RECENT ADVANCES IN POLYMERS FROM RENEWABLE RESOURCES

Alessandro Gandini

Grenoble Polytechnic (France) and
University of São Paulo at São Carlos (Brazil)

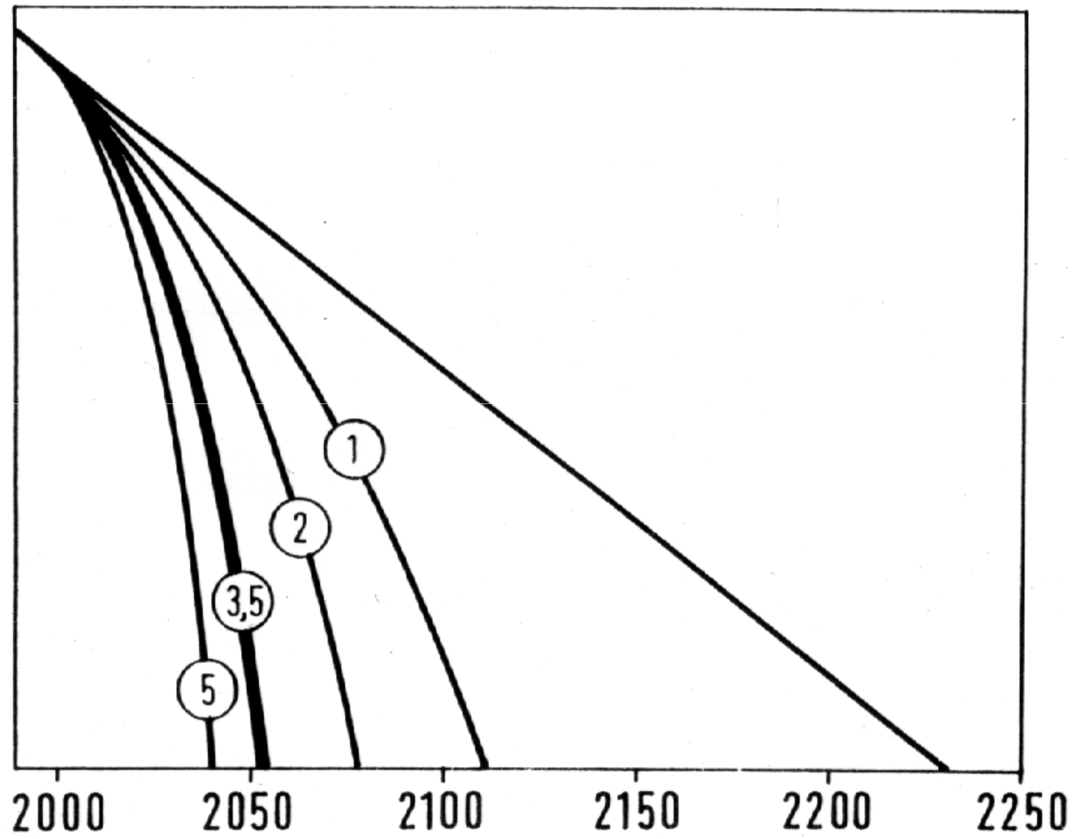
THE DWINDLING OF FOSSIL RESOURCES AND THE URGENT NEED TO IMPLEMENT SUSTAINABILITY HAVE SPURRED A VIGOROUS SURGE OF SCIENTIFIC AND TECHNOLOGICAL RESEARCH IN TWO DOMAINS:

- **THE SEARCH FOR ALTERNATIVE SOURCES OF ENERGY (NOT OUR DIRECT CONCERN IN THIS LECTURE!)**

- **THE USE OF RENEABLE RESOURCES TO PREPARE CHEMICALS AND POLYMERS AS AN ALTERNATIVE TO PETROCHEMICAL COUNTERPARTS:**

THIS IS THE PURPOSE OF THE LECTURE

Depletion of Natural Gas Resources



1 - 5 : % rise in consumption/annum

Canadian oil sands: dirtier than most oil on the market

Nature, 28 February 2012

RENEWABLE RESOURCES AS INDUSTRIAL RAW MATERIALS

-SUSTAINABLE

-CO_2 FIXATION

-UBIQUITOUS LOCAL SUPPLY (GLOBAL FAIRNESS COMPARED WITH PETROL!!)

-NEW PRODUCTS WITH IMPROVED BIOLOGICAL COMPATIBILITY AND (SOMETIMES) BIODEGRADABILITY

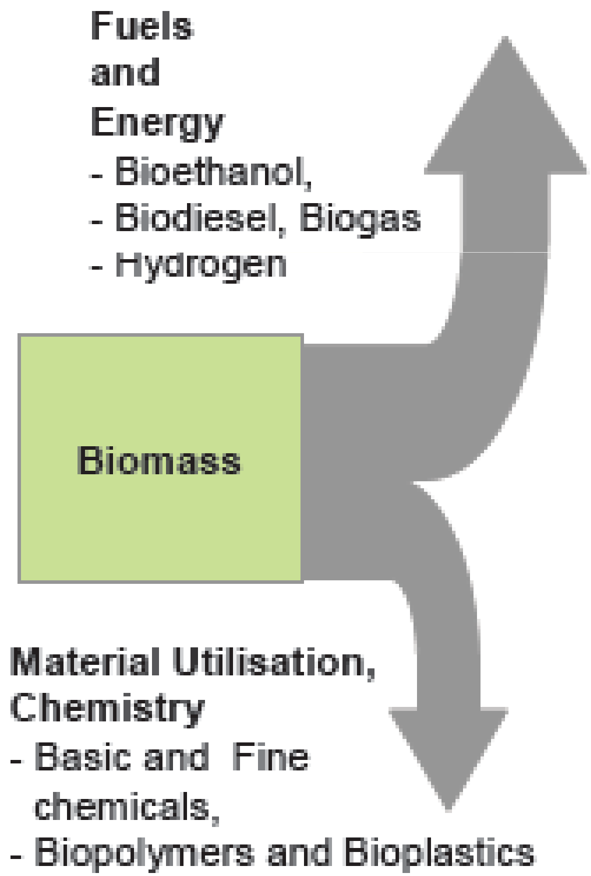
VEGETABLE BIOMASS REFINERIES

EFFICIENT SEPARATION OF THE BASIC COMPONENTS OF A GIVEN RENEWABLE RESOURCE IN VIEW OF THEIR RATIONAL EXPLOITATION FOR MAKING NEW MATERIALS, CHEMICALS, SYNTHONS, ETC.

EX. PAPERMAKING (*UP TO NOW, PRIORITY TO CELLULOSE*): STEAM EXPLOSION, ORGANOSOLV, TO SEPARATE AND EXPLOIT CELLULOSE, LIGNIN AND HEMICELLULOSES

The biorefinery paradigm

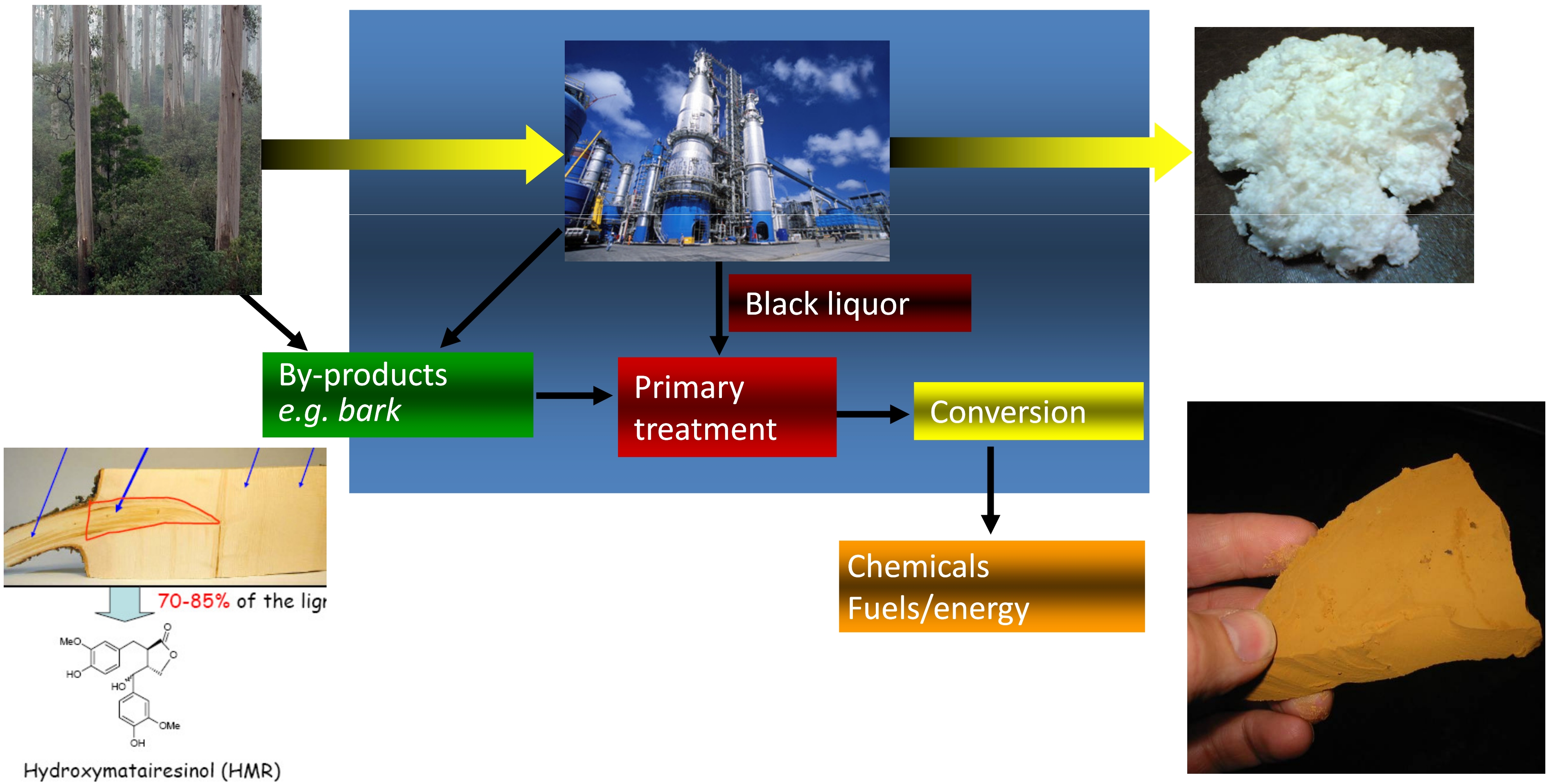
To replace oil refineries using biomass to produce:
- Chemicals and materials
- Fuels and energy



The concept is similar, but requires completely different approaches!

The lignocellulosic feedstock (LCF) biorefinery

- LCF-Biorefineries can be developed based on existing pulp mills
  - Reduced investment
    - Valorisation of waste streams



VEGETABLE BIOMASS

- **WOOD, ANNUAL PLANTS, AGRICULTURAL WASTES**
-
- **~10^{13} t, *renewed* at a rate of**
- **~3.10^{11} t per year**
- **MOSTLY:**
  - ***CELLULOSE (most abundant)***
  - ***LIGNINS (3rd most abundant)***
  - ***HEMICELLULOSES***
- **BUT ALSO:**
  - ***STARCH***
  - ***OILS, ROSIN, TANNINS***
  - ***TERPENES AND POLYISOPRENE,***
  - ***MARINE POLYSACCHARIDES (alginates)***
  - ***SUBERIN (from cork and birch),…***

ANIMAL BIOMASS

MOSTLY:

CHITIN (2nd most abundant) → CHITOSAN

PROTEINS

GELATIN

LEATHER

RESINS (Shellac, etc.)

