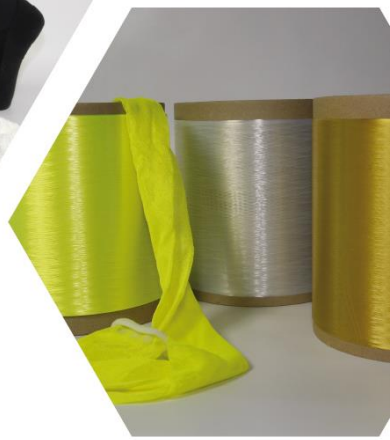
Current developments of biobased commercial products on cellulose basis



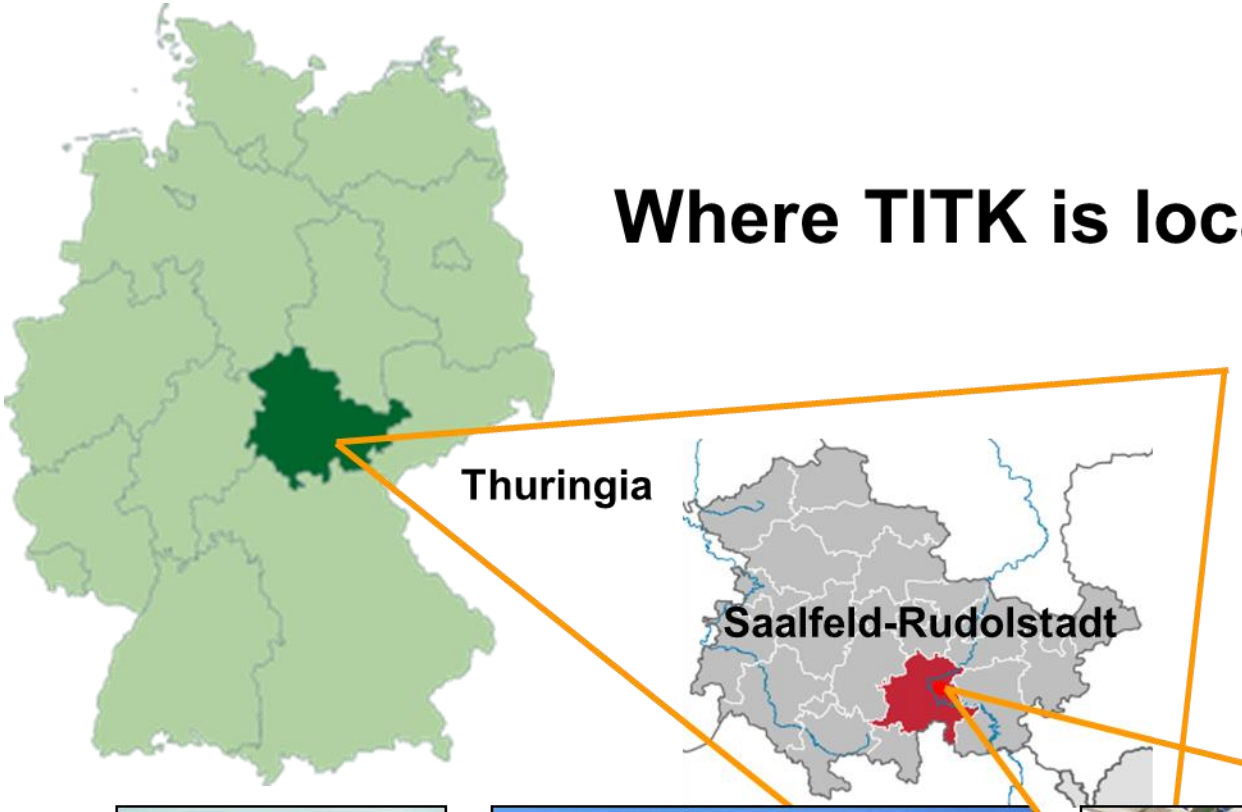
Frank Meister

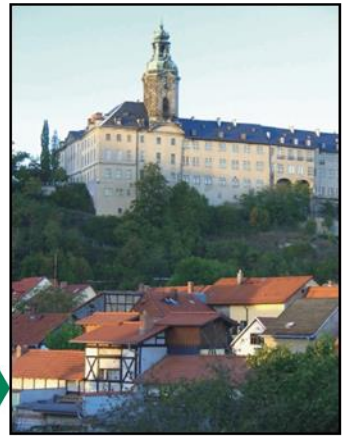
smartpolymer GmbH Rudolstadt,
Breitscheidstraße 97,
07407 Rudolstadt, Germany

TITK DIVERSITY IN POLYMERS

3rd BioEnergyTrainStudent Camp, CC for Wood Composites and Wood Chemistry Linz, February 25th to 28th, 2019

Where TITK is located ?

