystal
acetylated CN
TEMPO oxidative CN
silylated CN
ASA modified CN
PEG grafted onto CN
PEO grafted onto CN
Aliphatic polymers grafted onto CN
PCL grafted onto CN
Jeffamine macromolecules grafted onto CN
(ATRP) PMMAZO grafted from CN
PDMAEMA grafted from CN
(ATRP)
(ATRP) Polystyrene grafted from CN
(ATRP) PAA grafted from CN
PCL grafted from CN
PLA grafted from CN
PNIPAAm grafted from CN
(SI-SET-LRP)

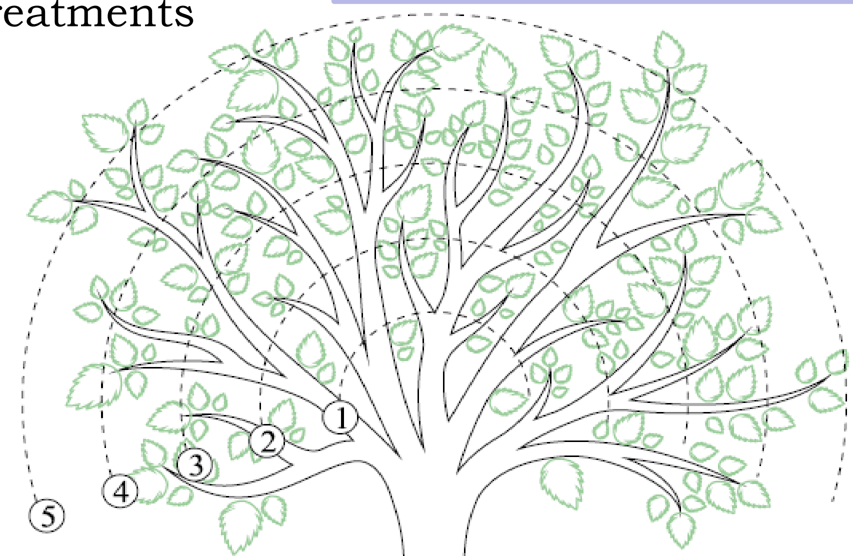
PULP SUSPENSION PRODUCTION

Chemical treatments:

- cooking
- bleaching

Mechanical treatments:
Recycling Treatments

➢ **50 types of CNF**



1 raw material
(wood, plants, agricultural wastes…)

CNF PRODUCTION

Pre-treatments:

- TEMPO oxidation
- carboxylation
- carboxymethylation
- sulfonation
- enzymatic hydrolisis

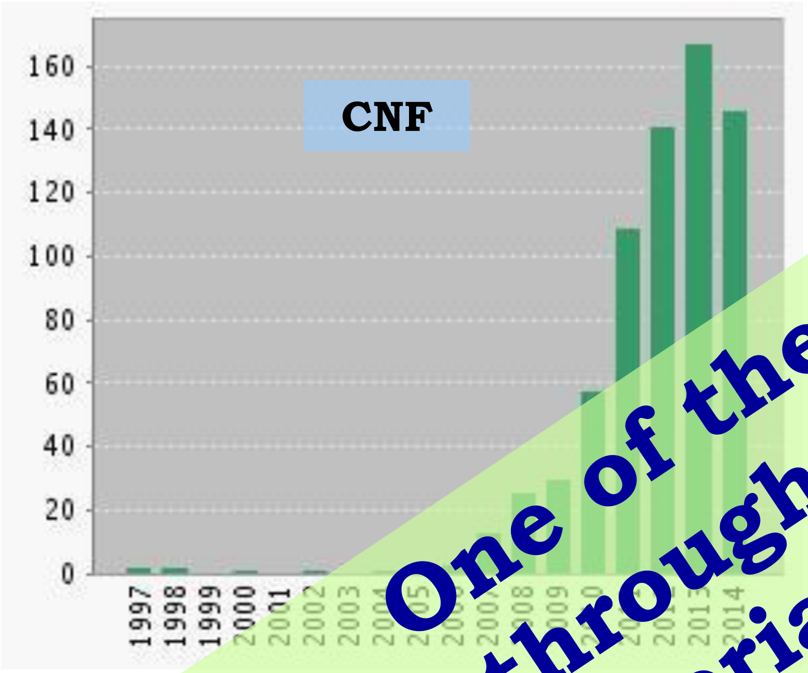
Mechanical treatment:

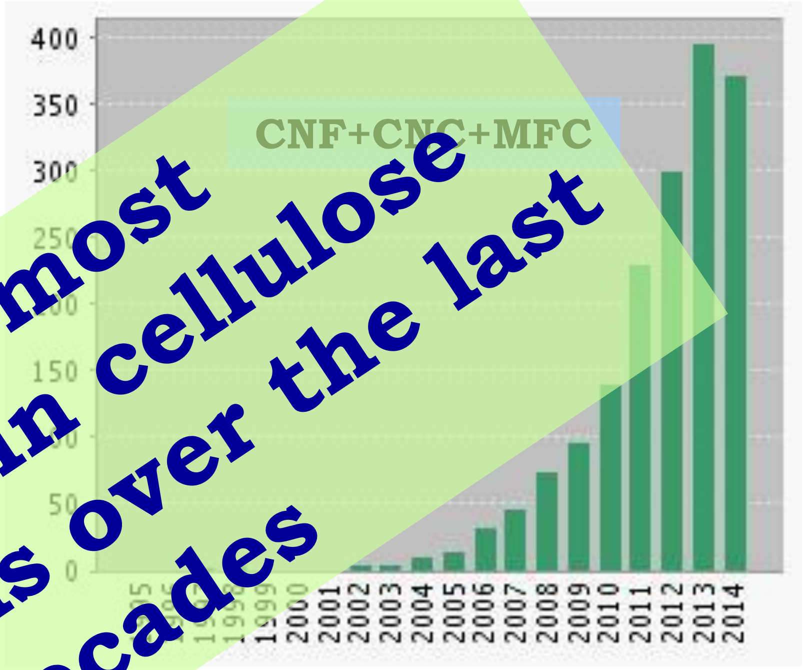
- homogenization
- microfluidization
- refining
- grinding
- electrospinning
- cryocrushing
- ultrasonication
- steam explosion

Post-treatments:

- chemical modification
- fractionation

NANOCELLULOSE EVOLUTION
INTEREST OF SCIENTIFIC COMMUNITY





One of the most breakthrough in cellulose based materials over the last two decades

Increasing interest in nanocellulose can be seen from the exponential rise in the scientific reports dealing with nanofibrillated cellulose and cellulose nanocrystals since 2000.

NC is unique among nanomaterials because it is bio-based, renewable, biodegradable and non-toxic.