FATS…

THREE STRATEGIES

1. CONVENTIONAL POLYMERS, BUT PREPARED FROM FROM RENEWABLE RESOURCES

2. THE CHEMICAL MODIFICATION OF NATURAL POLYMERS

3. NOVEL POLYMERS BASED ON MONOMERS FROM RENEWABLE RESOURCES

RECENT TRENDS AND ADVANCES

NATURE MAKES POLYMERS AND COMPOSITES

and

MAN USES THEM AS SUCH OR AFTER SUITABLE MODIFICATIONS

POLYSACCHARIDES

Cellulose

Hemicelluloses

Starch

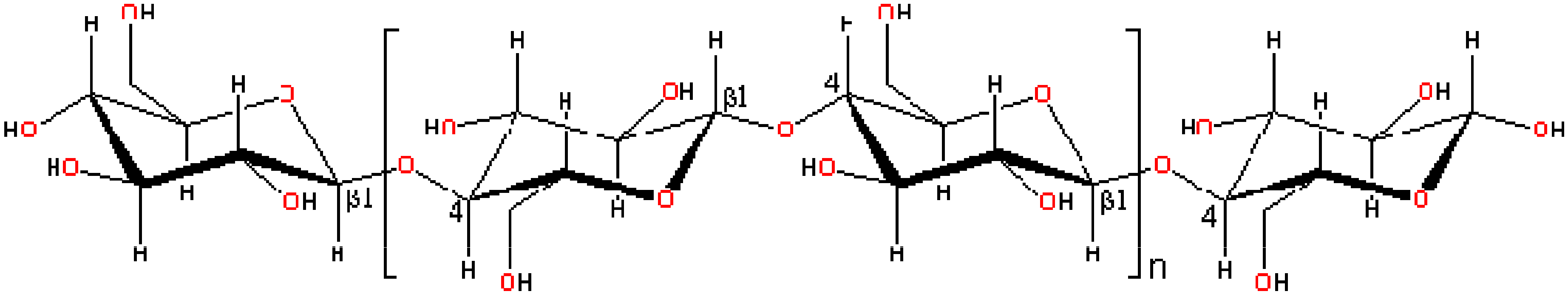
Chitin and Chitosan

CELLULOSE

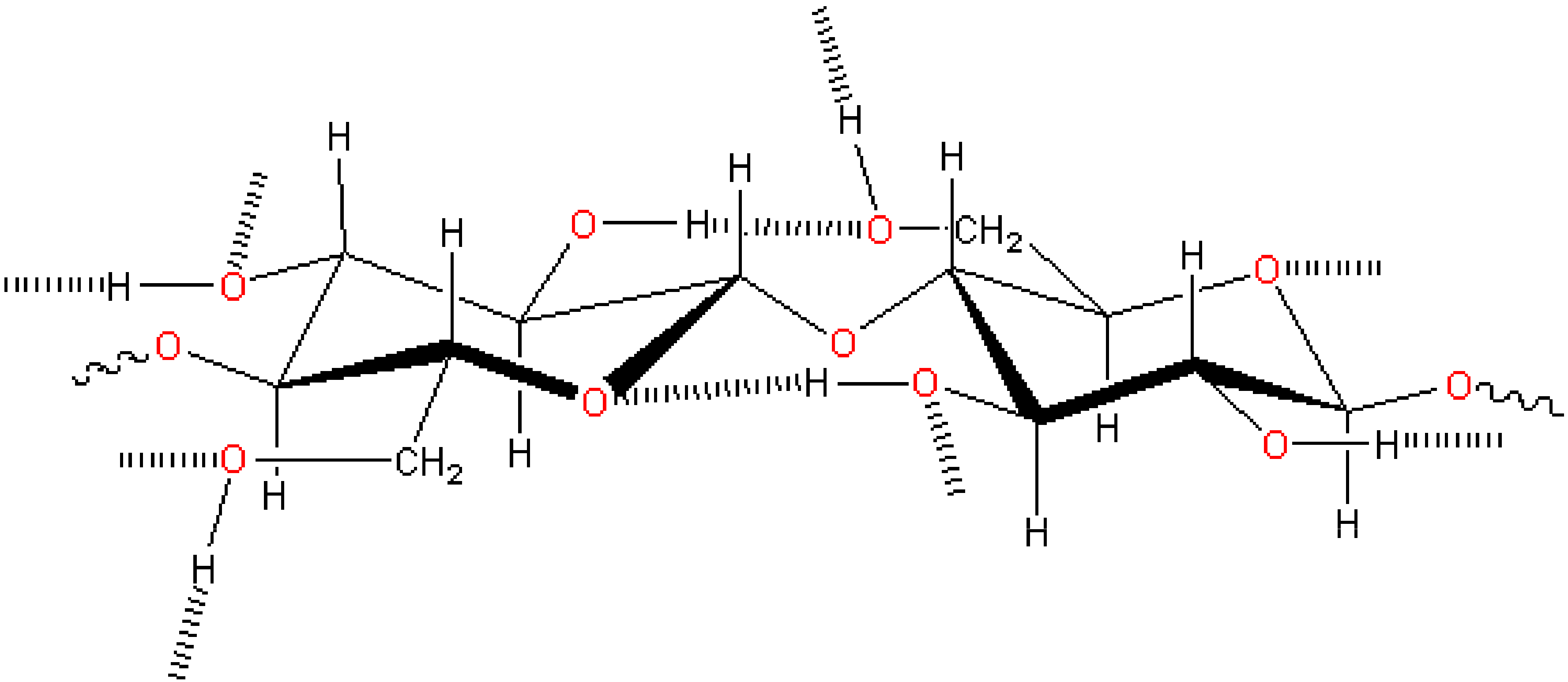
CELLULOSE IS THE MOST ABUNDANT NATURAL POLYMER ON EARTH

ITS MANIFESTATION IS ALMOST EXCLUSIVELY WITHIN THE VEGETABLE REALM

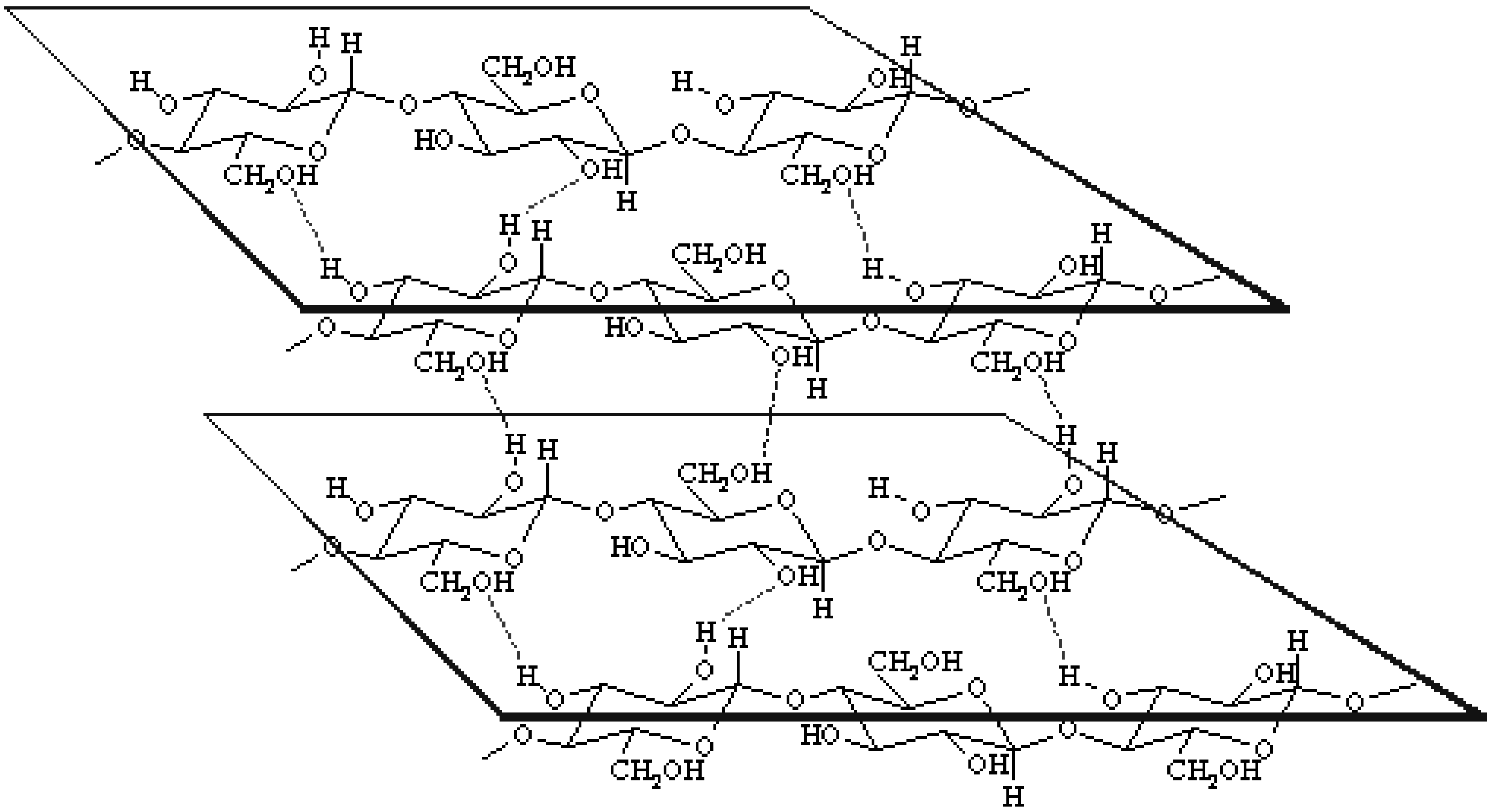
ALWAYS IN THE FORM OF FIBERS

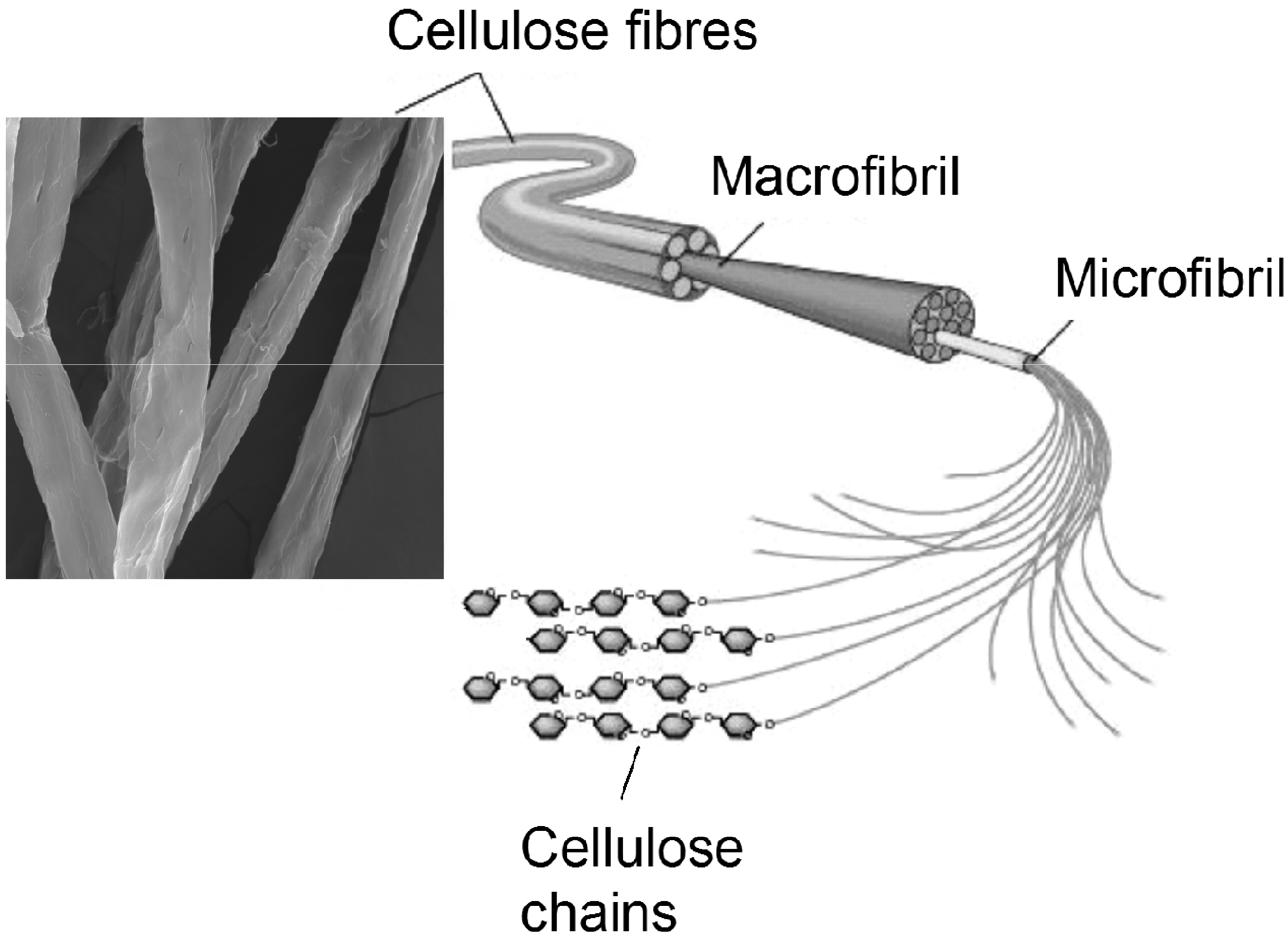


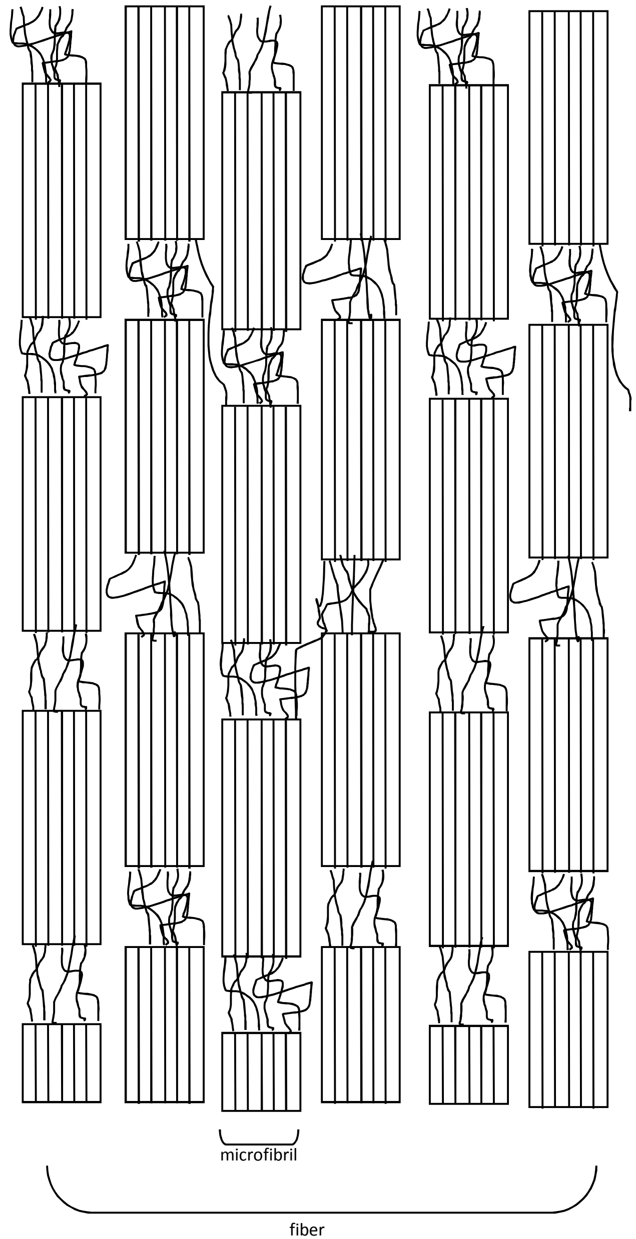
Cellulose is a linear polymer of β-(1→4)-D-glucopyranose units in $^{4}C_{1}$ conformation.