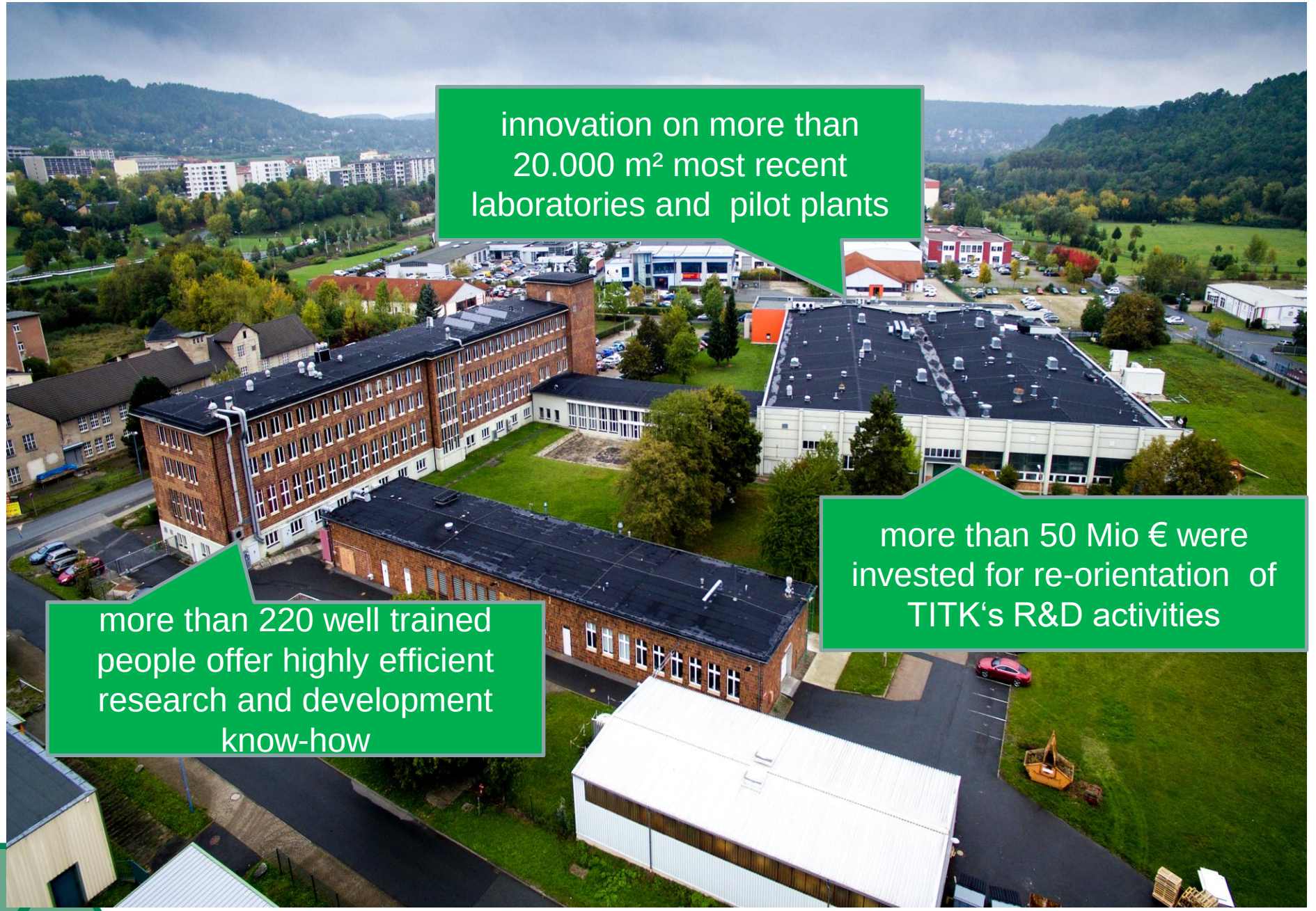




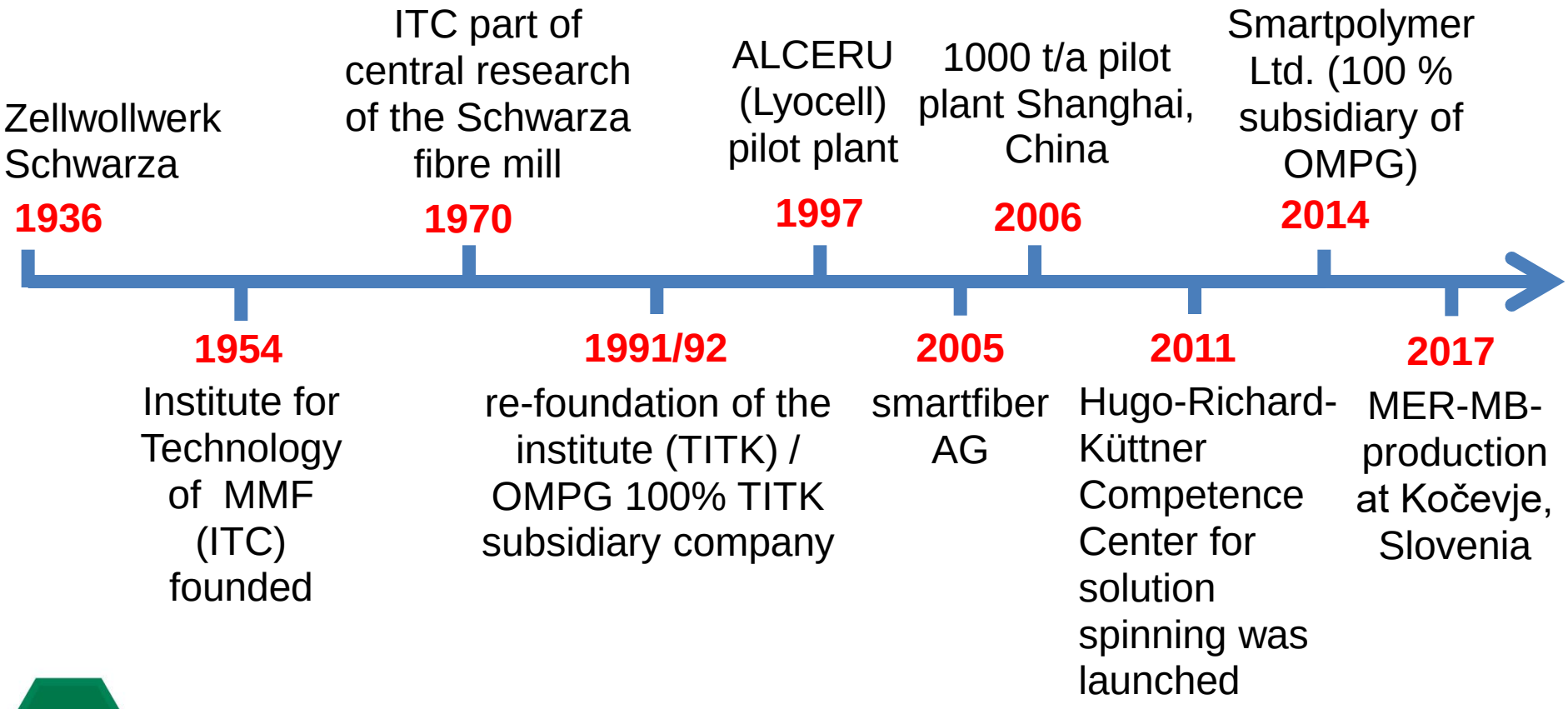
Castle Heidecksburg

TITK - main building

TITK - the whole institute campus


innovation on more than 20.000 m² most recent laboratories and pilot plants
more than 50 Mio € were invested for re-orientation of TITK‘s R&D activities
more than 220 well trained people offer highly efficient research and development know-how

A brief history …



TITK Group - today

TITK

Thuringian Institute for Textile and Plastics Research

Employees: 130
Members: about 90

→ Research and development projects on polymer materials, processing and technologies (50 R&D projects each year)

OMPG

East Thuringian Material Testing Company for Textiles and Plastics
(100 % subsidiary of TITK)

Employees: 31

→ analytical services (chemical, physical)
→ polymer and material testing
→ exclusive R&D orders

smart MELAMINE d.d.o.

(50 % subsidiary of smartpolymer)

Employees: 25

→ production and marketing of MER-MB non-woven

Smartpolymer GmbH

(100 % subsidiary of OMPG)

Employees: 31

→ product commercialisation and technology transfer

TITK's Core Competences, today

Native Polymers

Fibre reinforced Composites

Synthetic Polymers

Functional polymer systems

Outline

TITK in a nut shell

The cellulose gap

New developments in the pulp industry

- paper to dissolving pulp
- pulp from recycled textile fibres
- pulps from agricultural waste

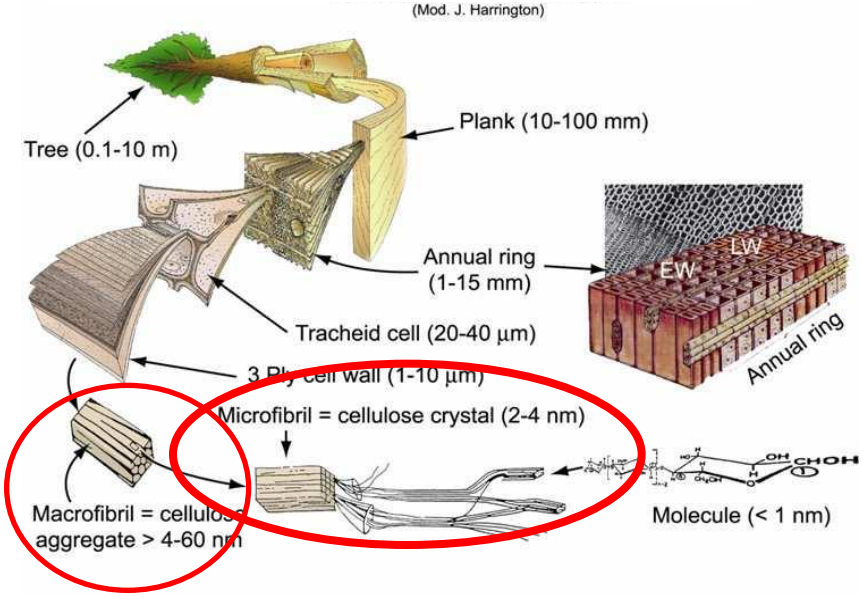
Functional Lyocell fibres

Lyocell technology options

Nano celluloses and innovative fibril fibres

Summary and prospects

Hierarchical structure of wood / cellulose



Cellulose (MMF) Gap

Multi-present global challenges:

1. Population growth

CAGR 2011-2020: 1.1 %[1]

[1] Forecasted **population growth** from UN Population Division

2. Prosperity growth

CAGR 2011-2020: 2.4 %[2]

[2] Forecasted **growth of global real GDP per capita** by Global Insight

3. Climate change

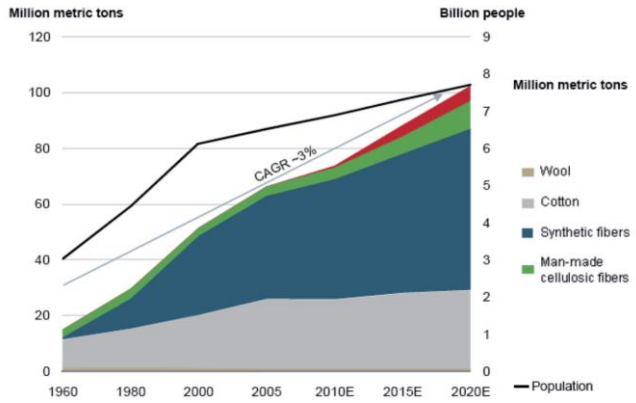
4. Marine micro plastics

→ **expected increase of cellulose fiber demand:** China, India, Indonesia, etc. will come in 2020 close to the current European level of fiber consumption of 25 kg/capita