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- **Cellulose nano-objects**
- **Cellulose nanomaterials (CN)**
- **Nanofibrillated cellulose (NFC)**
- **Nanofibrillar cellulose (NFC)**
- **Microfibrillated cellulose (MFC)**
- **Microfibrillar cellulose (MFC)**
- **Cellulose microfibril (CM…**
- **Cellulose nanofibre (…**
- **Cellulose nano…**
- **Cellulose …**
- **Cell… …aterials**
- **…ose (NCC)**
- **…rticles (CNP)**
- **…icrocrystal (CMC)**
- **C…ose nanowhiskers (CNW)**
- **Bacteria Nanocellulose**

ISO/TS 20477:2017 Nanotechnologies
Standard terms and their definition for cellulose nanomaterial

Cellulose Nanofibril (CNF)

Cellulose (3.2.4) nanofibre (3.1.6) composed predominantly of cellulose and composed of at least one elementary fibril (3.2.5), containing crystalline (3.2.1), paracrystalline (3.2.3) and amorphous (3.2.2) regions, with aspect ratio usually greater than 10, which may contain longitudinal splits, entanglement between particles, or network-like structures

- **The dimensions are typically 3-100 nm in cross-section and typically up to 100 µm in length.**
- **The terms nanofibrillated cellulose (NFC), nanofibrillar cellulose (NFC), microfibrillated cellulose (MFC), microfibrillar cellulose (MFC), cellulose microfibril (CMF) and cellulose nanofibre (CNF) have been used to describe cellulose nanofibrils produced by mechanical treatment of plant materials often combined with chemical or enzymatic pre-treatment steps.**

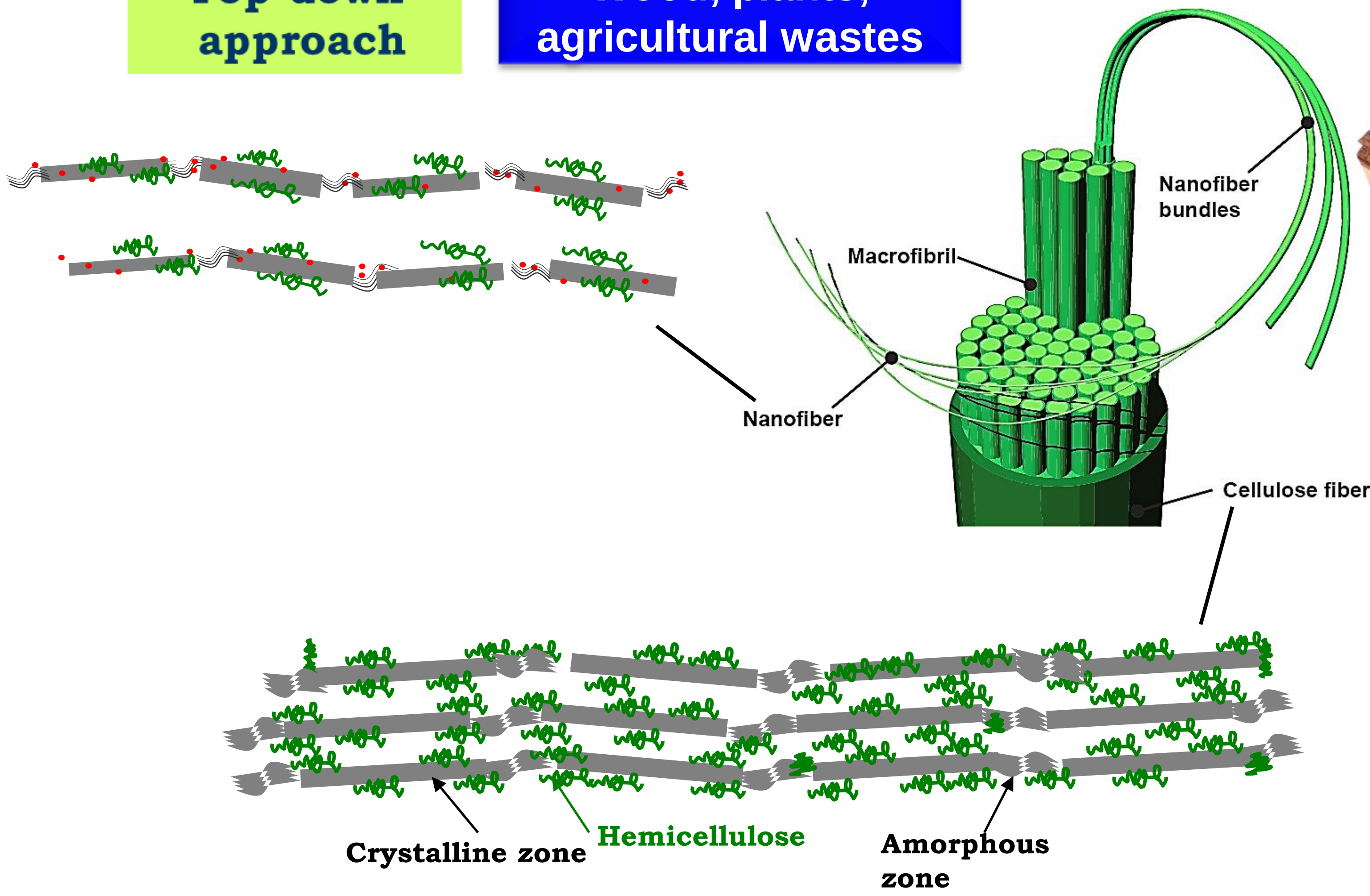
Cellulose Nanocrystal (CNC)

Nanocrystal (3.1.7) predominantly composed of cellulose (3.2.4) with at least one elementary fibril (3.2.5), containing predominantly crystalline (3.2.1) and paracrystalline (3.2.3) regions, with aspect ratio of usually less than 50 but usually greater than 5, not exhibiting longitudinal splits, inter-particle entanglement, or network-like structures

- **The dimensions are typically 3-50 nm in cross-section and 100 nm to several µm in length depending on the source of the cellulose nanocrystal.**
- **Historically cellulose nanocrystals have been called nanocrystalline cellulose (NCC), whiskers such as cellulose nanowhiskers (CNW), and microfibrils such as cellulose microfibrils; they have also been called spheres, needles or nanowires based on their shape, dimensions and morphology; other names have included cellulose micelles, cellulose crystallites and cellulose microcrystals.**