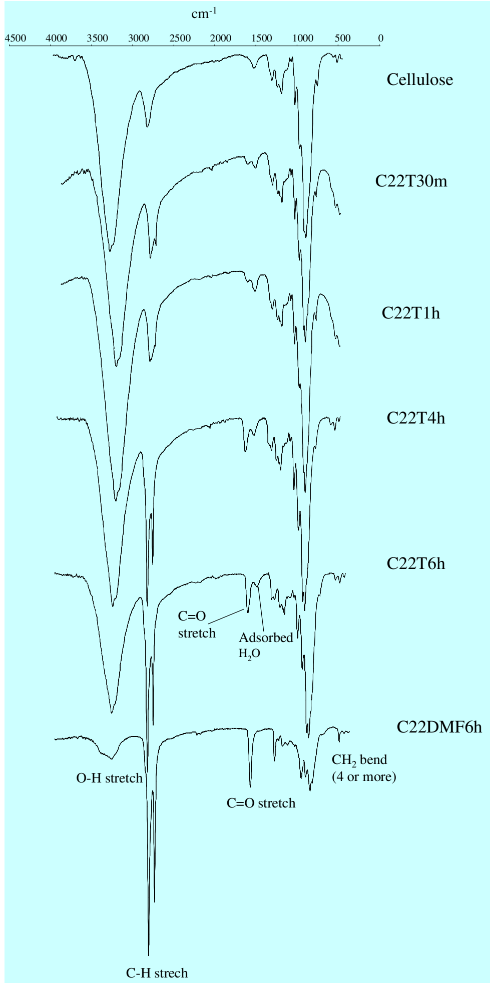
INTRA- AND INTER-MOLECULAR HYDROGEN BONDING

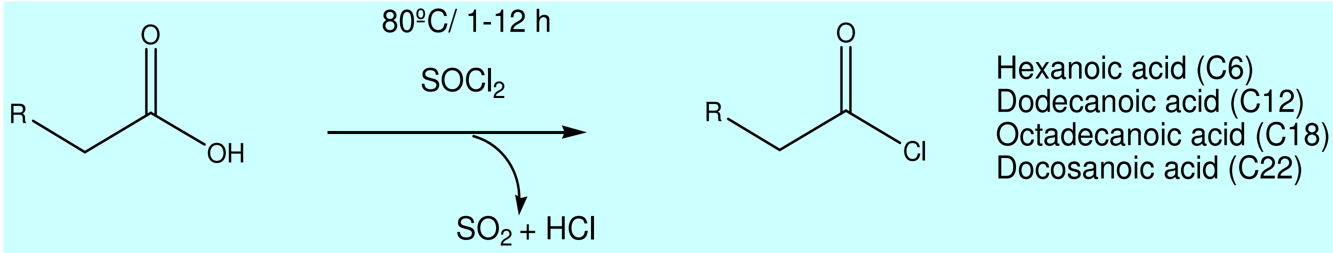


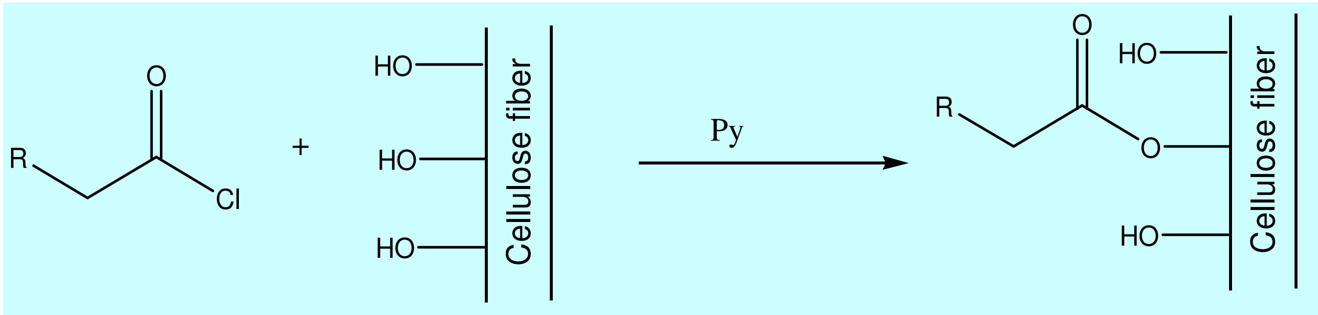

Cellulose fibres
Macrofibril
Microfibril
Cellulose
chains


microfibril
fiber

Controlled heterogenous modification of cellulose fibre surface with fatty acids (FA), i.e. another renewable resource



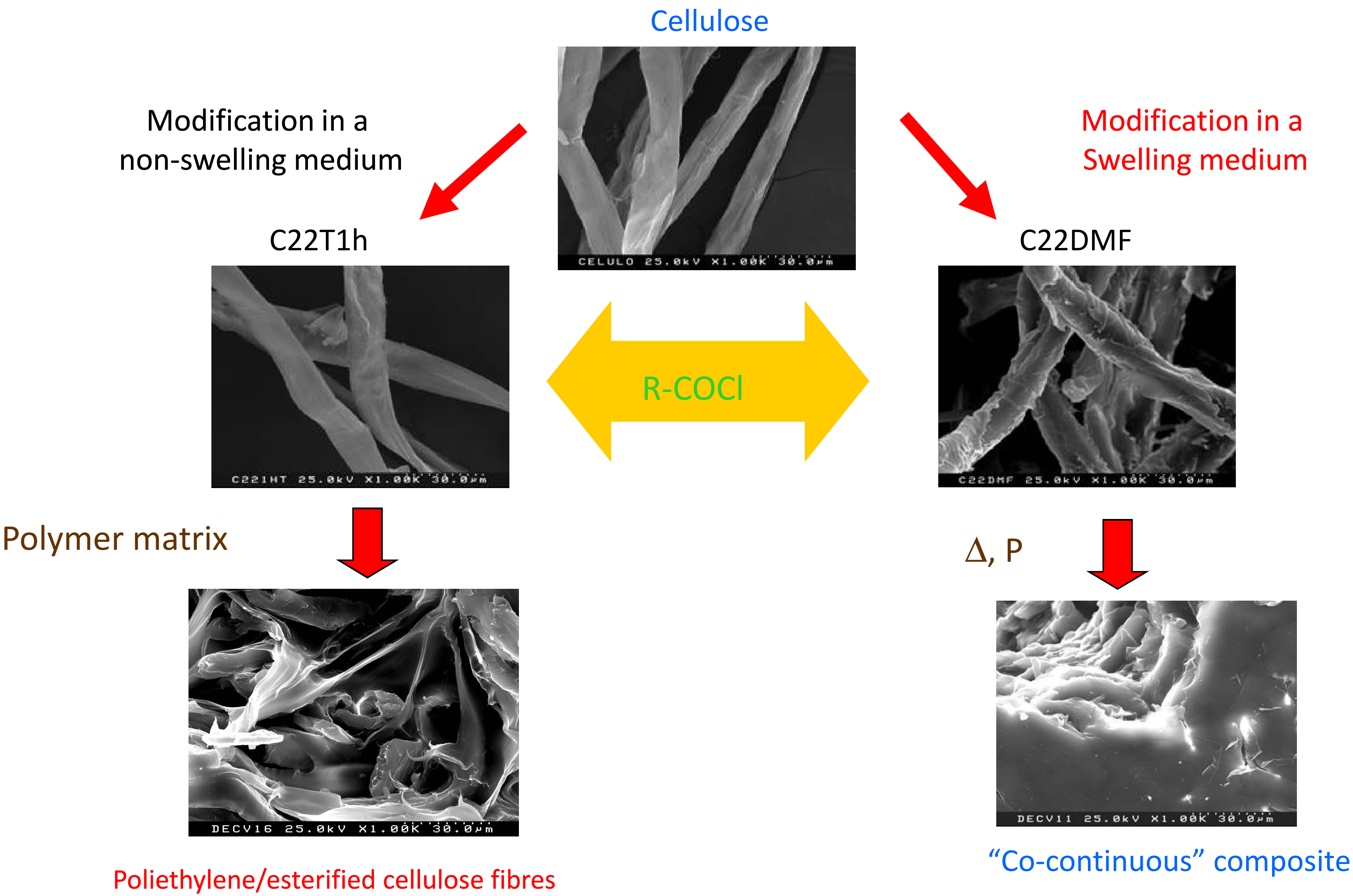




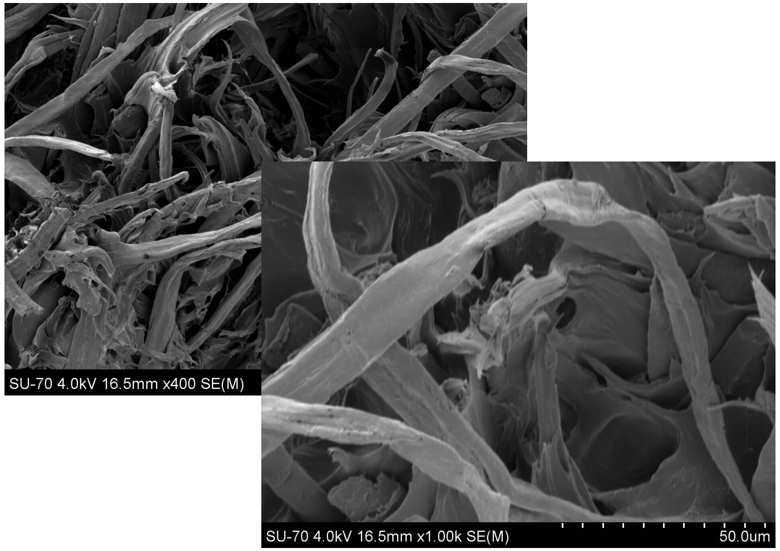
Reaction time: 30 min, 1h, 2h, 4h and 6h

Solvents: toluene or DMF

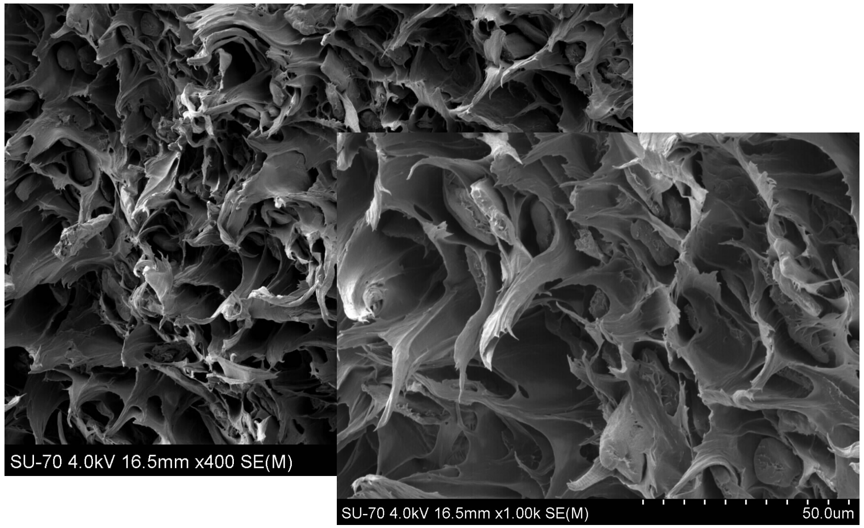
Carmen Freire, Aveiro University, Portugal


Cellulose
Modification in a
non-swelling medium
Modification in a
Swelling medium
C22T1h
C22DMF
R-COCl
Polymer matrix
Δ, P
Poliethylene/esterified cellulose fibres
"Co-continuous" composite

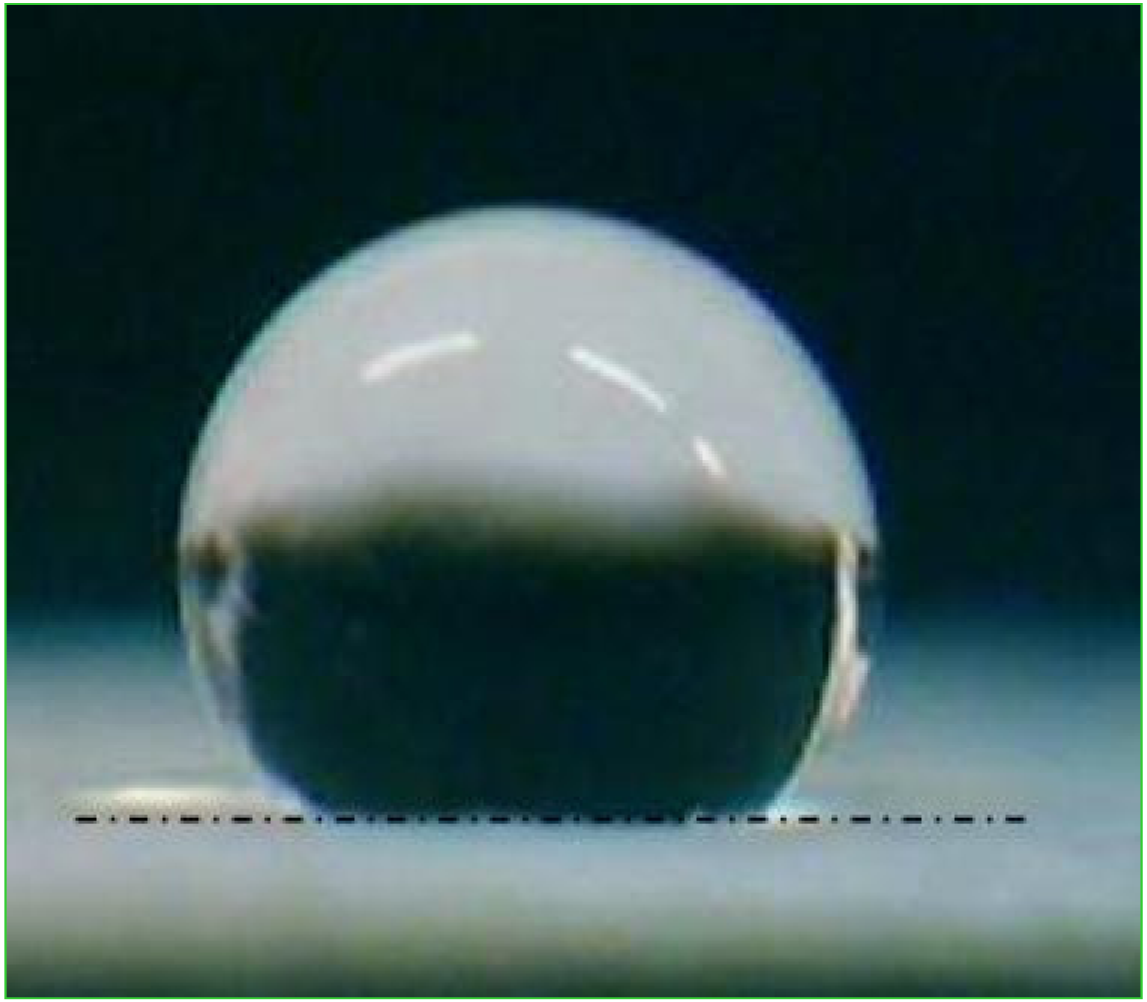
SEM ANALYSIS- Morphology



The interfacial adhesion between the unmodified cellulose fibers and the matrix was very poor