→ **stagnation of cotton production:** at about 28 Mio metric tons due to limitation of arable land for food production and of water availability

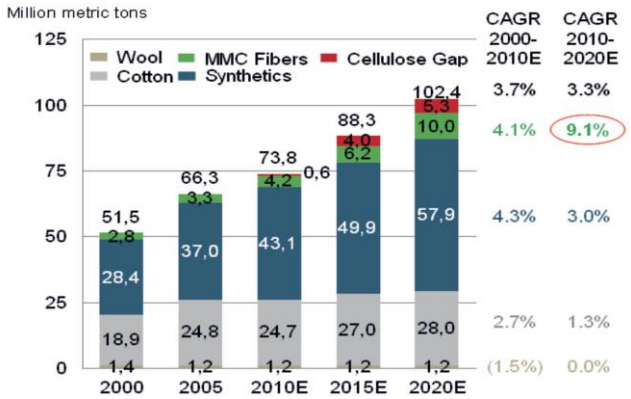
→ **expected disproportionately high demand for cellulose MMF, because of superior moisture management:** : 4.1% (CAGR 2000-2010) vs. 9.1% (CAGR 2010-2020)

→ demand for **product safety and sustainability** becomes really true



Fiber demand

vs.



Fiber production

Classification of marine micro-plastic according to their sizes

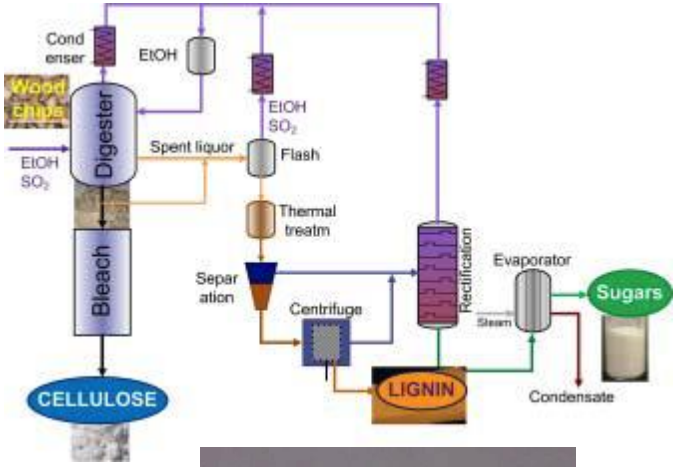
Particle Diameter	Accepted technical term	Affected organisms	Technical sources
> 25 mm	macro-plastic	vertebrates, birds	finished and semi-finished goods
5 - 25 mm	meso-plastic	birds, fishes	Semi-finished goods and plastic pellets
1 - 5 mm	large micro-plastic particles	fishes, crustaceans	pellets
< 1 (- 0.050 mm)	small micro-plastic particle	mussels, plankton, (all kind of animals and humans)	cosmetic micro particles, fragmented plastic pieces
< 50 - 0.100 µm	microscopic plastic pieces	every animate being in the sea, lakes, rivers and onshore	fragmented plastic pieces, fragmented synthetic fibres, plastic waste of coating, adhesive or painting dispersion

even though the last two categories are the lowest weight component of marine micro-plastic they bear the largest risk for every animate being !!!

Dissolving Pulps made of bio-refined paper pulps

TITK DIVERSITY IN POLYMERS

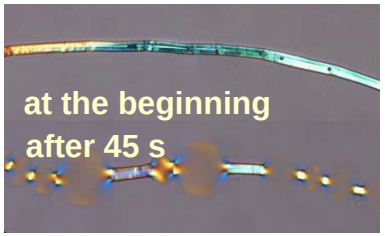
SO_2-Ethanol-Water



Promising Biorefinery for Rayon pulp and sugar-based Products

Reference: M. Iakovlev, Ph.D. thesis, Aalto University (2011)

Alkaline pulping and refining



High cellulose yield, narrow MMD, but inferior dissolution properties (ballooning, only)

Tunable solvent system:
IL + Co-Solv

Selective solubility window for any type of hemicelluloses

IONCELL process

Hemi - rich Kraft pulp → IL (+ co-solvent) → pure Hemi + pure Cellulose I

Easy conversion of hemi-rich paper to pure cellulose acetate grade pulp

Reference: H. Sixta, A. Roselli, M. Hummel, K. Ruuttunen: Advances in Dissolving Pulp Technology, 6th ICEP, Colonia del Sacramento, Uruguay, 27.11.2013

Dissolving Pulps made of recycled fibres

Process / Supplier	Worn again UK	Mistra SE	RE:newcell SE	Evrnu US	Lenzing AT	Recover® ESP	Relooping-fashion FI
approach	selective dissolution of polymers	catalytic caustic hydrolysis	selective dissolution of polymers	selective dissolution of polymers	pre-processing	mechanical	Pre-processing, dissolution
starting materials	PET-cotton blends	PET-cotton blends	pre- / post-consumer cotton, viscose, lyocell	pre- / post-consumer cotton, viscose, lyocell	pre-consumer cotton	pre-consumer cotton	mainly pre- / post-consumer cotton
solvents catalysts additives	several, among others DMSO, glycol, acetone, ionic liquids	NaOH, H_2SO_4, benzyltributhyl-ammonium chloride	NaOH, H_2SO_4	NaOH, H_2SO_4	NaOH, H_2SO_4	-	NaOH, H_2SO_4, carbon disulphide, Zn salts
products	cotton fibre / pulp for new cellulose MMF	cotton fibre / pulp for new cellulose MMF	dissolving pulp for new cellulose MMF	dissolving pulp for new cellulose MMF	dissolving pulp for new cellulose MMF	cotton fibre yarns	cotton fibre / pulp for new cellulose MMF
Process management	Batch	Batch	Batch (recently)	Batch	Continuous	Continuous	Continuous

Dissolving Pulp made of bast fibre plants

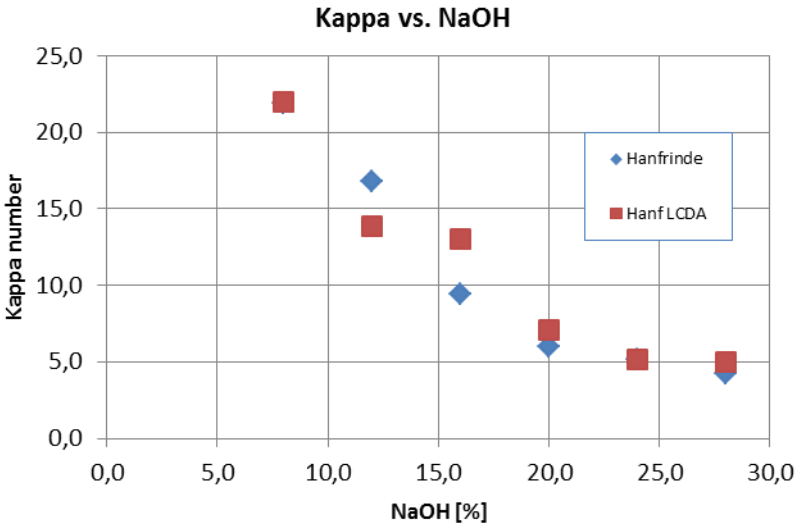
→ a two step process is required

a) Degumming for separation of all organic impurities (lignin, hemi's) from cellulose:

- raw material: a) HBS, dried (*"Hanfrinde")*
  b) hemp fiber tow (*"Hanf LCDA"*, max. 25 % shives)
- 60 minutes, 160° C
- 24% caustic soda (+ scale inhibitor)

b) Bleaching sequences to adjust DP:

- hydrogen peroxide / sodium hypochlorite for 120 minutes at 55° C (each)
- Actiron DP 950 and/or Masquol FEO were applied for complexation of heavy metal ions impurities and protection of hydrogen peroxide