Top-down approach

Wood, plants, agricultural wastes



Top-down approach

Wood, plants, agricultural wastes

Deslignification

Cellulose fibers

Acid hidrolysis

Nano-defibrillation

Cellulose nanocrystals

High cristallinity

D:3-10 nm, L:50-500 nm

Rigid needle-like structure

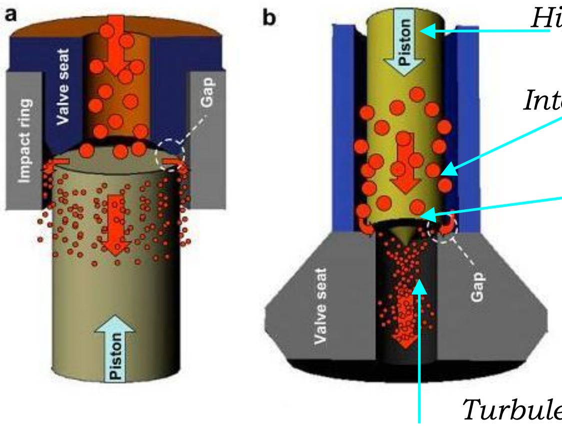
Cellulose nanofibers

High aspect ratio

D:5-50 nm, L: 0,2-2 μm

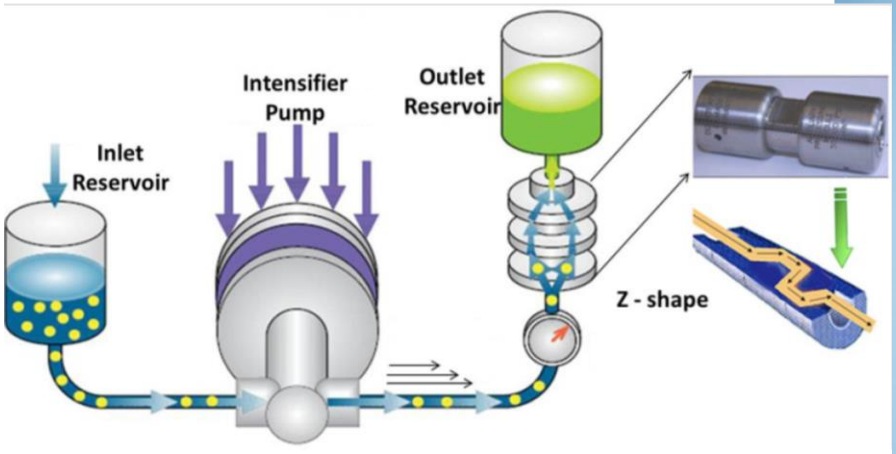
Flexible

Homogenizer



Scheme illustration of the principle of homogenization
lab-scale homogenizer (GEA niro-soavi),

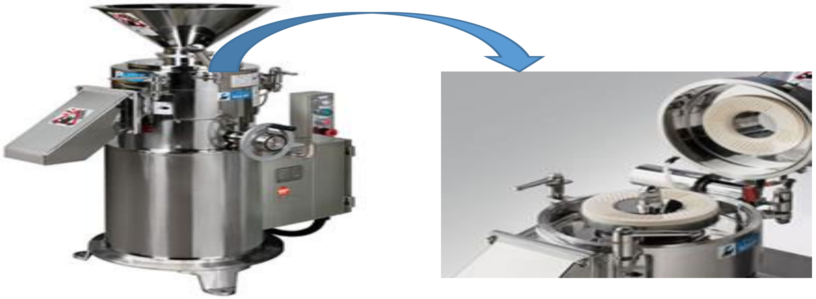
Microfluidizer



Basic concept of the single pump microfluidizer functionning

Refining

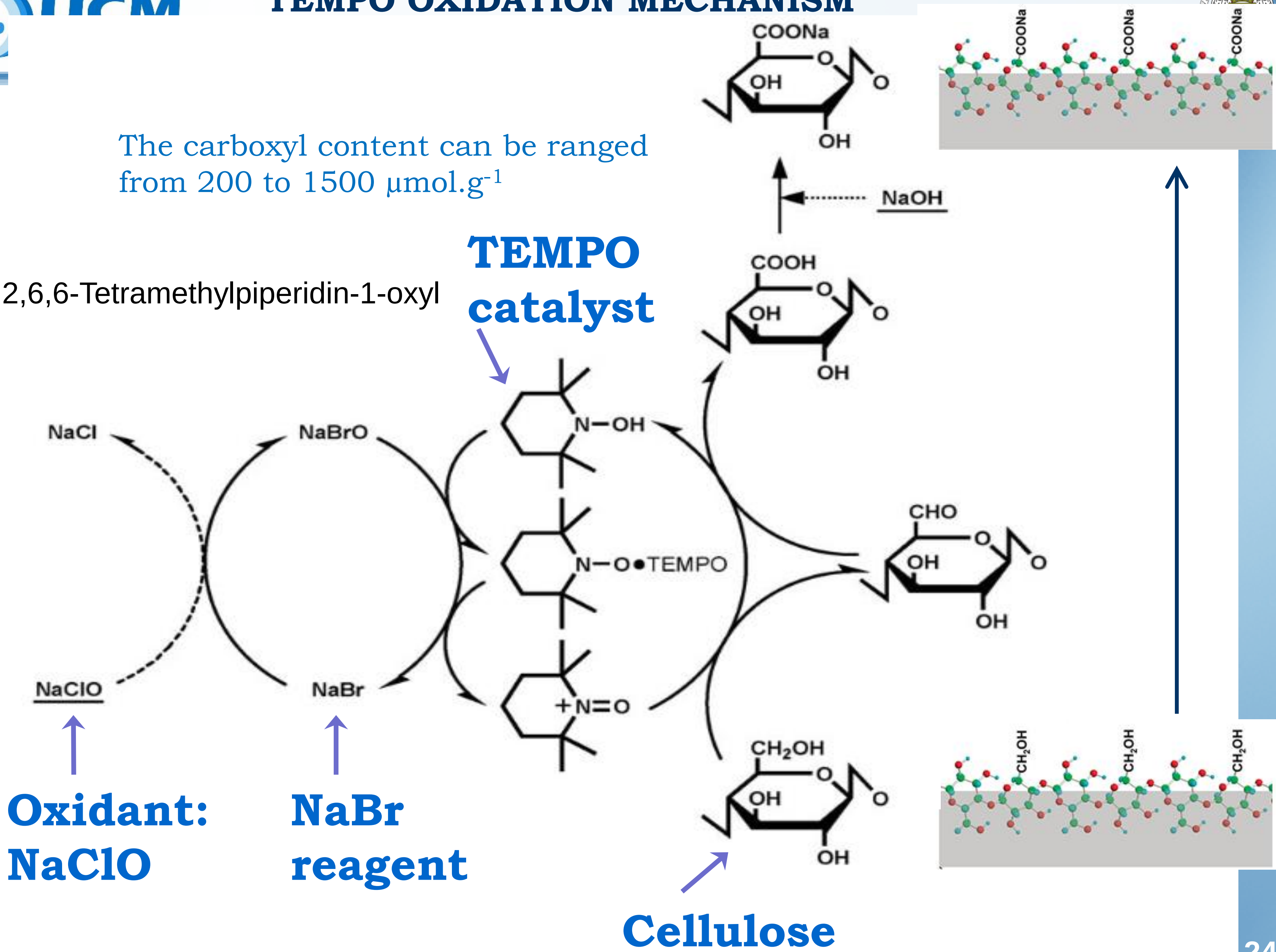
Grinding



TEMPO OXIDATION MECHANISM

The carboxyl content can be ranged from 200 to 1500 $\mu mol.g^{-1}$

2,2,6,6-Tetramethylpiperidin-1-oxyl



CELLULOSE NANOFIBRES

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Virgin Pulps	Agroforestry Wastes	Recovered Papers