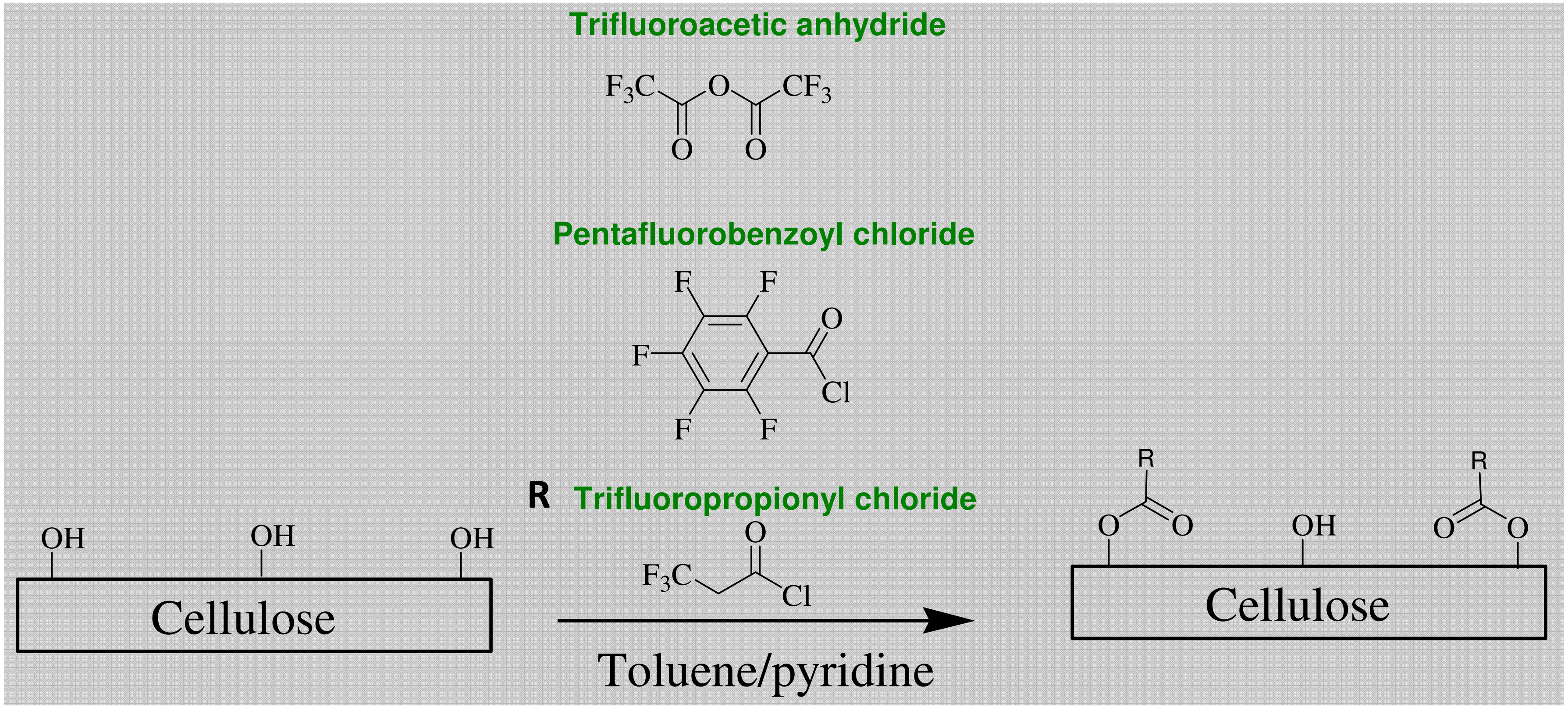


The modified fibers-based composites present a strong interfacial adhesion between the two components:



CREATION OF AN OMNIPHOBIC SURFACE

(High contact angles with both water and non-polar liquids)



Optimization of the reaction conditions:

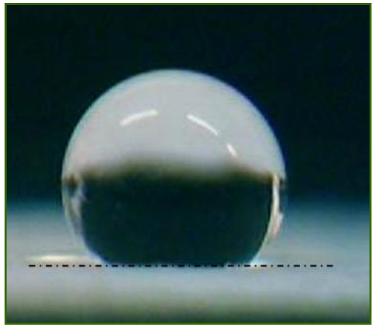
- Reaction time
- Temperature

Characterization of the ensuing cellulose derivatives:

- FTIR, XRD, TGA
- Surface Analysis
- Hydrolytic stability....

Gisela Cunha, Aveiro

Contact angles (θ) - Surface energy



	TFAA	PFBz	TFP
Contact angle with water (θ_w)	126	124	122
Contact angle with diiodomethane (θ_d)	103	73	91
Polar component of the surface energy (γ_s^p) / $mJ.m^{-2}$	0.1	0.6	0
Dispersive component of the surface energy (γ_s^d) / $mJ.m^{-2}$	7.2	21.8	12.3

High hydrophobicity

High lipophobicity

An extensive surface coverage is not necessary

Even for degree of substitution (DS) as low as 0.006

Low surface energies

(native cellulose ≈ 30+30mJ.m^{-2})

☑ Drastic reduction of the polar component
☑ Predominance of the dispersive component

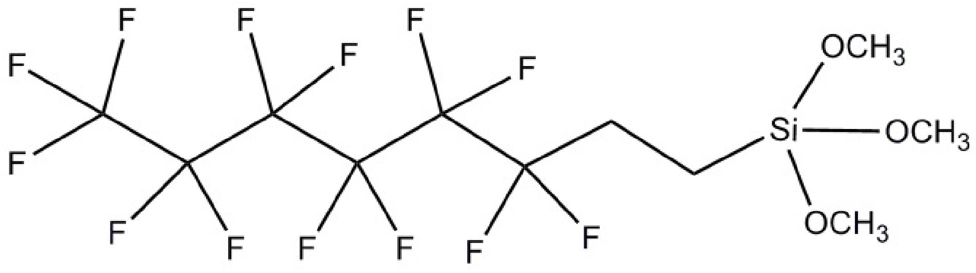
*TFAA – Trifluoroacetic anhydride
PFBz – Pentafluorobenzoyl chloride
TFP – Trifluoropropanoyl chloride

AN ALTERNATIVE APPROACH

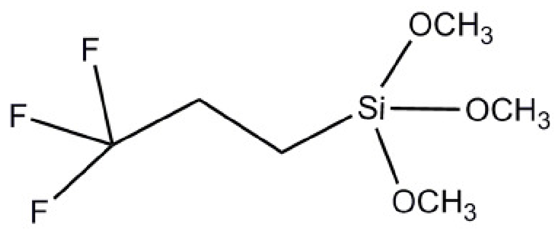
Gil Gonsalves Aveiro

Cellulose fibre surface modified by several steps: SiO_2 particles, five PDDA/SS and fluorosiloxanes.

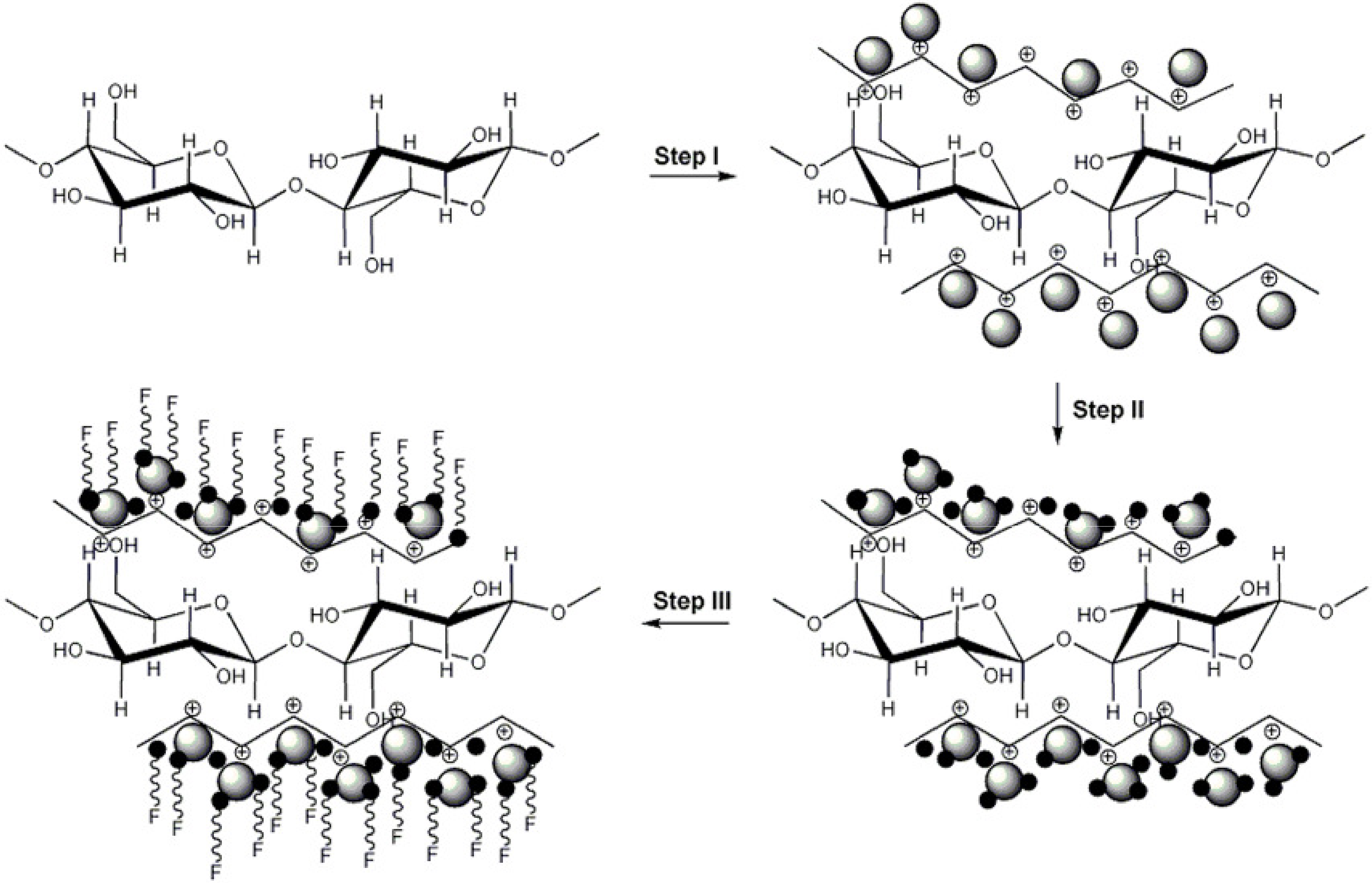
Sample	SiO_2 (800nm)	PDDA/SS	FPTS	FOTS	Water CAº
A-FPTS			*X*		***119.3***
B-FPTS	*X*		*X*		***126.2***
C-FPTS	*X*	*5X*	*X*		***136.3***
A-FOTS				*X*	***124.3***
B-FOTS	*X*			*X*	***136.3***
C-FOTS	*X*	*5X*		*X*	***146.8***