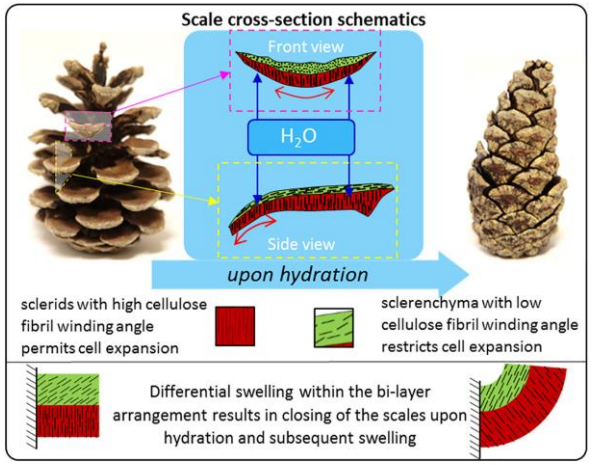


Composition of dissolving pulp (OG hemp tow)

Measured Parameter		OPP Hanf HP
cuoxam-DP		670
a-cellulose content	%	97.8
carboxyl group	µmol/g	13.3
carbonyl group	µmol/g	12.5
heavy metal ions	ppm	25
thereof $Fe^{3+}/Cu^{2+}/$	ppm	20 / 0.26
$Ni^{2+}/Cr^{3+}/Mn^{2+}$	ppm	0.26 / 3.0 / 0.87
alkali/ earth alkali ions	ppm	452
thereof Na^{+}/K^{+}	ppm	207 / < 1
Mg^{2+}/Ca^{2+}	ppm	41 / 203

Cellulose pulp-hydrogels for biomimetic inspired thermo-regulation

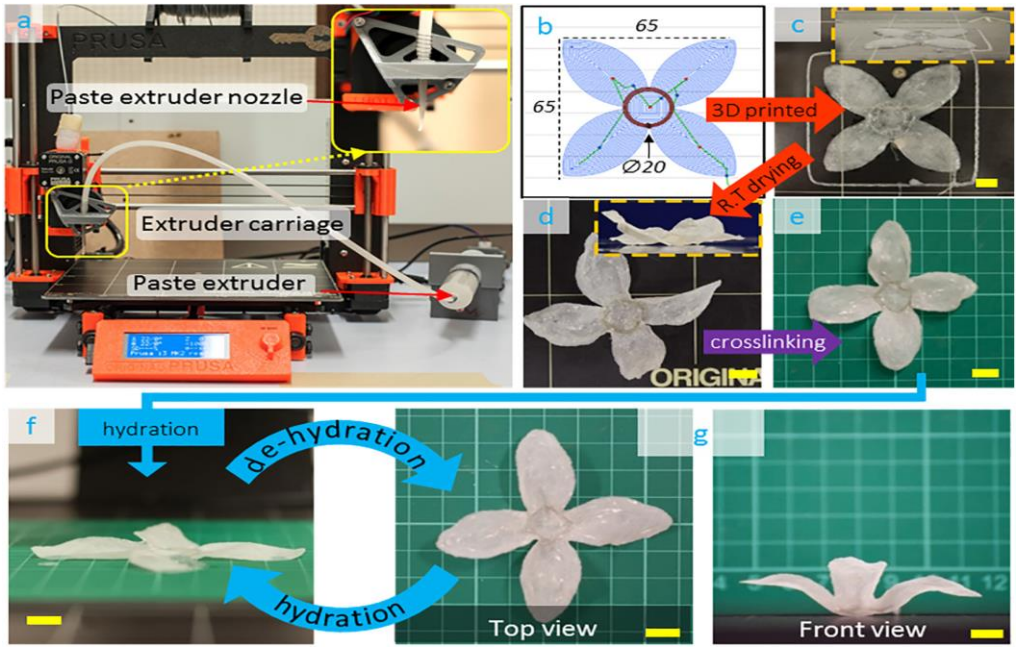
Reference: Mulakkal, M., Trask, R., Ting, V. P., Seddon, A.: *"Responsive Cellulose-Hydrogel Composite Ink for 4D Printing"*, Materials and Design, 160, (2018), 108-118.



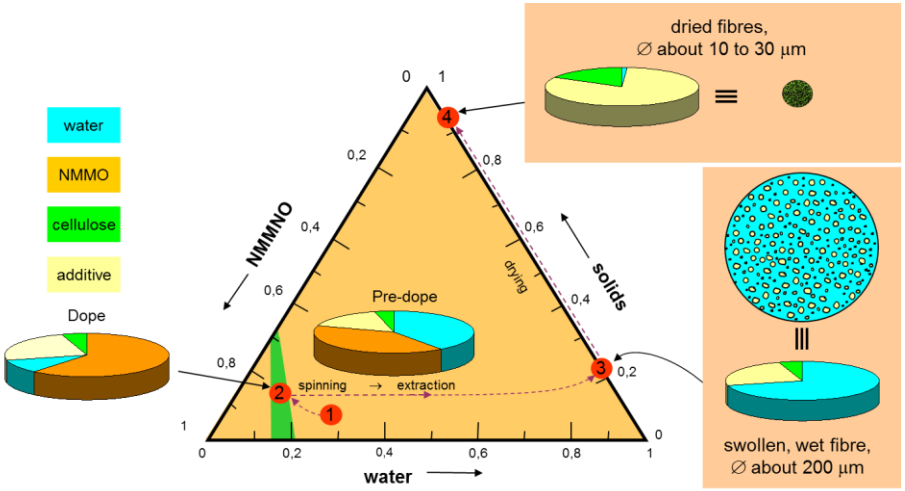
→ differences in the fibril winding angles in the top and bottom layers of the cells (sclerids in red and sclerenchyma in green) control the expansion of these cells during hydration / dehydration

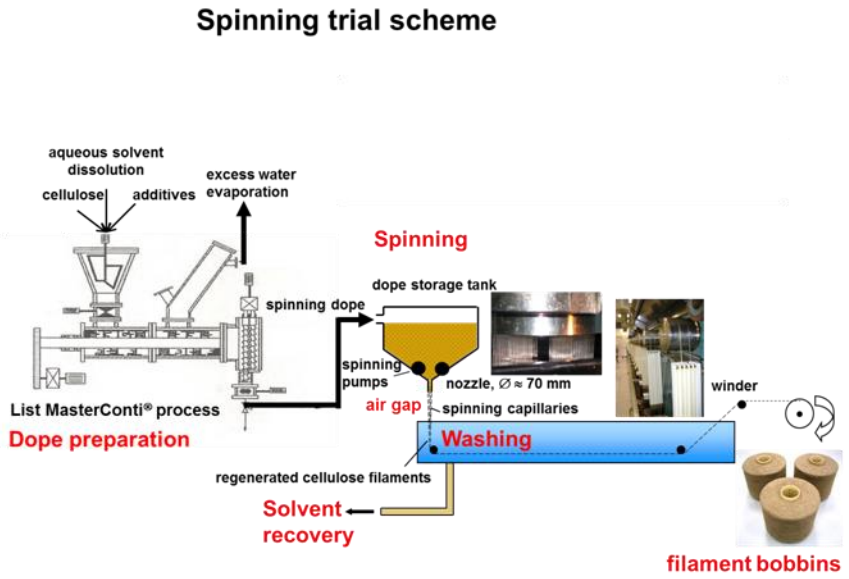
→ the cooperative anisotropic expansion of these differentiated cells result in the opening and closing of pinecone scales in response to hydration

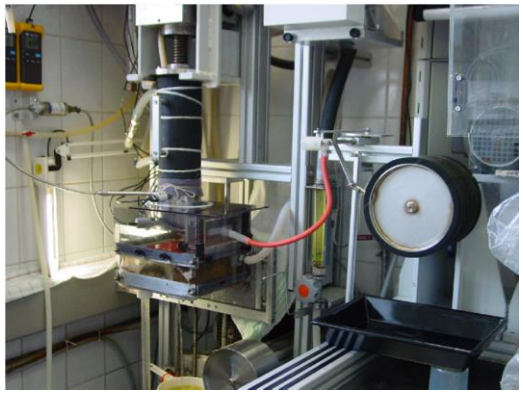
→ the same principle will be applied for innovative protective, sport, leisure and out-door clothes to regulate temperature and humidity