PULPS

- ❑ Pine
- ❑ Eucaliptus

- ❑ Corn Stalk
- ❑ Rapessed Straw

- ❑ Pine Sawdust
- ❑ Eucaliptus Sawdust
- ❑ Triticale Straw

- ❑ NP

ECF

Organosolv

NaOH/AQ Bleached

PRETREATMENTS

Bleached NaClO

Refine

TEMPO NaBr + NaClO (pH=10)

TEMPO NaBr + NaClO (pH=10)

HOMOGENIZATION

CELLULOSE NANOFIBRE

- AFM
- Nanofibrillated Yield
- Transmittance
- Carboxilic Content
- Zeta Potenial
- Cationic Demand
- Polymerization Degree

Cellulose (2016) 24(2), Cellulose (2017); BioResources (2016) 11 (4), 8123; BioResources (2016) 11 (2), 3416; Industrial Crops and Products (2017) 97, 374

Methodology

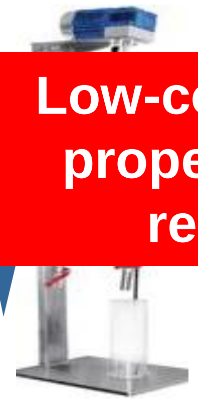
LOW-COST CNF

E-CNF
(1.5-5.0 wt%)

P-CNF
(1.5-5.0 wt%)

T-CNF
(1.5-5.0 wt%)

Recycled pulp: 100 % ONP
1.5 wt% consistency



Low-cost CNF to control linting propensity (High filler-loaded recycled papers): ONP

PCC
(20-60 wt%)

CNF-PCC suspension

Retention system:
Coagulant: 1.25 mg/g
cPAM: 0.75 mg/g
Bentonite: 1.7 mg/g

Drainage measurements sheets 60 g/m^2

Mechanical and physical characterization

Linting propensity (LintView)

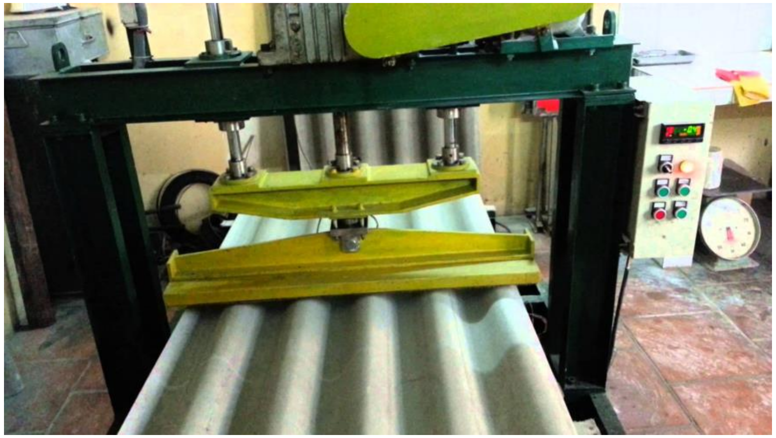
Dynamic drainage analyser (DDA)

A. Balea, et al.
Cellulose,Vol 25, No 2, February 2018

2. As additive

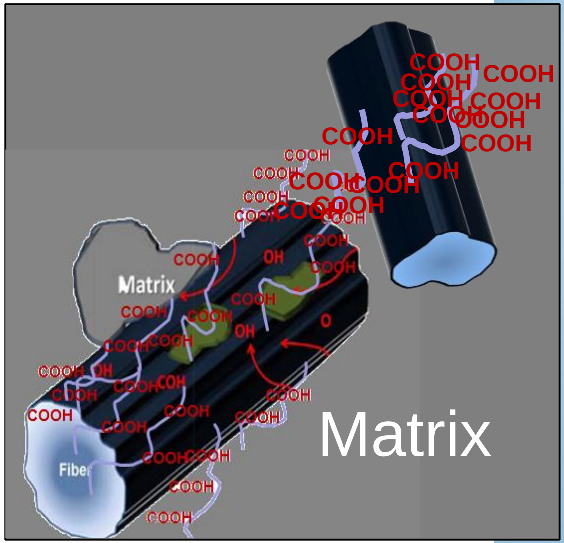
- **Improvement of bonding strength: MOE and MOR**
- **Enhancement of hardenning after 7 days**
- **Reducing of pull out**
- **Reducing porosity**

✓ **Low CN doses are enough for high improvements**



2.- Why does NC improve FC mechanical properties?

1. NC increases the interactions fibers ←→ matrix



NC has high hydrogen bonding ability

↓

↑ affinity for cellulosic fibers

↓

NC attaches on fiber surface and interacts with matrix and other fibers →

- ✓ **Improvement of bonding strength, MOE and MOR**
- ✓ **Contribute to reduce pull out**

2.- Why does NC improve FC mechanical properties?