FOTS



FPTS


Step I
Step II
Step III

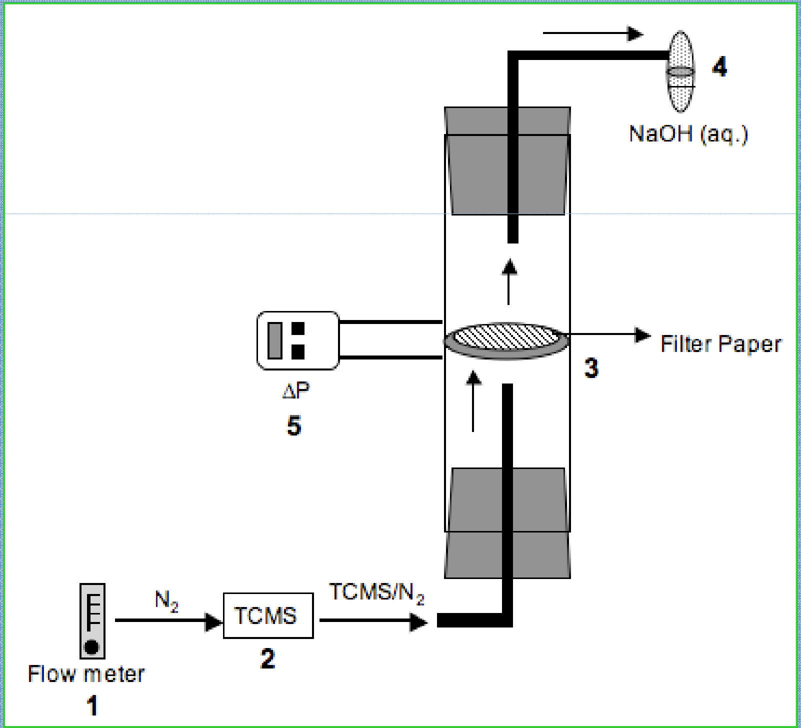
THE MOST RECENT

AND BY FAR THE SIMPLEST

DEVELOPMENT

Gisela Cunha Grenoble, France

System for the vapor phase reactions



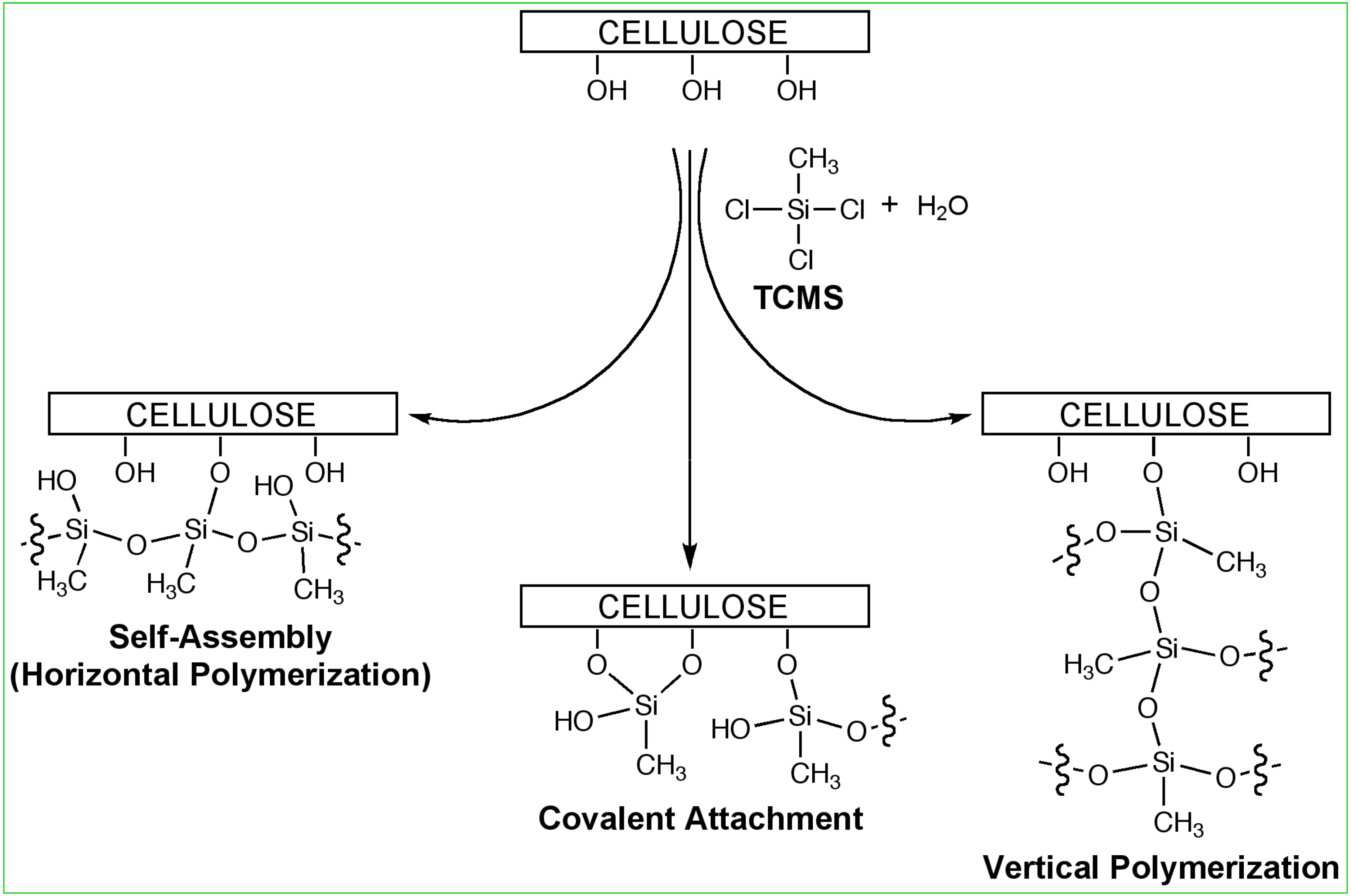
1. The N_2 (carrier gas) stream is controlled with the flow meter

2. The N_2 stream passes through the flask containing the TCMS, dragging its vapors

3. The N_2/TCMS stream is flushed towards the filter paper (placed in the middle of the reactor) for a given period of time

4. The excess of TCMS and the HCl formed (by-product) are removed from the gaseous waste by bubbling through a aqueous NaOH solution at the exit of the system

5. ΔP is measured with the digital manometer



CELLULOSE
OH OH OH
CH3
Cl Si Cl + H2O
Cl
TCMS
CELLULOSE
OH O OH
HO HO
Si O Si O Si
H3C H3C CH3
Self-Assembly
(Horizontal Polymerization)
CELLULOSE
O O O
HO Si
HO Si O
CH3 CH3
Covalent Attachment
CELLULOSE
OH O OH
O Si CH3
O
H3C Si O
O
O Si O
CH3
Vertical Polymerization

Contact angles measurements

Sample	θ_{water} (º)	$\theta_{glycerol}$ (º)	$\theta_{diiodomethane}$ (º)	$\theta_{1\text{-}bromonaphtalene}$ (º)
FP	36	41	37	23
FP1	134	98	106	62
FP2	136	127	109	71
FPh1	40	43	39	25
FPh2	125	121	106	82

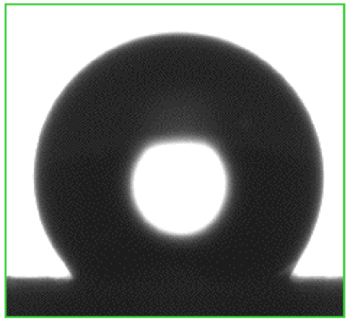
- Drastic increase in both the **hydrophobicity** and **lipophobicity** of the samples (except for FPh1)
- High contact angles, even for sample treated for only 30 sec (FP1)

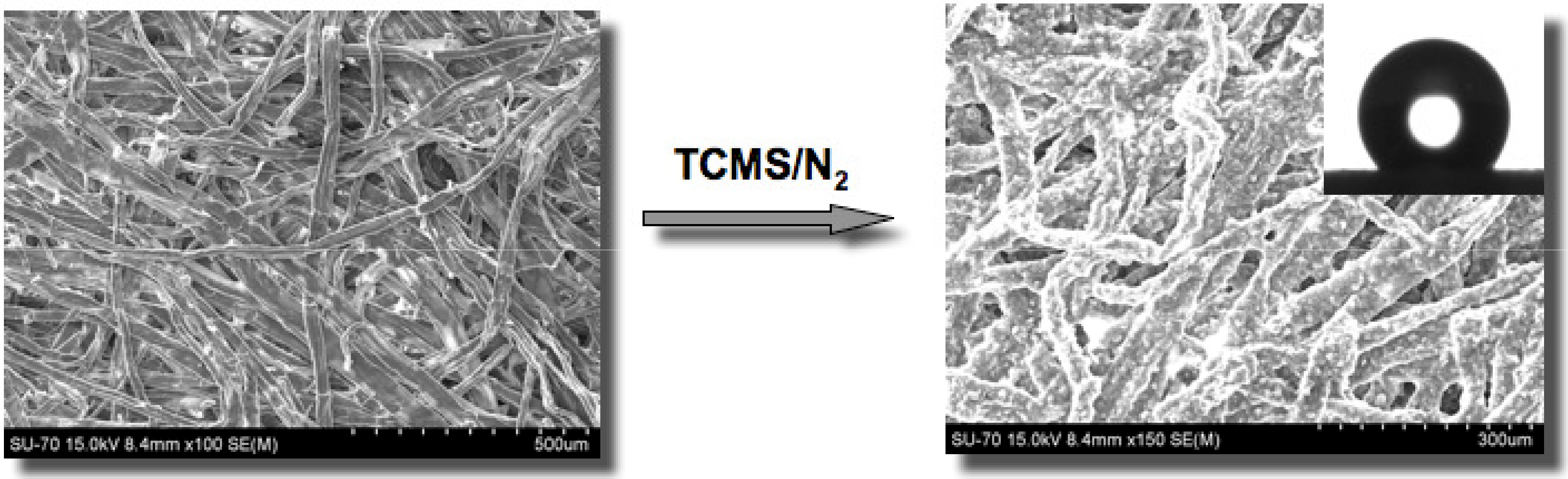
  Diffusion of excess of TCMS through the samples

An extensive surface coverage is not necessary

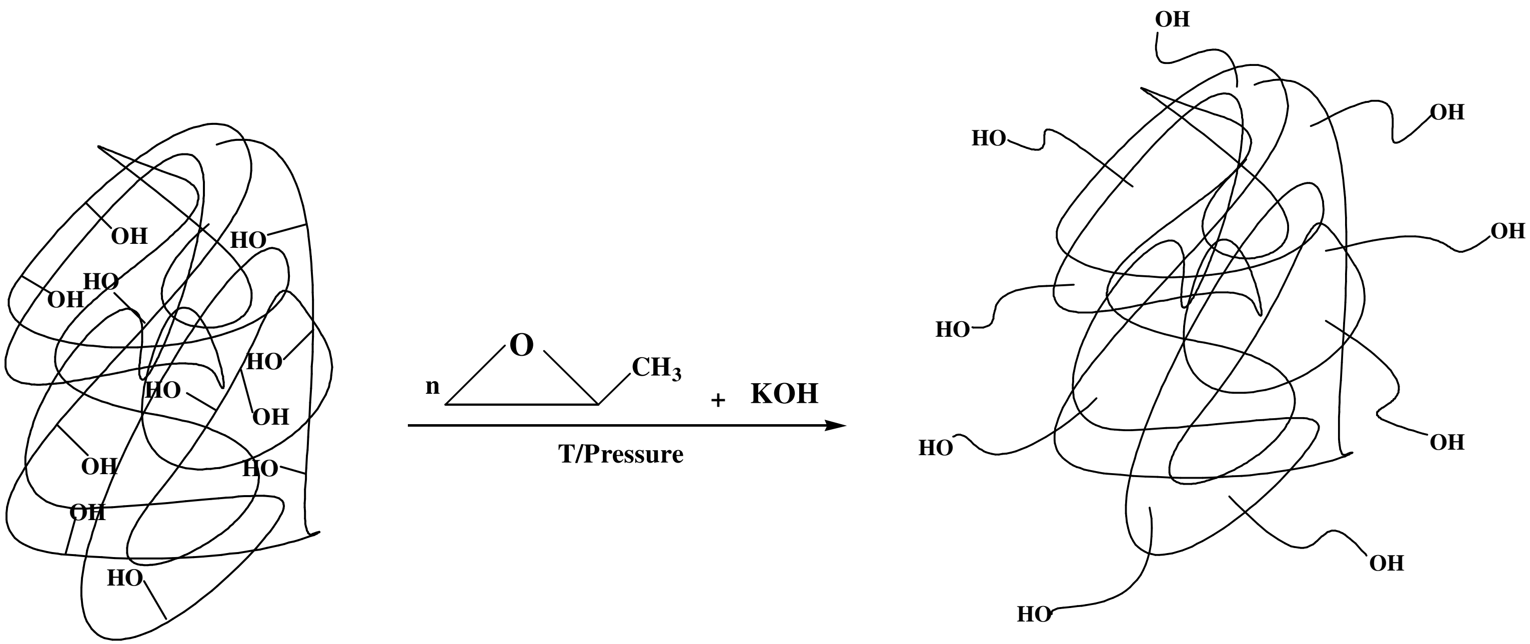
- Very low surface energies

  Drastic reduction in the polar component




SU-70 15.0kV 8.4mm x100 SE(M)
500um
TCMS/N2
SU-70 15.0kV 8.4mm x150 SE(M)
300um

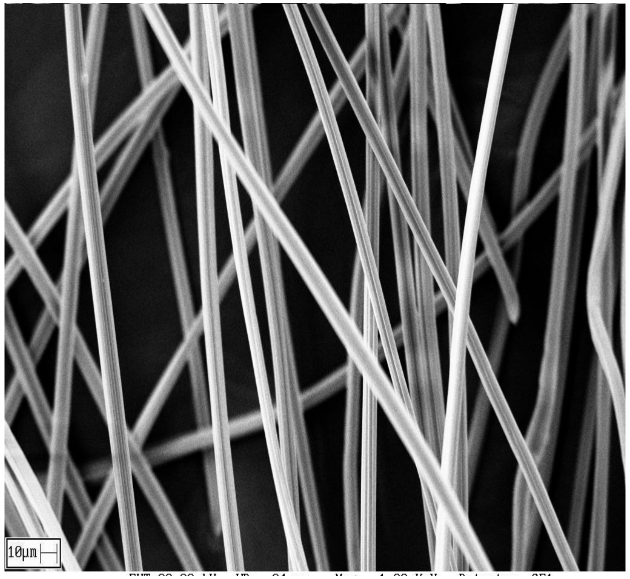
Direct Transformation of Cellulose Fibers into Self-reinforced Composites by Partial Oxypropylation