Dry-jet-wet spun functional fibres

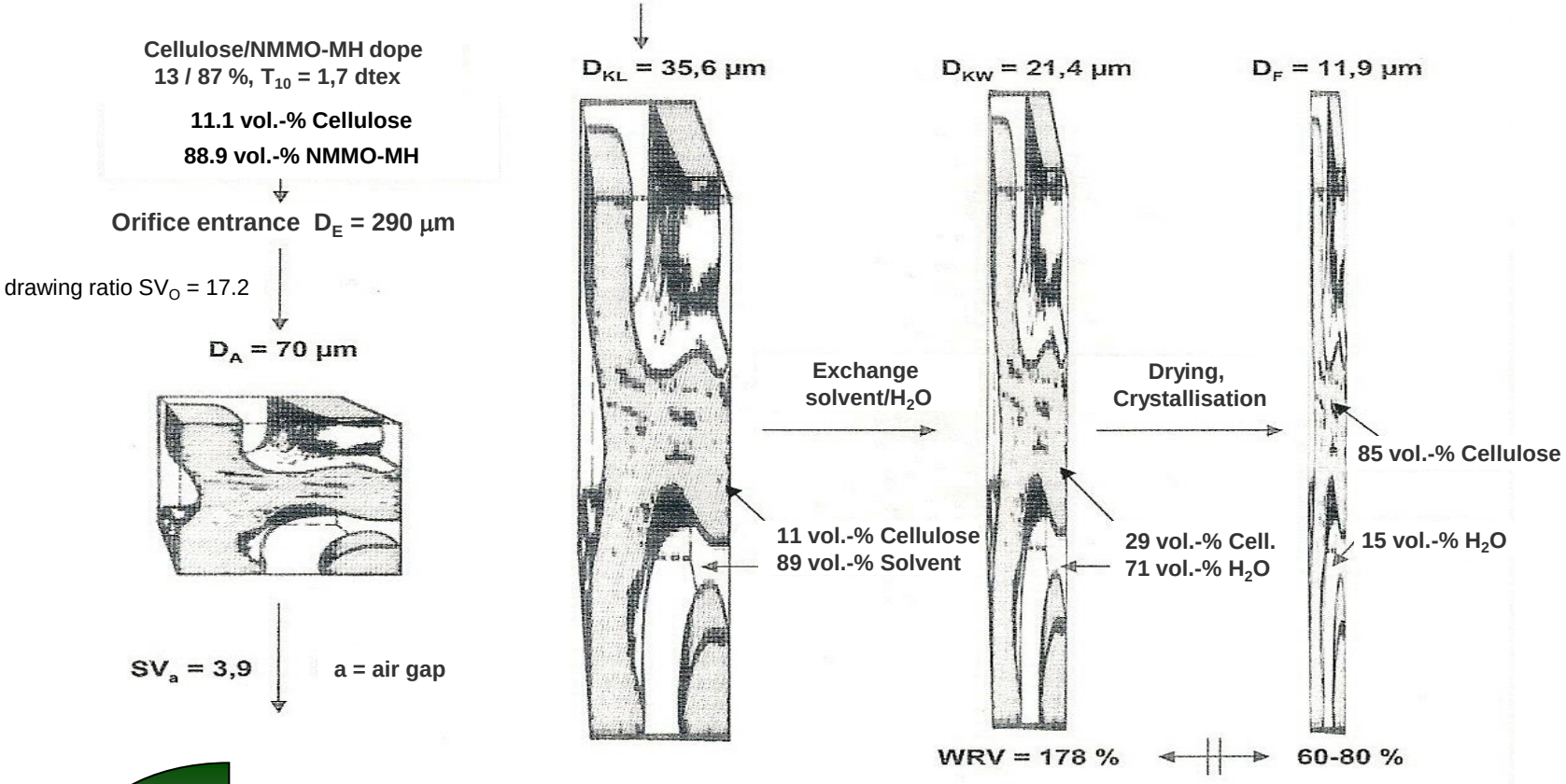






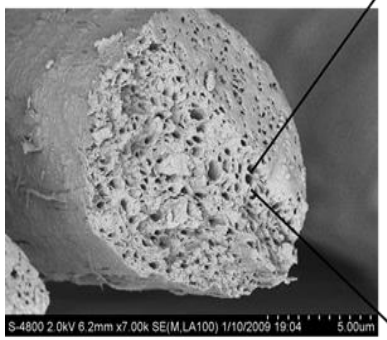
Fibrillar morphology of air-gap spun fibres

C. Michels, B. Kosan; Lenzinger Berichte, 86 (2006) 144-153

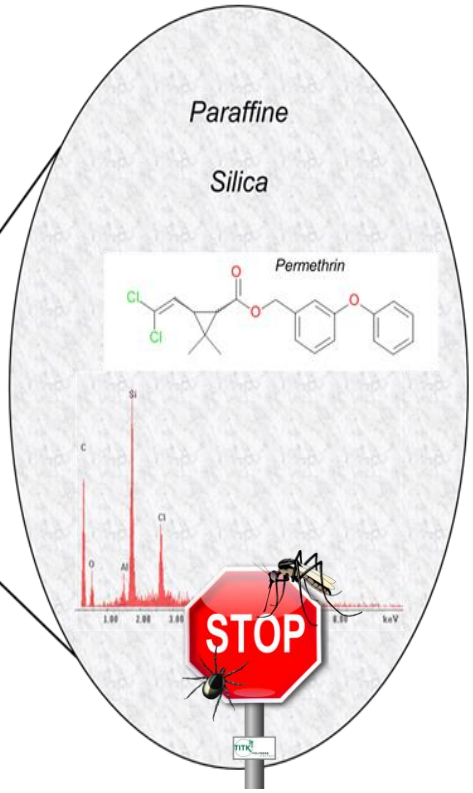


- **temperature change in the spun capillaries (and addition of non-solvent) in the air gap causes spinodal phase separation of the dope and subsequent a porous, highly oriented, crystalline fibre structure yields by drawing, solvent exchange and drying**
- **permanent fibres hydrophilic properties are caused by continuous capillary system along the whole fibre**