2. Enhances hardenning near NC

Interaction with Ca++ → **NC swelling**

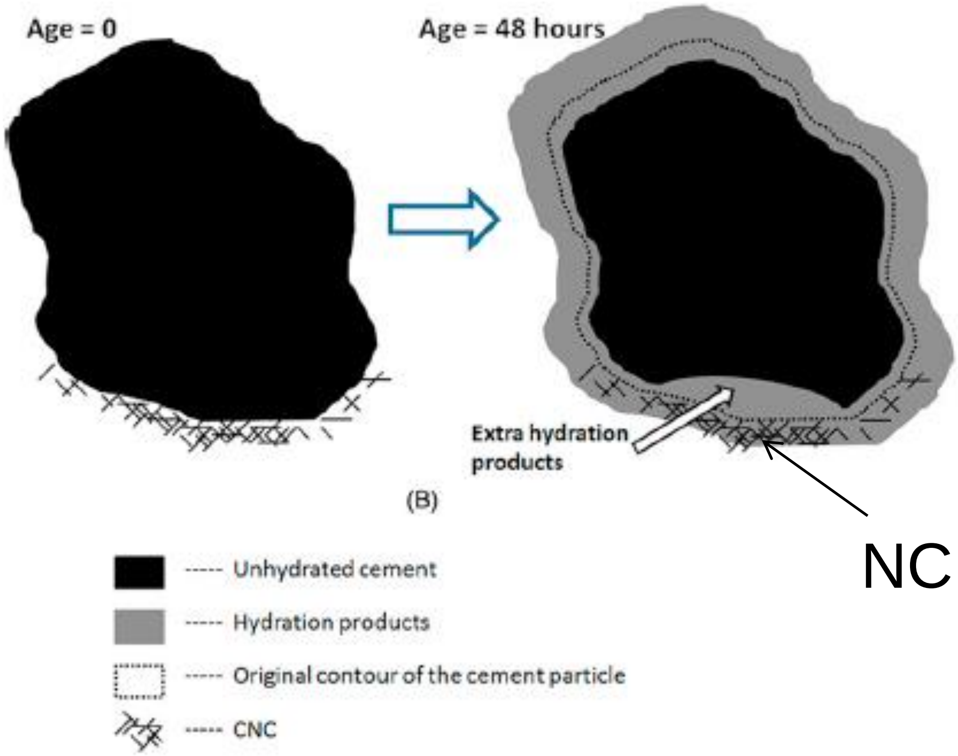
↑ H_2O and Ca^{++} in interface
Better difusión of H_2O in NC network

Accumulation of hydration products in interface

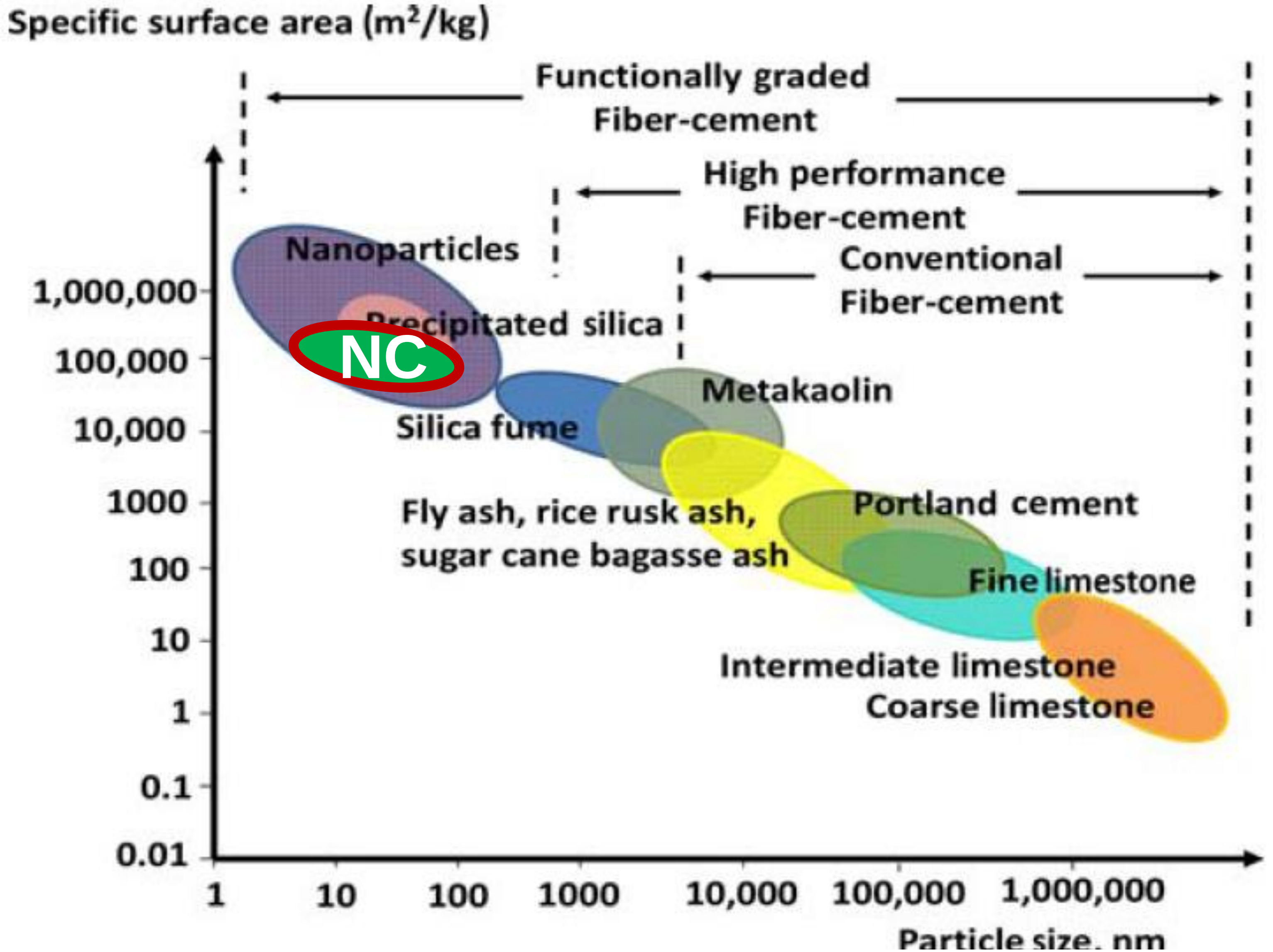
Block pores of fibers

Increase interaction fiber-matrix

Control of water in matrix



Parveen et al. (2017). Macro-and nanodimensional plant fiber reinforcements for cementitious composites. In Sustainable and Nonconventional Construction Materials using Inorganic Bonded Fiber Composites (pp. 343-382).



Sanchez and Sovolec. Nanotechnology in concrete – A review.
Construction and Building Materials
Volume 24, Issue 11, November 2010, Pages 2060-2071

Functionalised NC aerogels as superinsulation materials for buildings: synthesis, characterisation and integration

Interactions of functionalised NC aerogel powder and the components of the fibercement

Aerogel

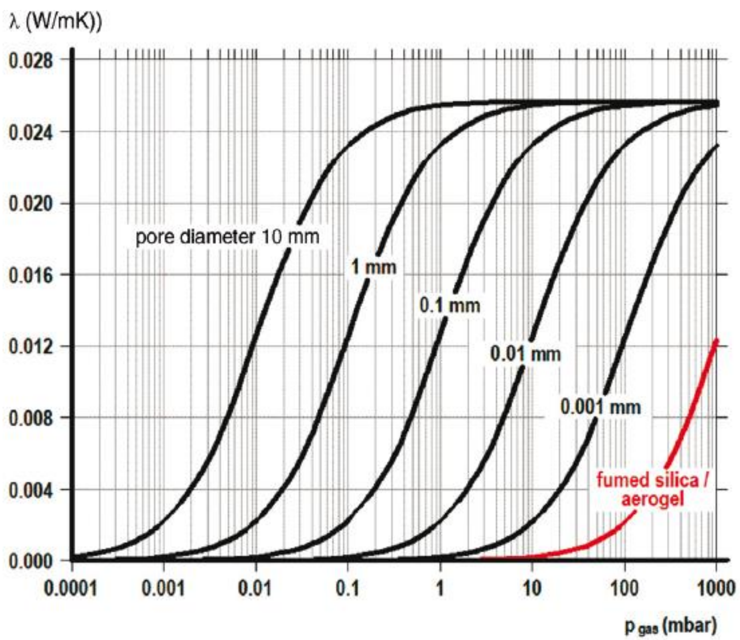
Polystyrene, phenolic resins, polyurethane, nylon…