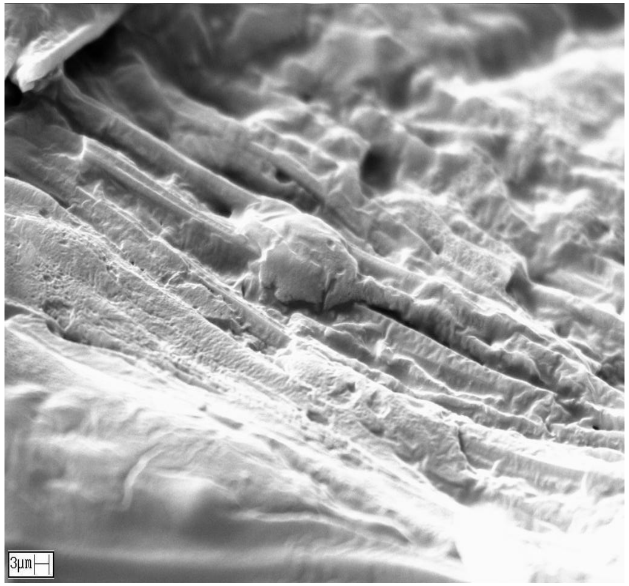


NATURAL SUBSTRATE

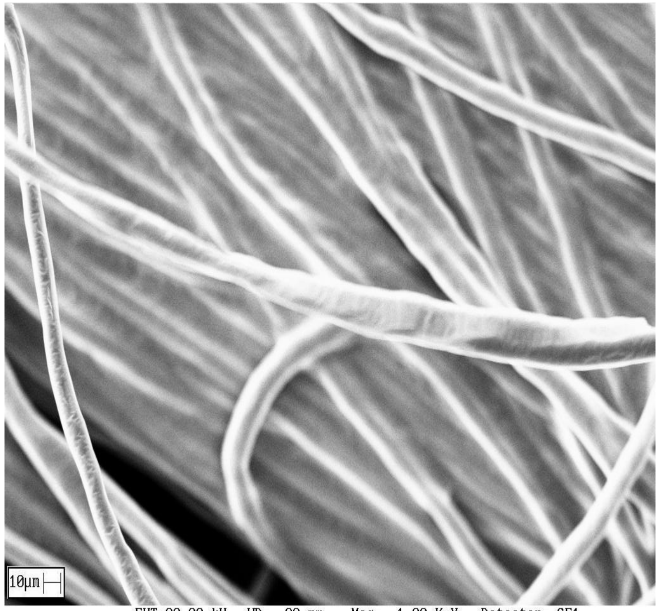
LIQUID POLYOL

Daniel Pasquini, São Carlos, Brazil





Regenerated fibres as such, after partial oxypropylation and after pressing

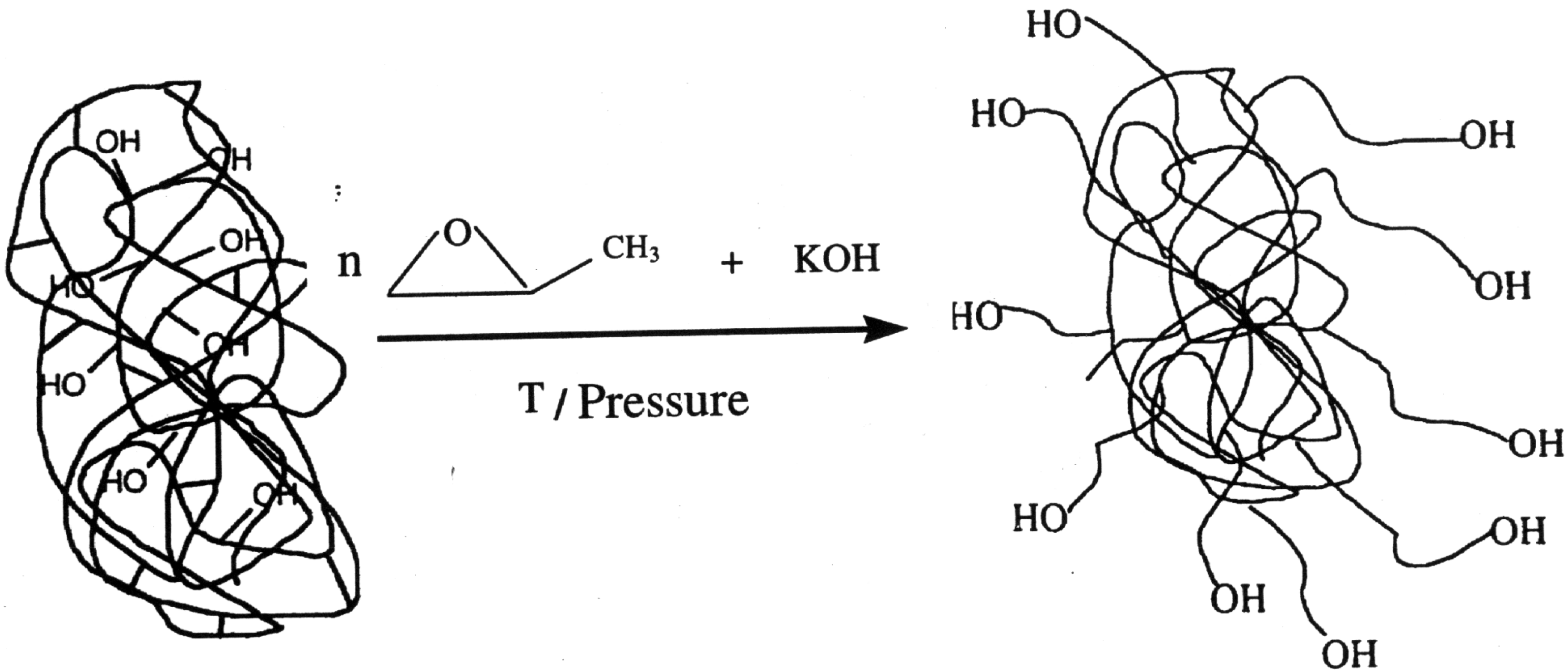


“TOTAL” OXYPROPYLATION

BULK REACTIONS LEADING TO THE TRANSFORMATION OF AN OH-BEARING SOLID SUBSTRATE INTO A

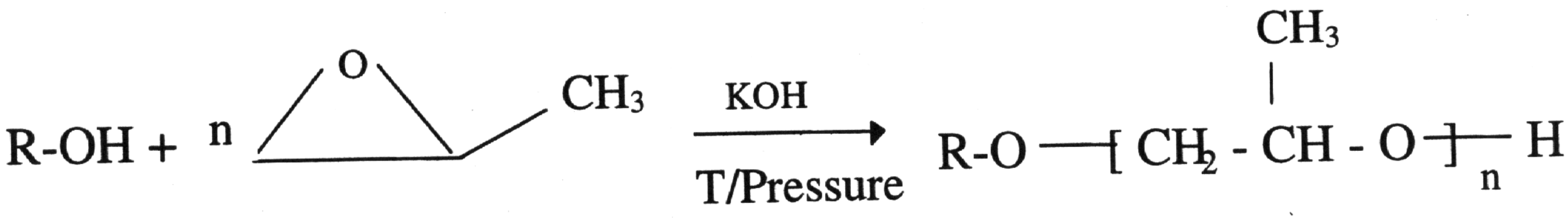
VISCOUS POLYOL

Filomena Barreiro, Bragança Polytechnic, Portugal
and Naceur Belgacem, Grenoble, France

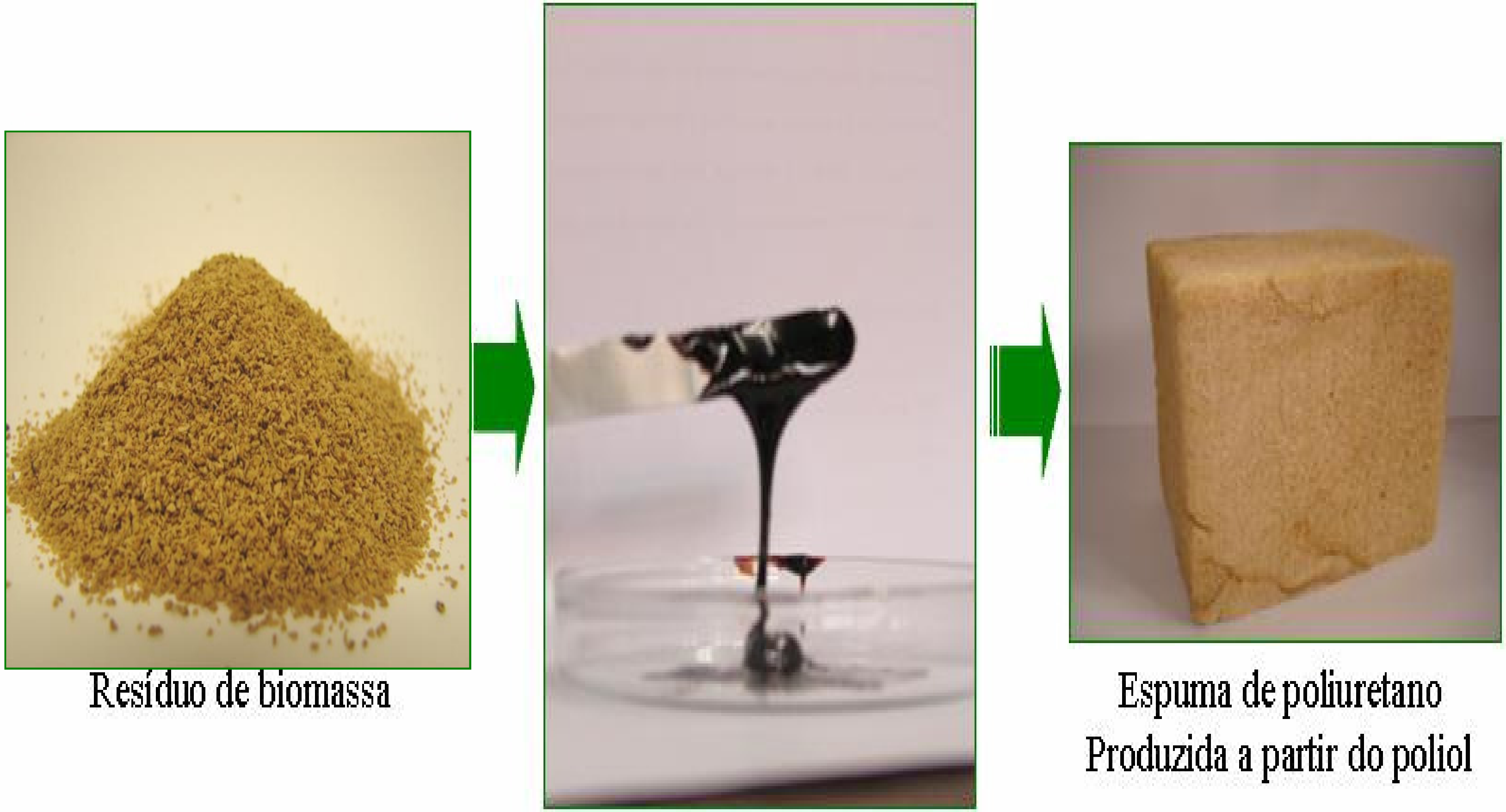


OH-bearing macromolecules

Liquid polyol



Homopolymerisation



Resíduo de biomassa

Poliol obtido a partir do resíduo

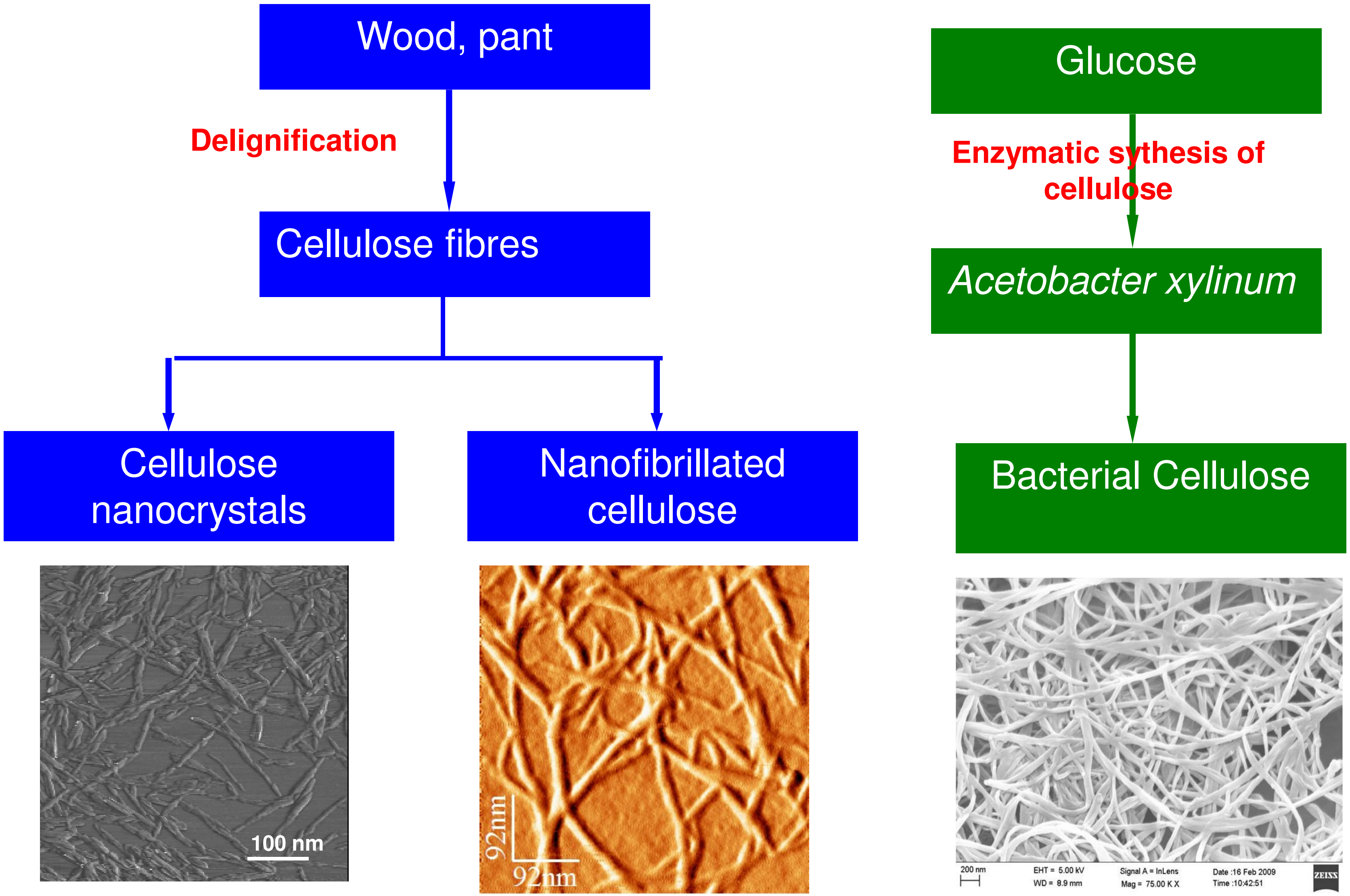
Espuma de poliuretano
Produzida a partir do poliol

THIS SIMPLE PROCESS WAS SUCCESSFULLY APPLIED TO SEVERAL NATURAL SUBSTRATES:

-LIGNINS
-CORK
-SUGARBEET PULP
-CHITIN (AND CHITOSAN)
-OLIVE STONES
-BARLEY RESIDUES
-COFFEE RESIDUES…

TO PRODUCE VISCOUS POLYOLS SUITABLE FOR THE SYNTHESIS OF NOVEL POLYURETHANES AND POLYESTERS BASED ON RENEWABLE RESOURCES

THE ADVENT OF NANOCELLULOSES



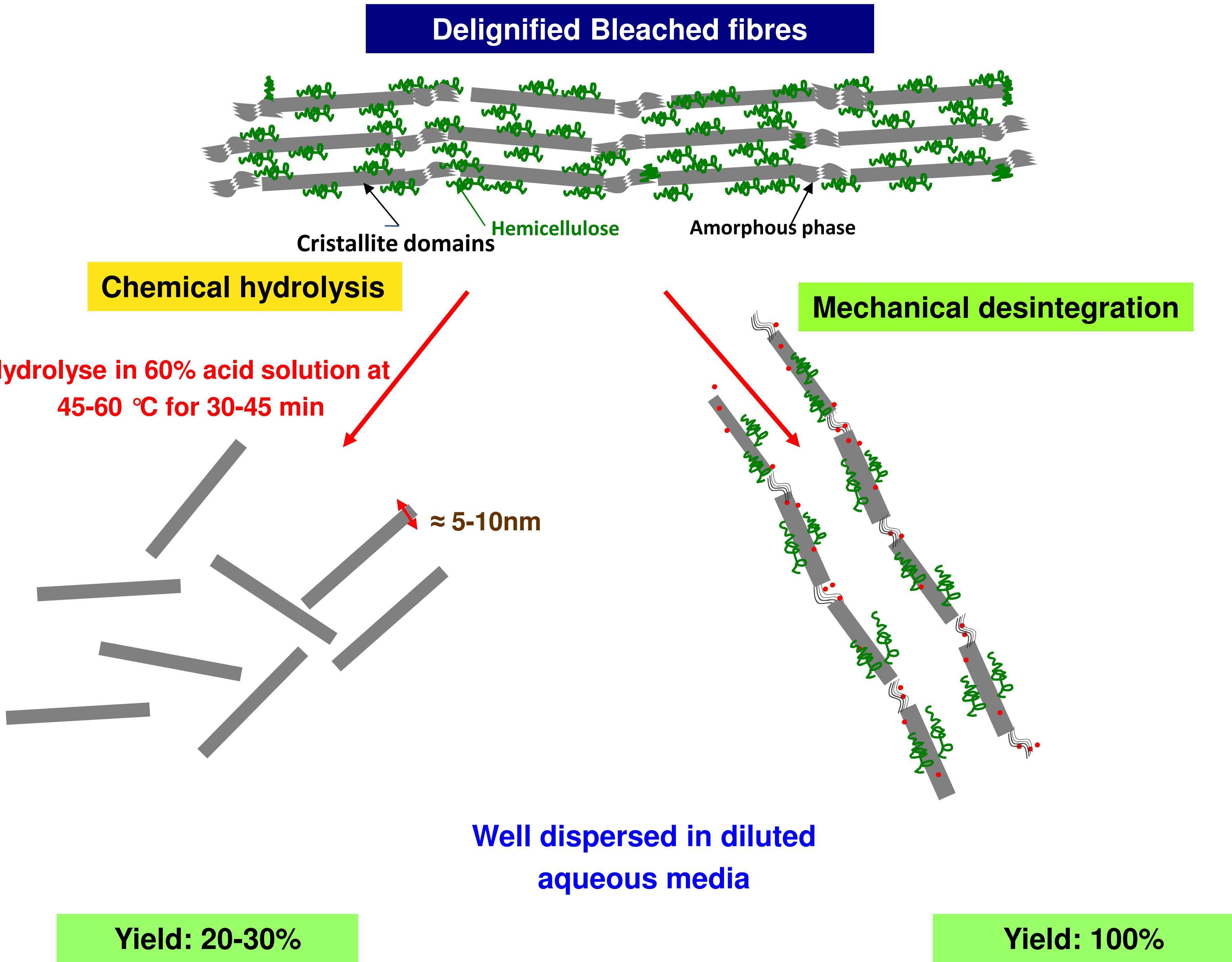
Rigid Rod like structure

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

Flexible Nanofibrils

D:5-50 nm, L: 0.2-2 µm

Pure cellulose in the form of nanofibrils
D:3-10 nm, L> µm

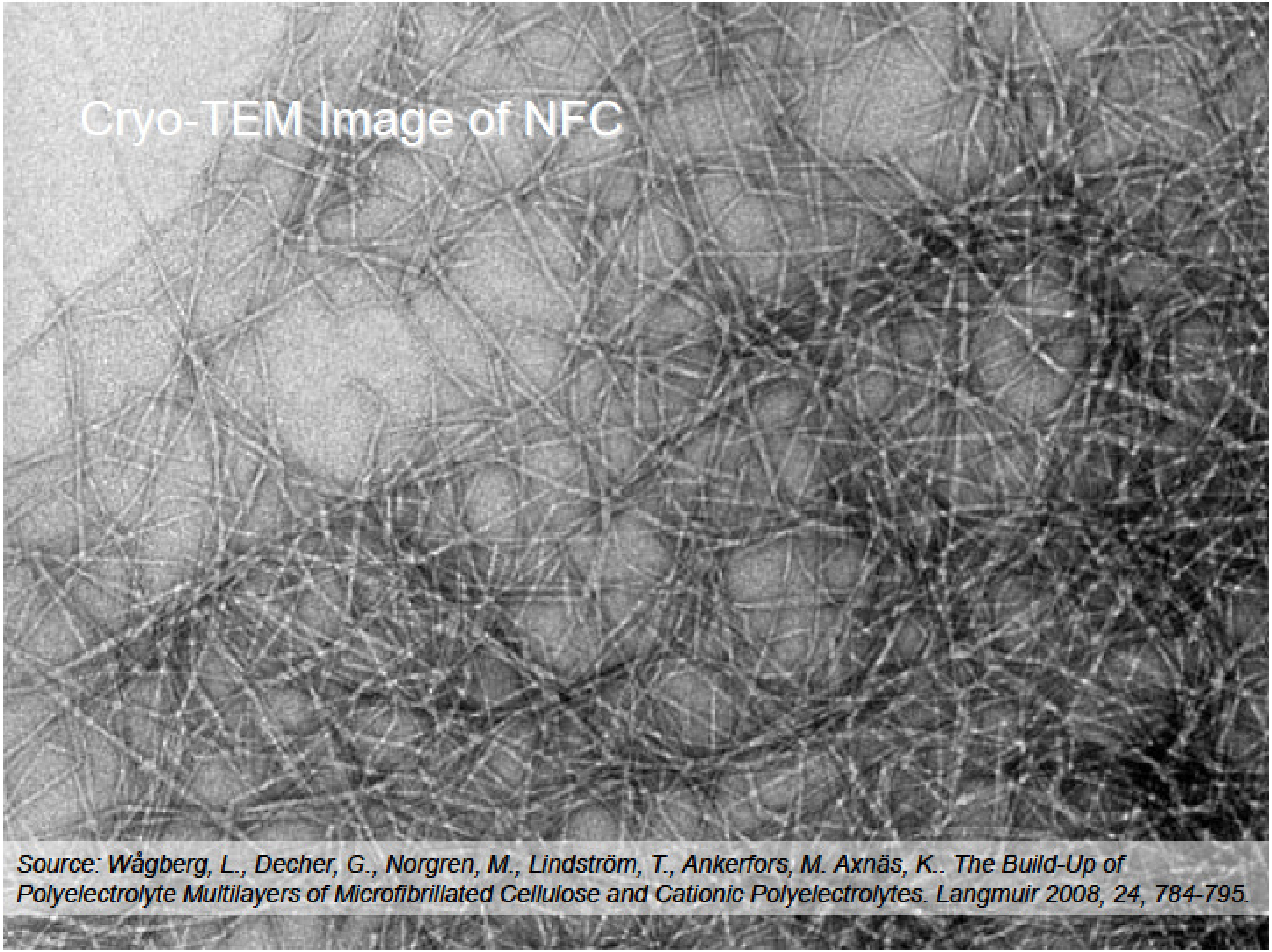

Delignified Bleached fibres
Cristallite domains
Hemicellulose
Amorphous phase
Chemical hydrolysis
Hydrolyse in 60% acid solution at
45-60 ℃ for 30-45 min
≈ 5-10nm
Mechanical desintegration
Well dispersed in diluted
aqueous media
Yield: 20-30%
Yield: 100%

1.

NANOFIBRILLATED CELLULOSE

(MFC, NFC)

Cryo-TEM Image of NFC

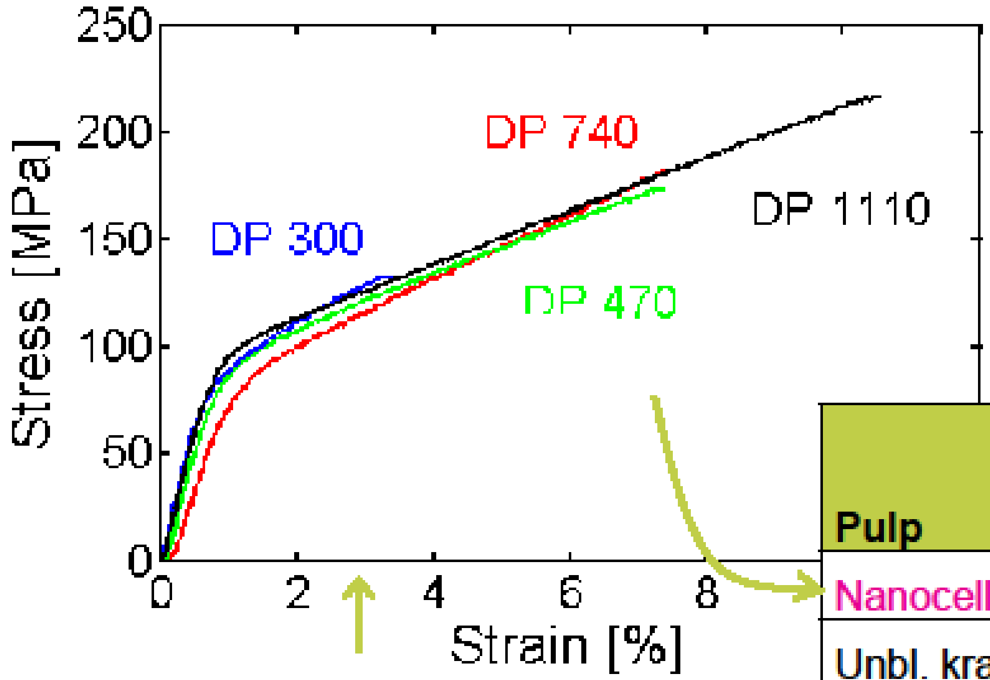


Source: Wågberg, L., Decher, G., Norgren, M., Lindström, T., Ankerfors, M. Axnäs, K.. The Build-Up of Polyelectrolyte Multilayers of Microfibrillated Cellulose and Cationic Polyelectrolytes. Langmuir 2008, 24, 784-795.


MFC gen. 2
2 w-%


MFC gen. 2
7 w-%

Stress-strain curves for Films of different NFCs



Source: Henriksson, M., Berglund, L.A., Isaksson, P., Lindström, T., Nishino, T. Cellulose Nanopaper Structures of High Toughness. Biomacromolecules 2008, 9, 1579-1585.

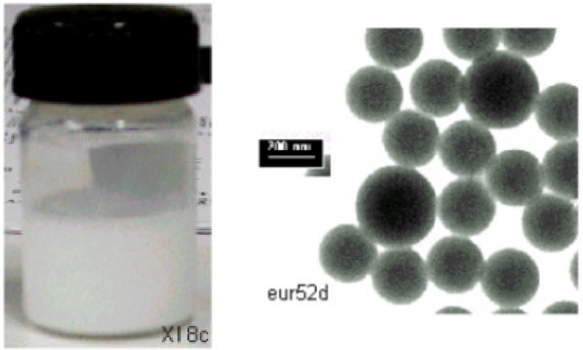
"Nanopaper": Strongest cellulose-based material made by man.

Pulp	Stress at brake [MPa]	Young's Modulus [GPa]	Strain at break [%]
Nanocellulose	~200	10-20	6-12
Unbl. kraft	64	5	4
Bl. kraft SW	54	5	5
Bl. kraft HW	34	4	4
Newsprint	16	2	2
Ground wood	6	1	1

Source: Fellers et al. (1983) Carton board. Profitable use of pulps and processes.

POTENTIAL USES OF NFC

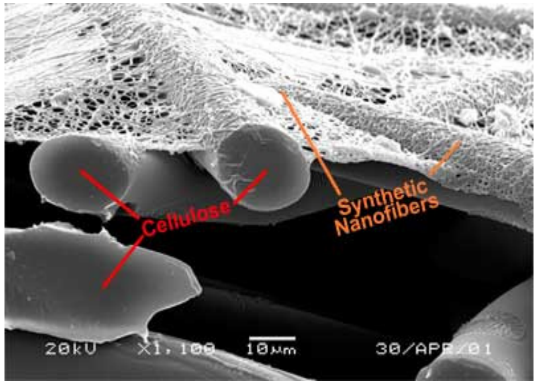
Colloidal stabilizer for emuslion



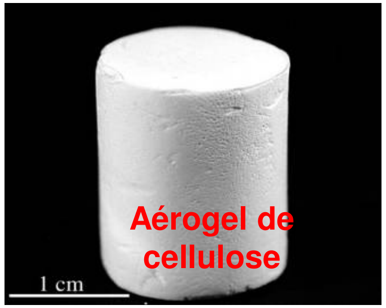
Reinforcing nanofiller

Transparency-high reinforcing potential

Strength additive for paper



Aeorgel



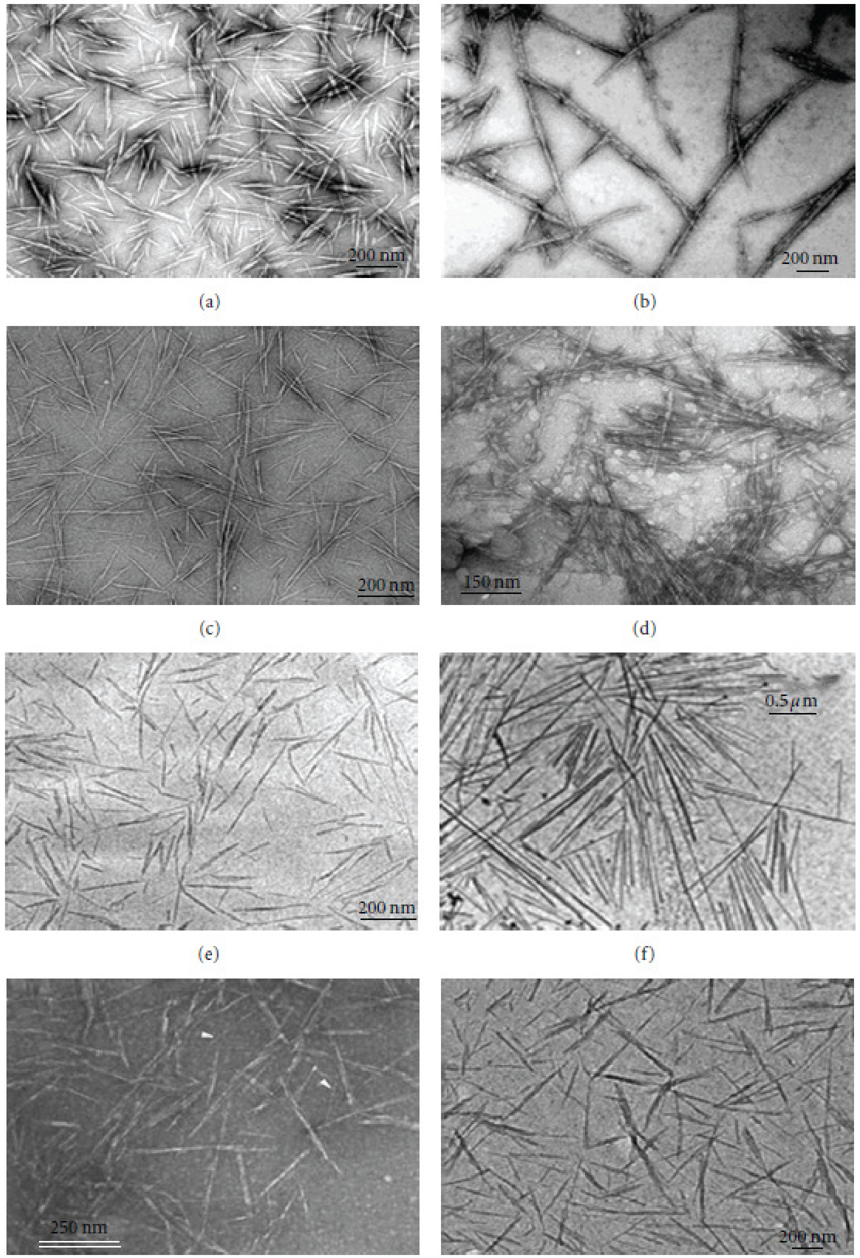
Foams, adsorbent, membrane

Stronger Paper Materials Always Needed

2.