Cellulose-paraffin blend fibres

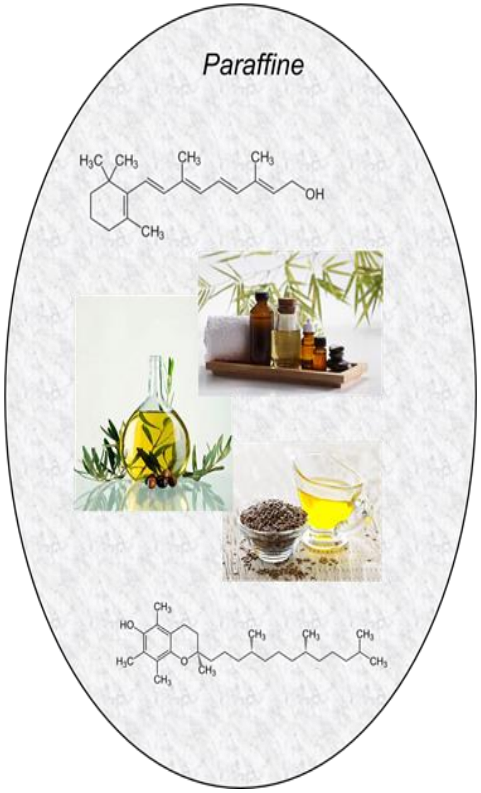


Cell Solution™ protection



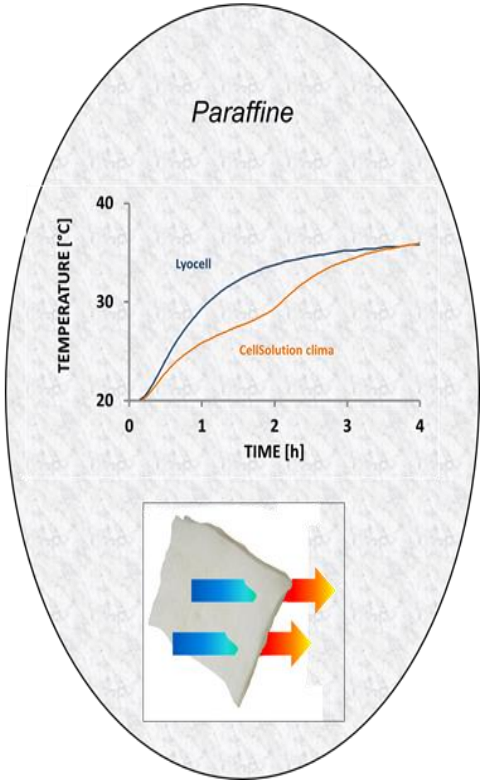
… against biting insects

Cell Solution™ skin care



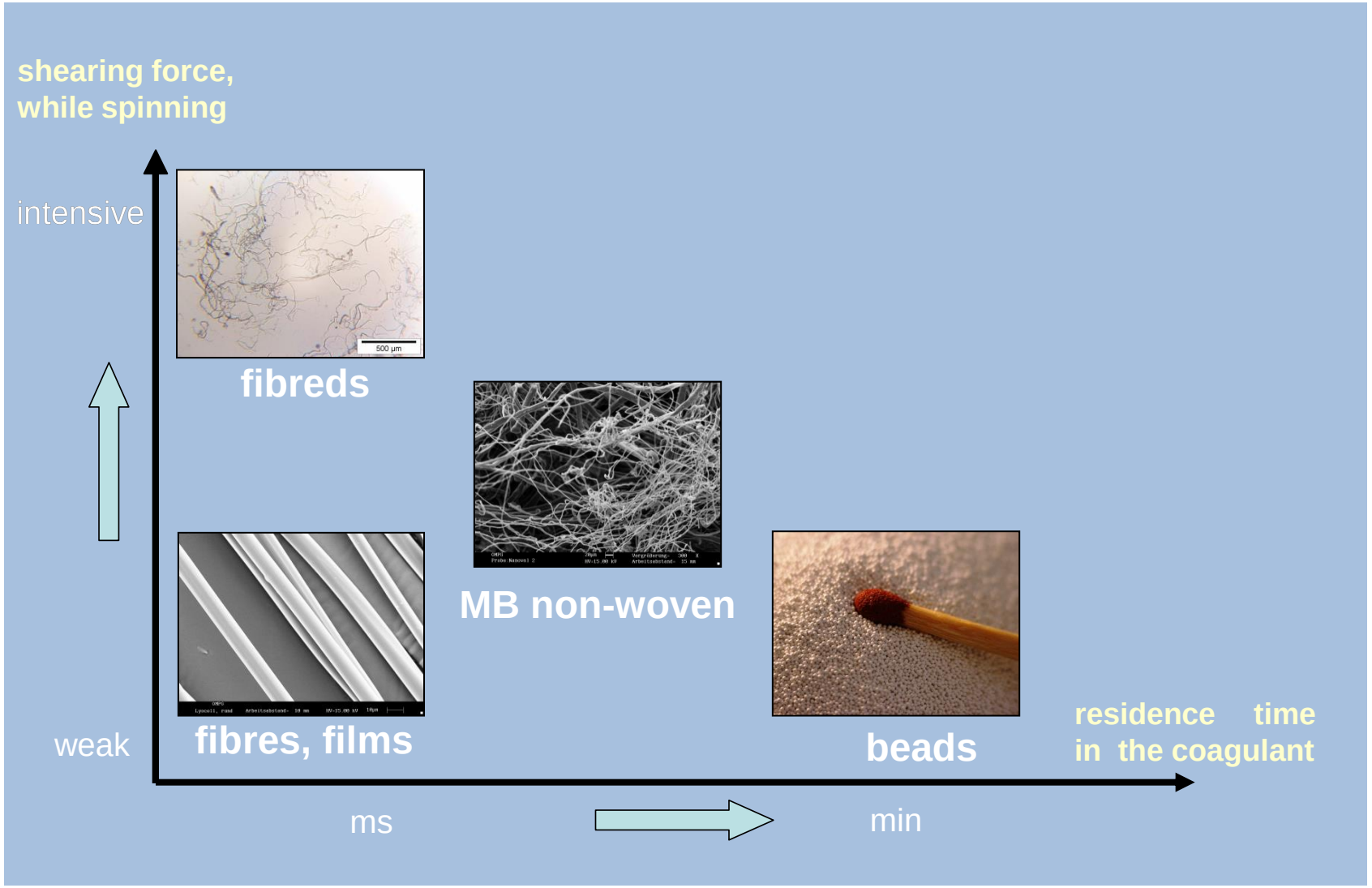
for human skin care

Cell Solution™ clima



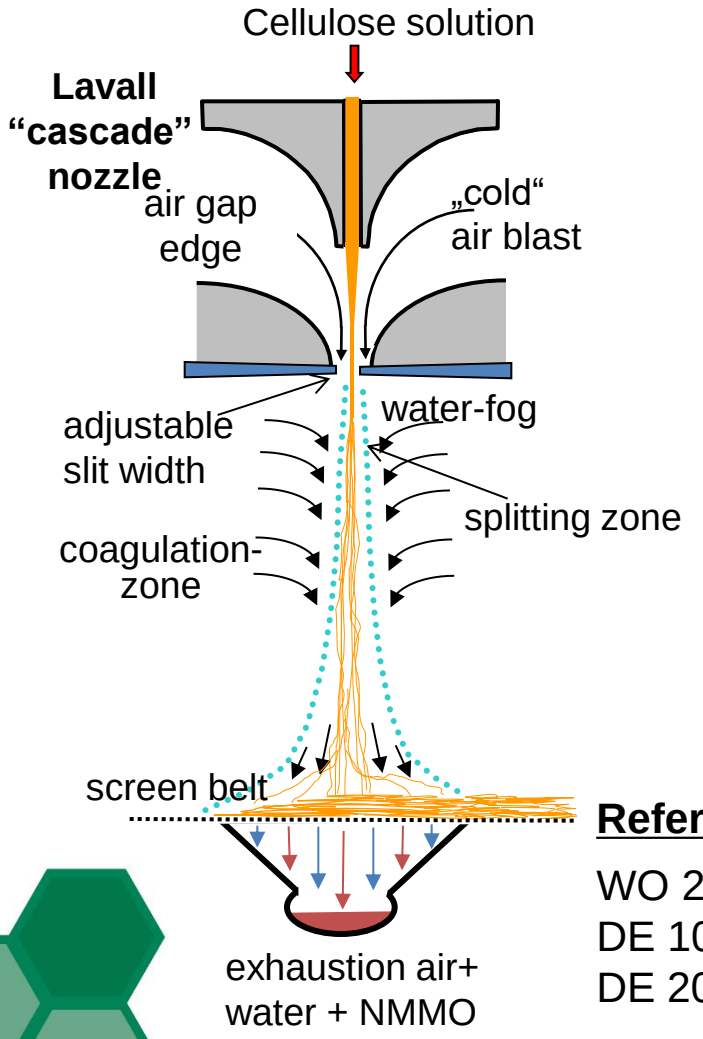
for excess heat storage

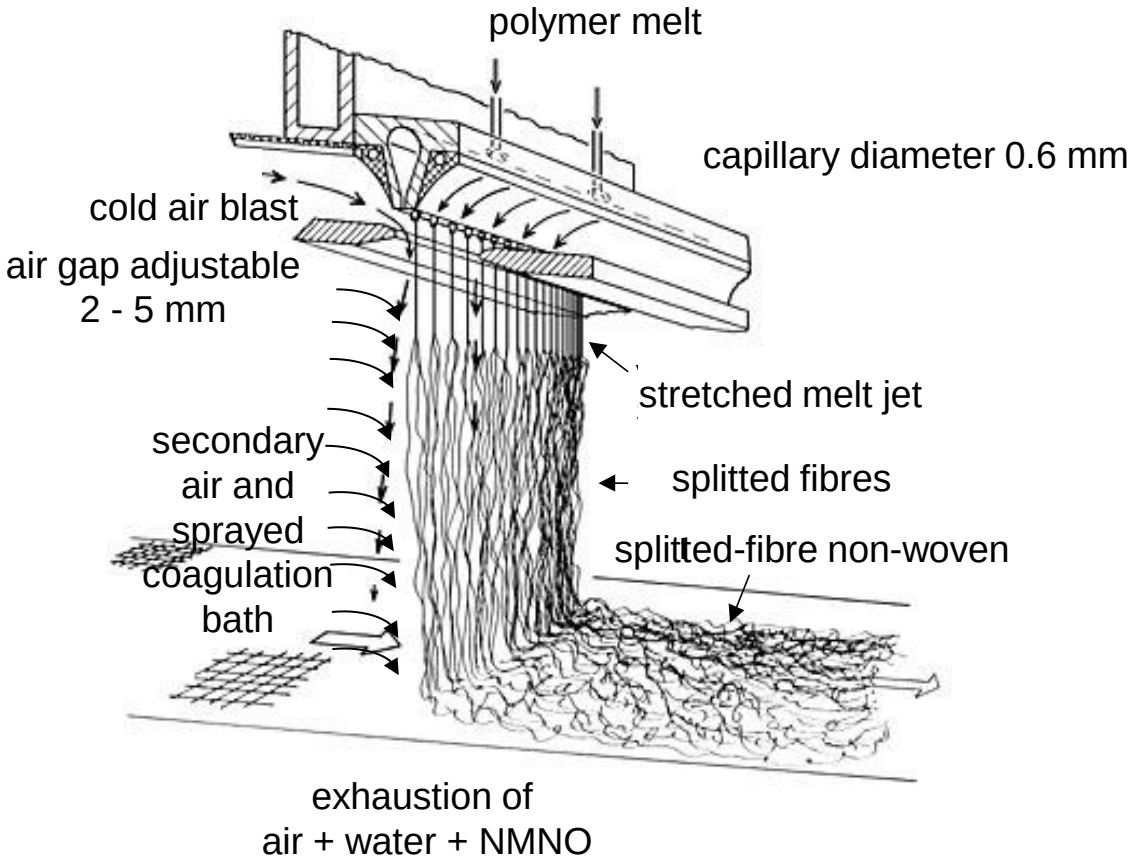
Technical options to spin new cellulose shapes



Lyocell non-woven by adapted MB spinning

= Nanoval (splitt fibre) process





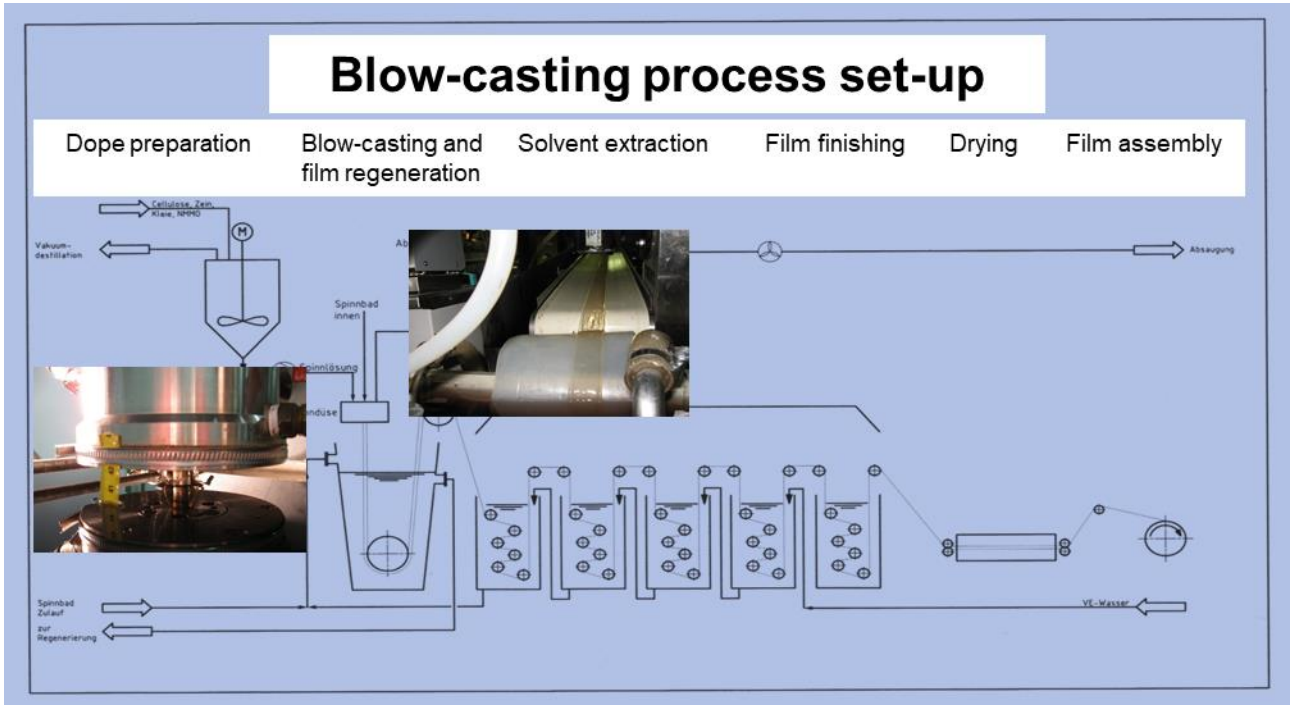
References Nanoval:

WO 2001/138056, Nov. 10, 2011
DE 102006012052, Sept. 13, 2007
DE 202005014604, Jan. 05, 2006

References Biax/Reicofil:

US 8029260, Oct. 04, 2011
US 0258562, Oct. 15, 2009