Synthetic polymers

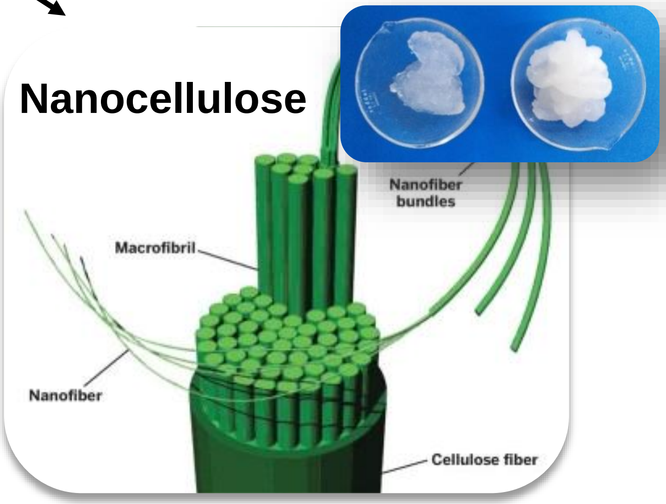
Renewable resources

Environmental concerns

Insulation material (<0.025 W/mK)



Nanocellulose



NC AEROGEL SUPERINSULATION

Aerogel

Synthetic polymers →

Polystyrene, phenolic resins, polyurethane, nylon…

Environmental concerns

CELLULOSE

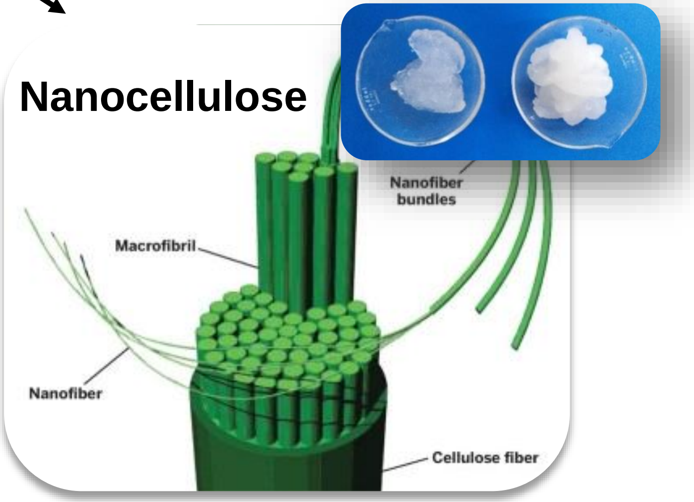
- High strength & modulus
- Flexible
- Lightweight material
- Electrically charged
- Chemically reactive
- Dimension stability
- Water absorption
- Barrier properties
- High aspect ratio
- Transparent and translucent
- Builds network structures

NANO

- Very strong
- Large specific area
- Highly reactive
- Less Defect
- Thermal stability
- Unique optical, electrical, magnetic properties

urces

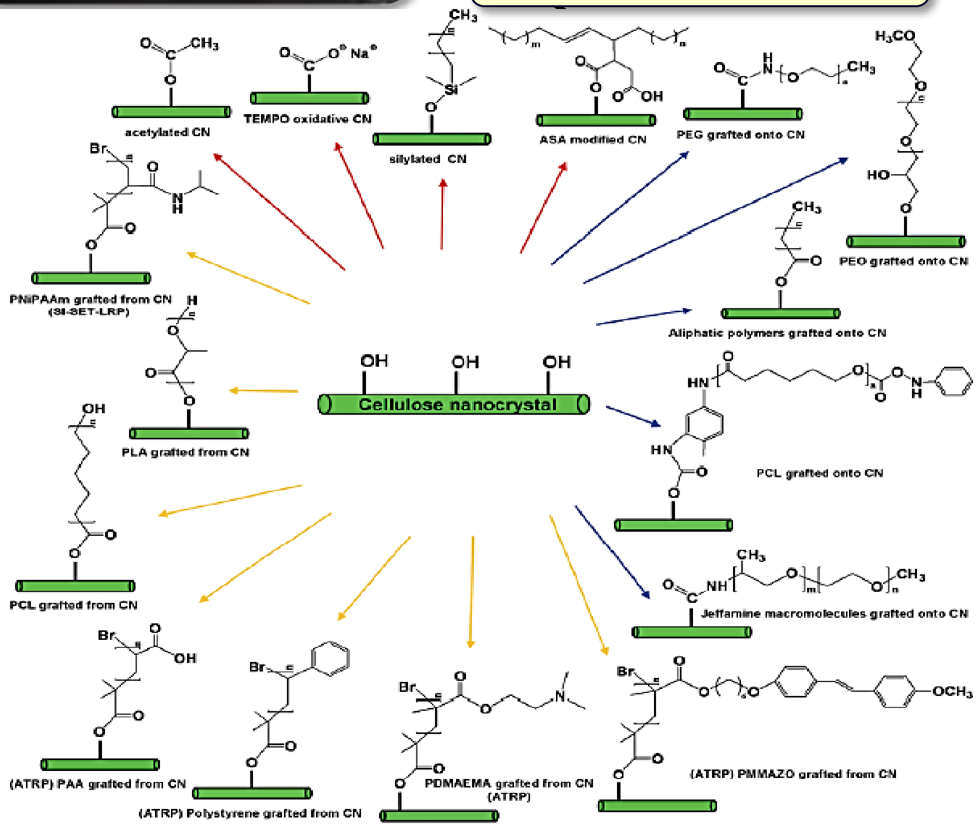
Nanocellulose



Aerogel

Synthetic polymer

Functionalised NC



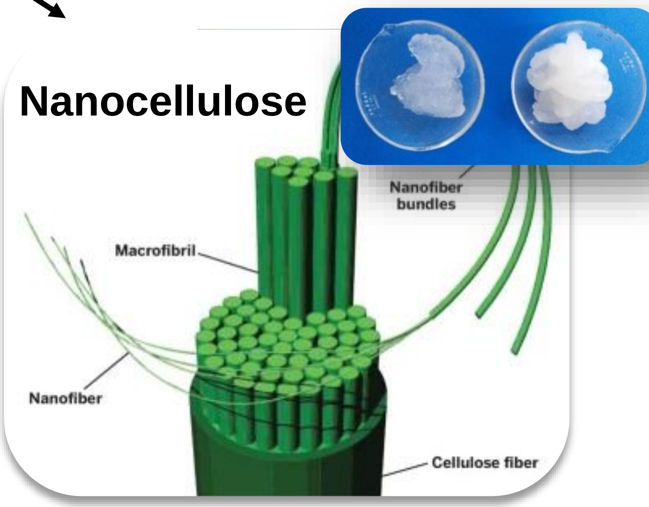
Functionalised NC aerogels:

Increasing:

- Dimensional stability
- Interfacial compatibility with the matrix
- Reinforcing capacity
- Adhesion of NC aerogel to the adjacent layers
- Durability

Decreasing:

- Water absorption of NC
- Cost production



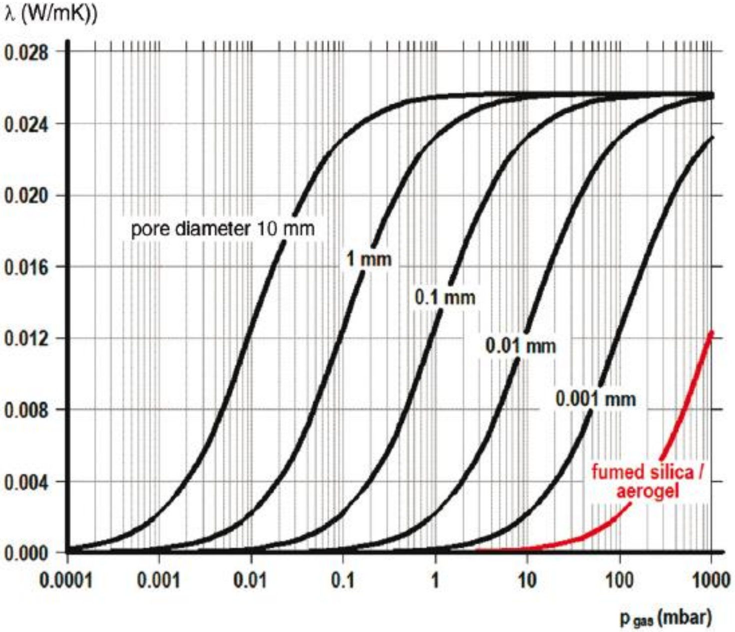
NC AEROGEL SUPERINSULATION

Aerogel

Building sector

Development "zero energy buildings"

Insulation material (<0.025 W/mK)



Piping, vessels, heat and cold storage appliances and devices

Functionalised NC aerogels as superinsulation materials for buildings: synthesis, characterisation and integration

A1) Production and characterisation of non-fuctionalised hydrogels of NC:

- Raw material: residual lignocellulose sources (e.g. agrowastes residues, recycled pulp).
- Production: mechanical/chemical pre-treatment+high-pressure homogeneization.
- Characterization: e.g. AFM, carboxylic groups, nanofibrillation yield, transmittance, zeta potential, cationic demand, polymerization degree, WRV.

A2) Production and characterization of non-fuctionalised aerogels (reference):

- Production: freeze-drying.
- Characterization: e.g. porosity, WRV, hidrofobicity, thermal conductivity, nanoestructure (pore distribution).

A3) Production and optimisation of functionalised NC hydrogels and aerogels:

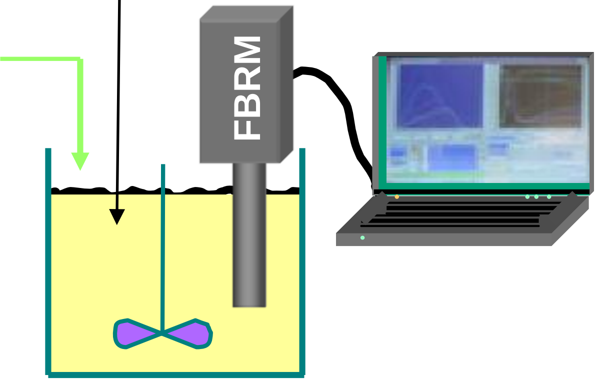
- Production: e.g. sylilation, grafting
- Characterization hydrogel/aerogel: idem A1 and A2

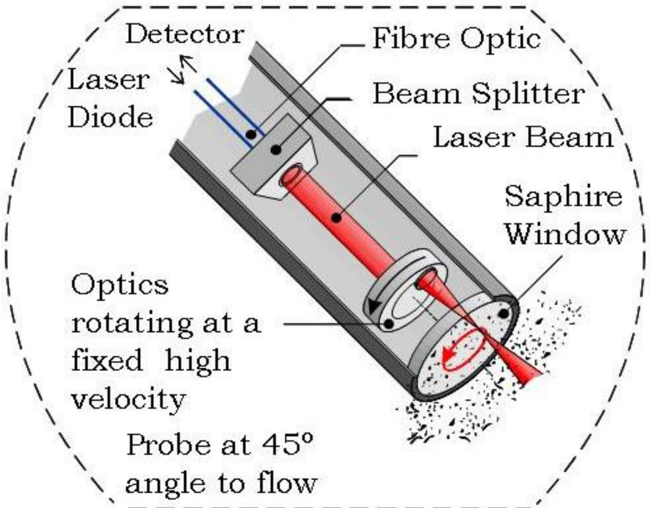
A4) Integration in non-residential building insulation: monolithic and divided materials.