CELLULOSE NANOCRYSTALS

(WHISKERS)



(a) (b) (c) (d) (e) (f) (g) (h)

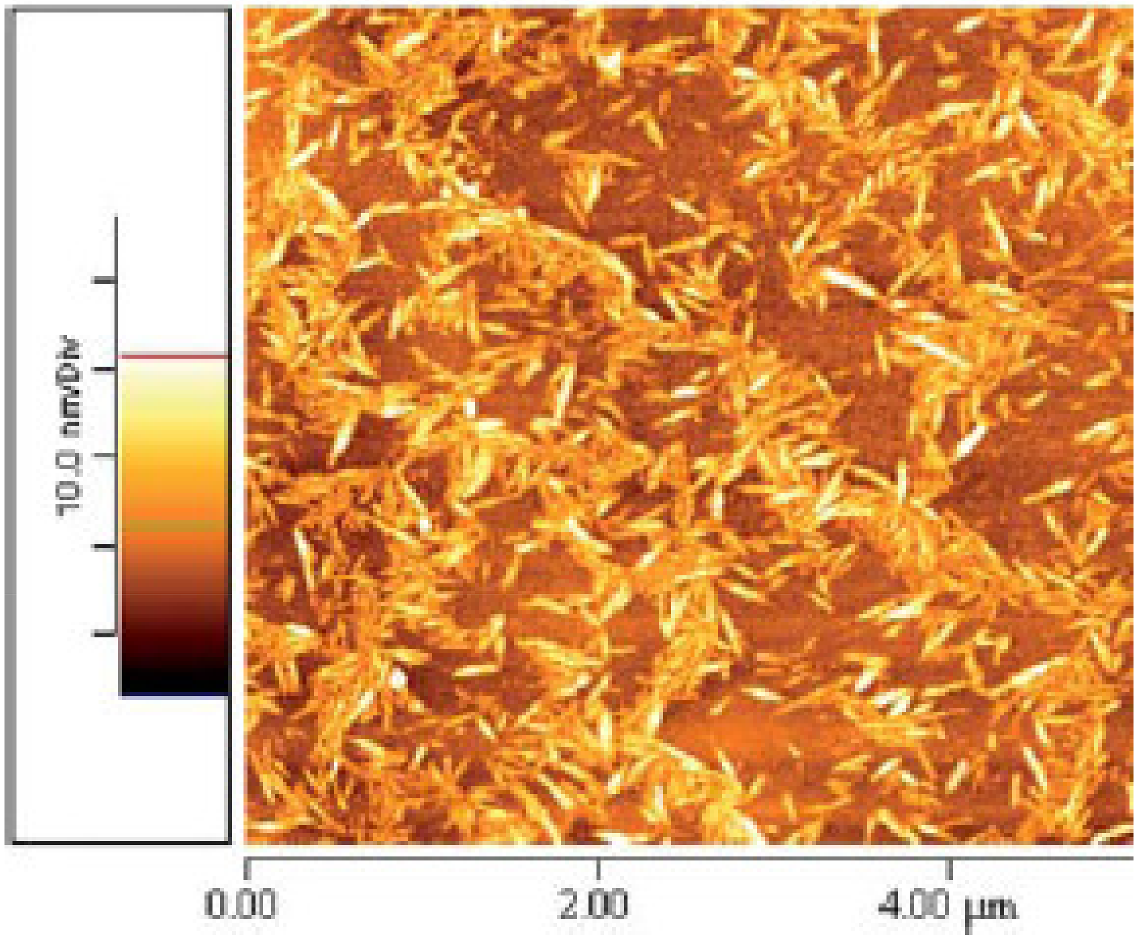


Fig. 2 Atomic Force Microscope image of cellulose nanowhiskers produced using acid hydrolysis of cotton. The left hand scale gives height information (units: nm Div^{-1}). Image courtesy of Mrs Rafeadah Rusli, University of Manchester.

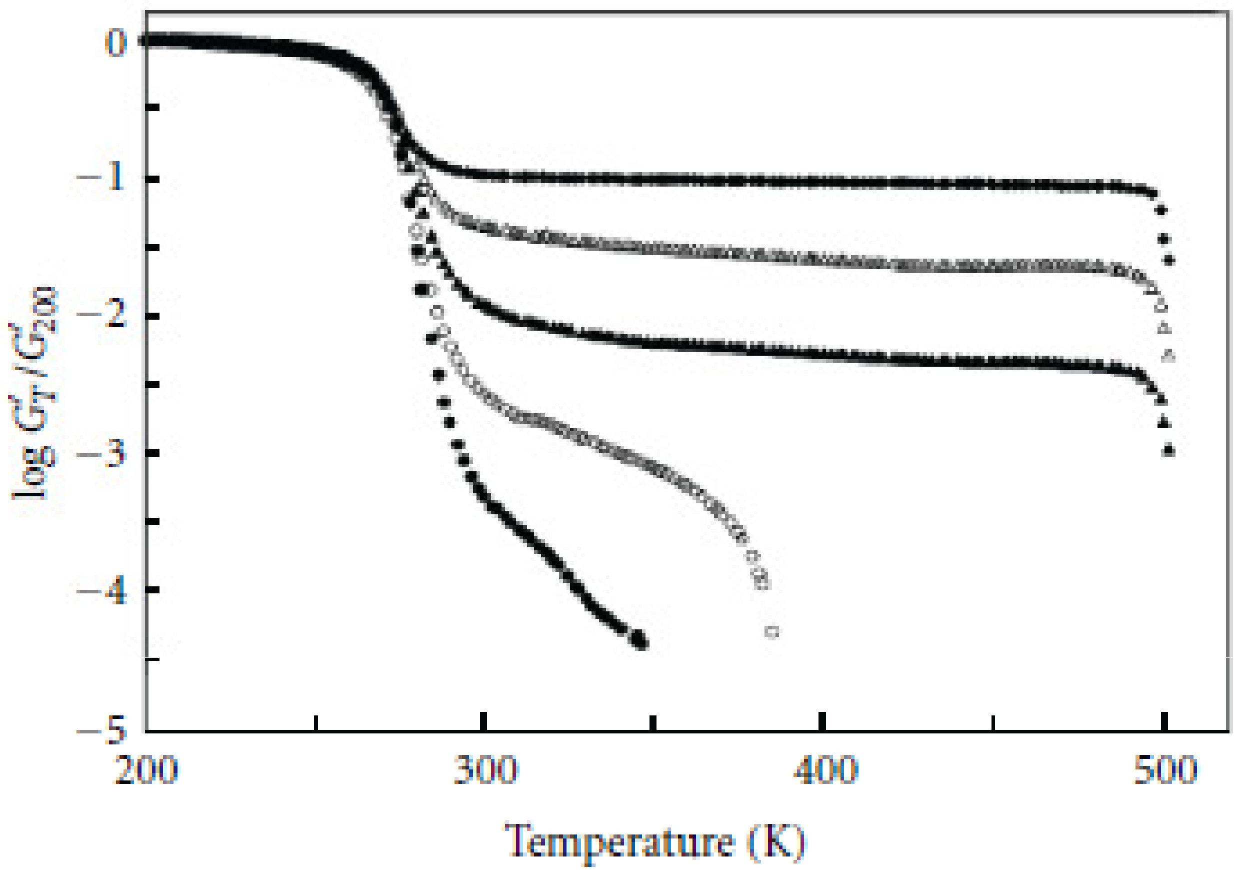
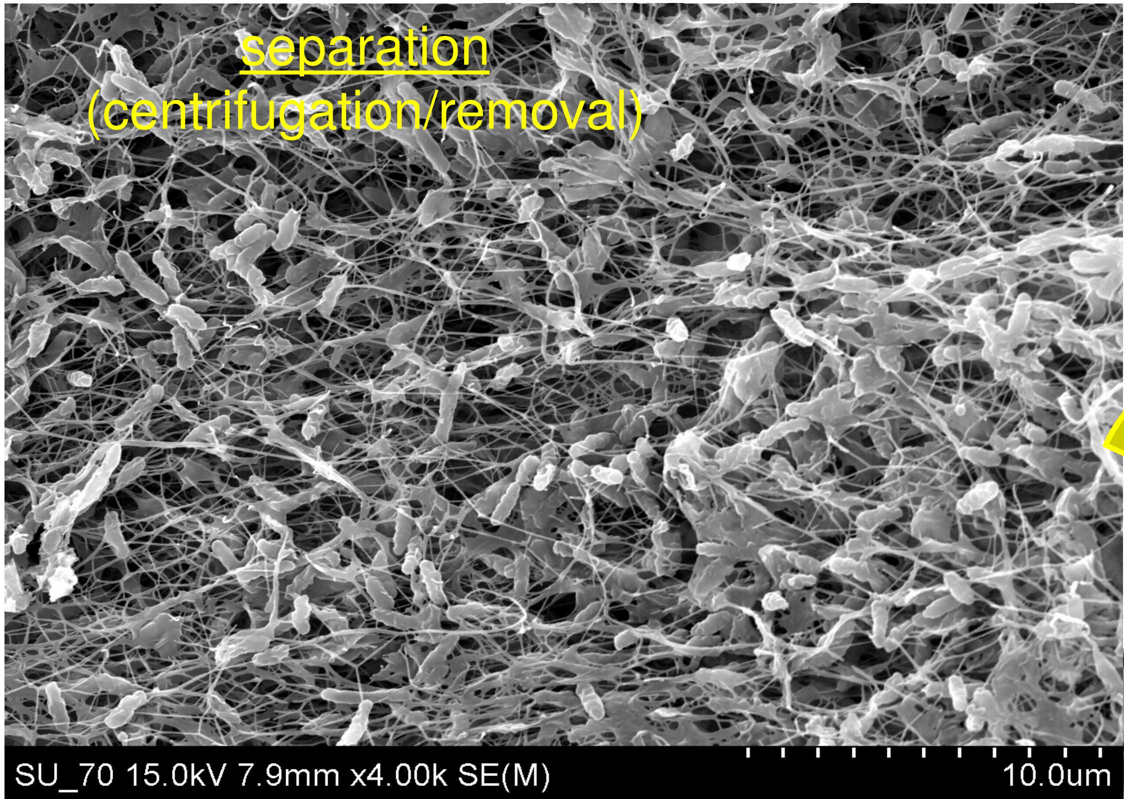


FIGURE 13: Logarithm of the normalized storage shear modulus (log G'_T/G'_{200}, where G'_{200} corresponds to the experimental value measured at 200 K) versus temperature at 1 Hz for tunicin whiskers reinforced poly(S-co-BuA) nanocomposite films obtained by water evaporation and filled with 0 (●), 1 (○), 3 (▲), 6 (△) and 14 wt% (♦) of cellulose whiskers [140].

3.

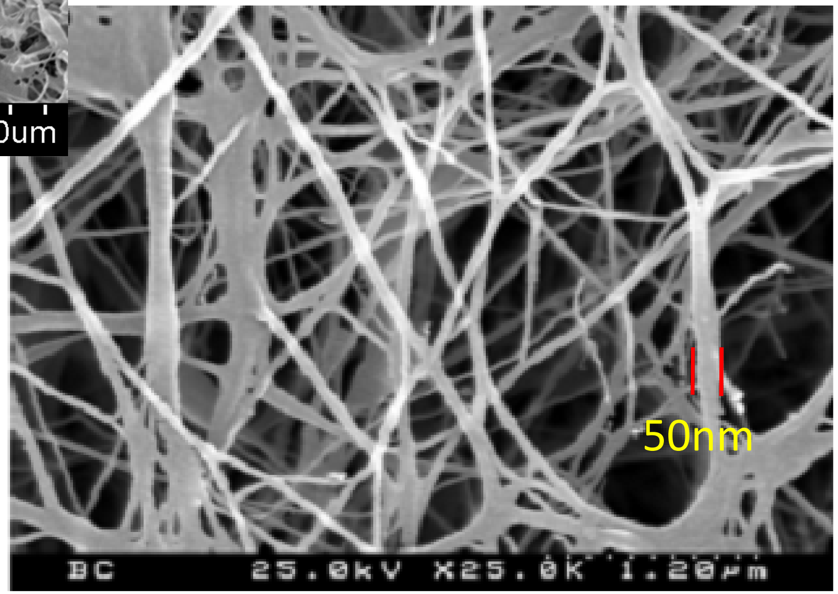
BACTERIAL CELLULOSE

Separation/Purification



-bacteria + resídues from the production process

purification
(0.1M NaOH, 60°C/4 h)



-high purity

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ERROR: undefined
OFFENDING COMMAND: ‘~

STACK:
```