EP 2108719, Oct. 14, 2009
US 0056956, Mar. 17,2005

Film blow casting – peeling sausage skins



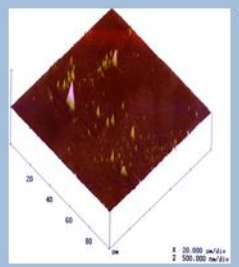
Shirred peeling skins,

parameter	unit	NMMO	Viscose	IL
cellulose concentration	[%]	9 - 12	7 – 9	14 – 18
skin thickness	[mm]	35 – 45	40 – 45	20 – 30
weight	g cell/m^2	30 – 40	30 – 40	30 – 40
swelling	[%]	110 – 120	150 - 180	100 – 110
tenacity, MD	[N]	25 – 28	18 – 20	n. d.
Elongation, MD	[%]	40 - 50	45 - 48	n. d.

Atomic force microscopy
(surface roughness)

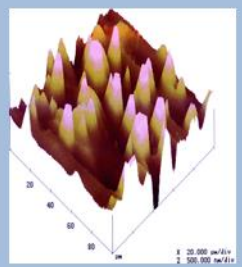
Lyocell peeling skin

5 – 14 nm

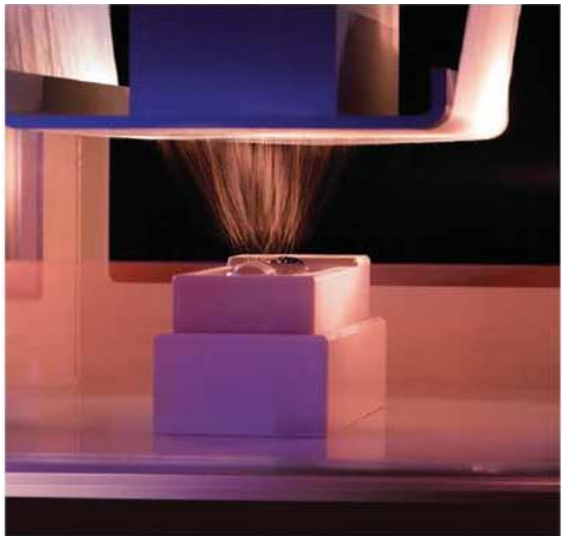


viscose peeling skin

70 – 140 nm

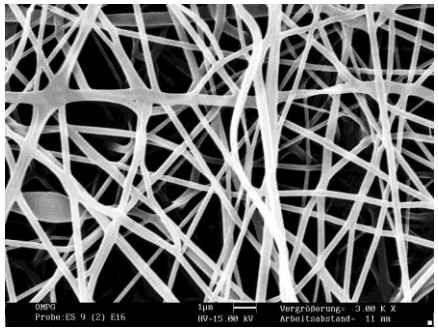


Nano fibre non-woven
by electro spinning of cellulose solutions



State of the art:

- shaping of cellulose or derivatives from aqueous or volatile organic dissolutions (DMAc/LiCl)
- need of low viscosities inhibits a shaping of higher concentrated cellulose dopes
- small conversion rate (up to g/h), only
- high added values at lowest material consumption in filtration, tissue engineering, cosmetic tissues, pharmacy, paper reinforcement



$\square_{fibre} \approx$ 60-500 nm

Most competitive to MB non-woven and BNC

Nano cellulose - ambitious product application in the high-tech sector

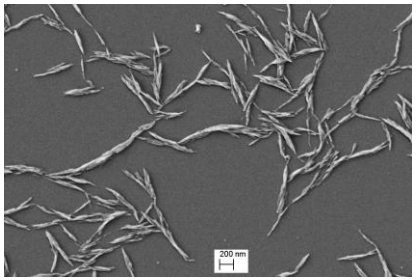
Micro fibrillated cellulose (MFC)

- high pressure homogenisation
- length = 0.1μm to some micron
- ∅: 5 – 60 nm

Application area:

- ❖board and paper
- ❖plastic reinforcement (such as starch foams)
- ❖cosmetics
- ❖filtration / oil production

Nano crystalline cellulose (NCC)

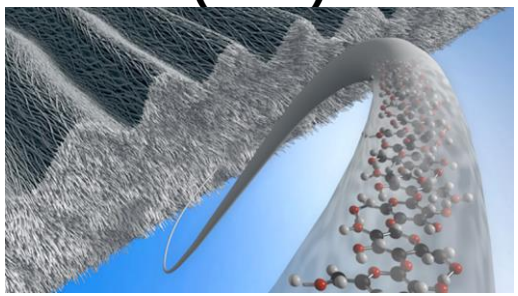


- fractional acidic hydrolysis
- length = 0.1 μm to some micron
- ∅: 5 – 60 nm

Application area:

- ❖aero gels
- ❖plastic reinforcement
- ❖high performance films
- ❖protective clothes (high impact glass and textiles)

Bacterial nano cellulose (BNC)



- biotechnological process
- different lengths according to applied technology
- ∅: 20 - 100 nm

Application area:

- ❖cosmetic masks
- ❖wound care (burns)
- ❖medical implants (blood vessels, artificial skin, etc.)

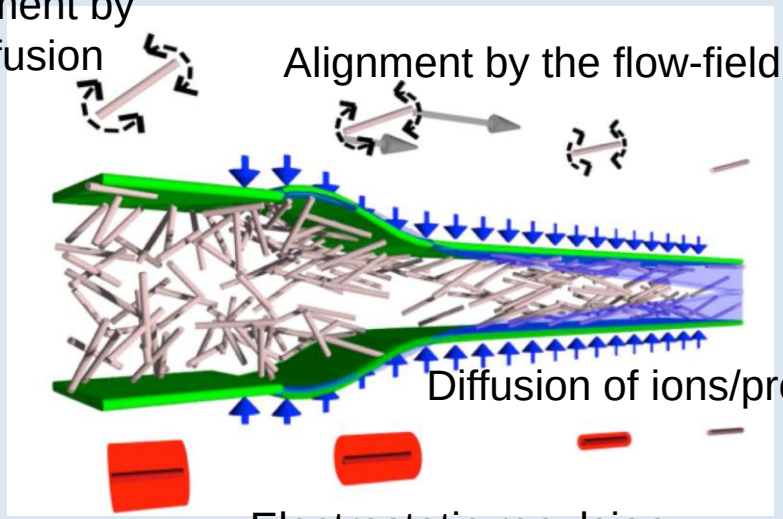
Wet spinning of cellulose nano fibrils

Reference: Håkansson et. al., “Hydrodynamic alignment and assembly of nanofibrils resulting in strong cellulose filaments”,. Nat. Comm (2014)

Process concept

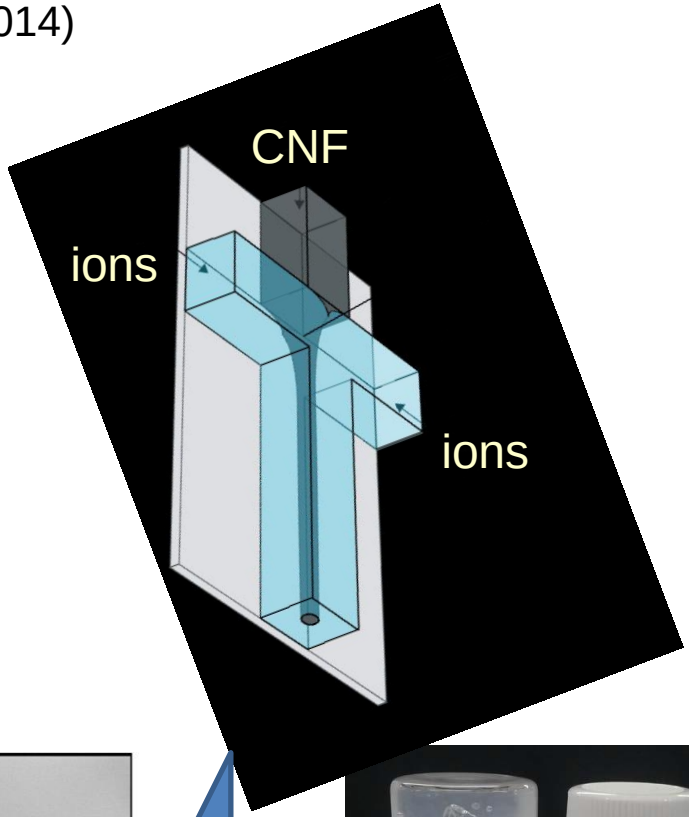
De-alignment by rotary diffusion

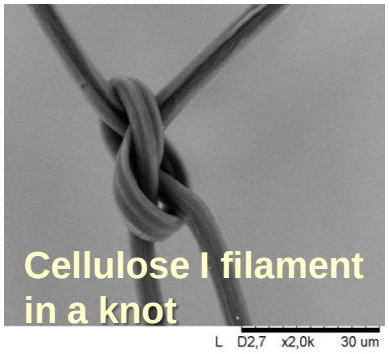
Alignment by the flow-field

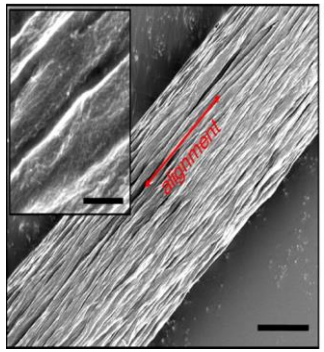


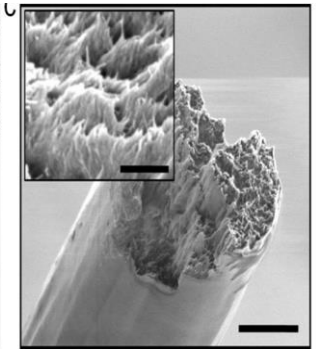
Diffusion of ions/protons

Electrostatic repulsion









Conclusion and perspectives

- Cellulose undergoes recently a renaissance as sustainable and environmental friendly material in technical application
- Global mega trends induce higher demand for cellulose man-made fibres, especially in fast developing Asian countries
- New approaches are developed to manufacture cellulose pulps without increase of cotton production
- Innovative and sustainable MMF technologies are developed for functional fibre, non-woven and film manufacturing
- Cellulose nano-structures like MFC, NCC and BNC are on the way into commercial production, innovative applications and reasonable priced goods
- Innovative fibre spinning technology based on nano-structures will allow more improved sustainability without any danger for environment

Thank you very much for your kind attention !

Comments or any questions ?

Contact:

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