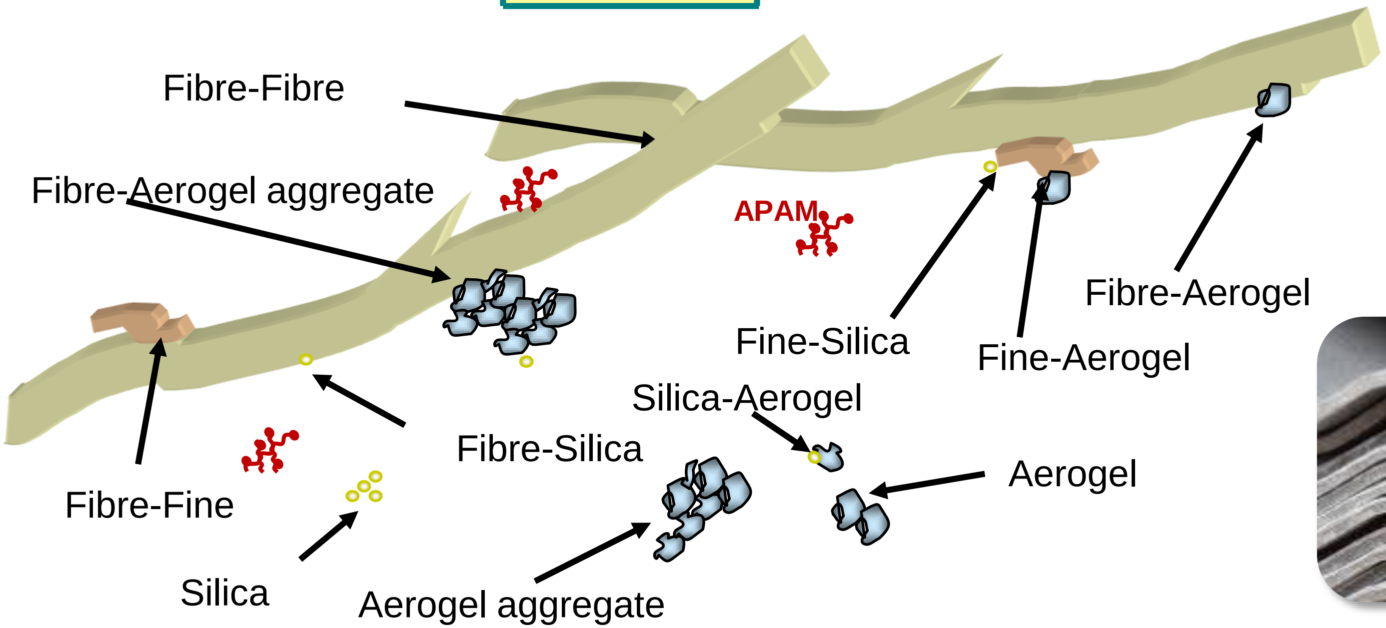
INTERACTION FUNCTIONALISED NC AEROGEL POWDER

Cellulose fibers
Cement
Silica
PVA
Functionalised NC aerogel powder

Flocculant: APAM







ACTIVITIES

Interactions of functionalised NC aerogel powder and the components of the fibercement

A1) Selection the funcionalised aerogels based on two criteria: low thermal conductivity and high hydrofobicity.

A2) Production and characterisation of fuctionalised NC aerogels powder:

- Production: grinding
- Characterization: e.g. particle distribution, WRV, hidrofobicity, thermal conductivity, nanoestructure (pore distribution).

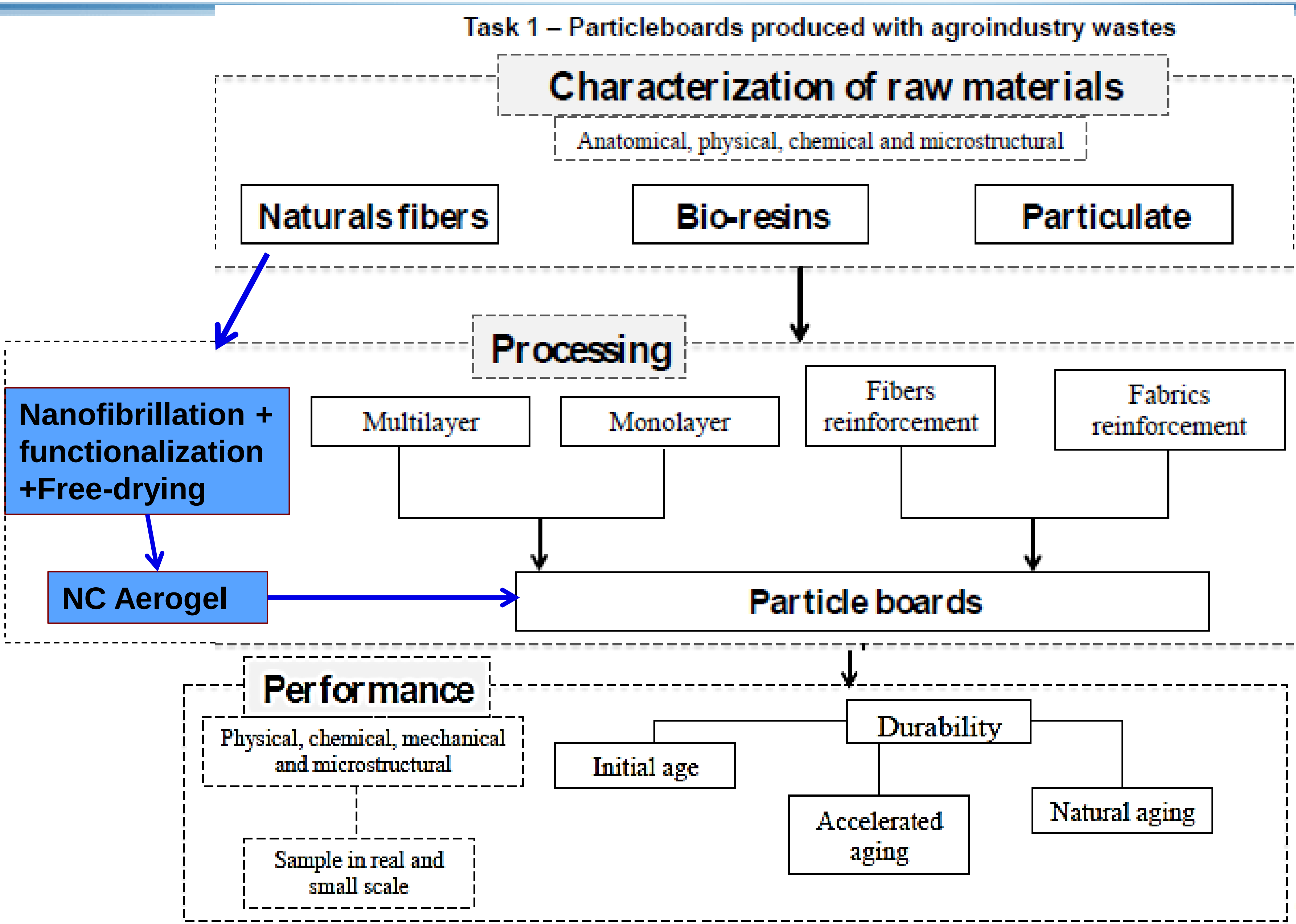
A3) Interaction of fuctionalised NC aerogels powder with fibercement component using FBRM (e.g. cellulose fibers, cement, silica…).

- Single interaction without flocculant (e.g. NC aerogel powder + cement; NC aerogel poder+cellulose fibers…)
- Interaction with APAM (e.g. NC aerogel powder + cement + APAM)

A4) Preparation and characterization of fibercement-aerogel composites.

- Preparation of probes of FC containing aerogel powder by mixing, casting, pressing and curing.
- Characterization of physical, mechanical and thermal properties
- Microstructure (SEM)

INTEGRATION IN THE PROJECT



INTEGRATION IN THE PROJECT