Aalto University
School of Chemical
Engineering

Cellulose: regenerated fibres

CHEM-E2140 - Cellulose Based Fibres

Michael Hummel

Learning outcomes

After this lecture you know

- **4 different spinning principles**
- **the key-properties of biobased man-made fibers**
- **basics of yarn spinning**
- **the difference between viscose and Lyocell**
- **principles and applications of the Ioncell™ process**
- **problems associated with chemical cotton recycling**

Fibers

- **Natural**
- **Man-made**

Man-made fiber from natural polymers

Cellulose	
Cellulose acetate	CA
Cellulose triacetate	CTA
Cellulose nitrate	CN
Rayon fibers:	
Cupro	CUP
Viscose	CV
Modal	CMD
Lyocell	CLY

Other natural polymers	
Alginate	ALG
Elastodiene	ED

Fiber production 2017

Natural

Cotton: 25.6 Mt

Wool: 1.17 Mt

Jute: 3.1 Mt

Coir: 0.50 Mt

Sisal: 0.30 Mt

Hemp: 0.27 Mt

Man-made

Natural polymers

Cellulose staple fiber: 6.6 Mt

- Viscose: 5.5 Mt
- Acetate: 0.85 Mt
- Tencel: 0.2 Mt

Cellulose filament: 0.35 Mt

Synthetic polymers

Polyester

- staple fiber: 15.4 Mt
- filament: 38.2 Mt

Acrylic

- staple fiber: 1.7 Mt

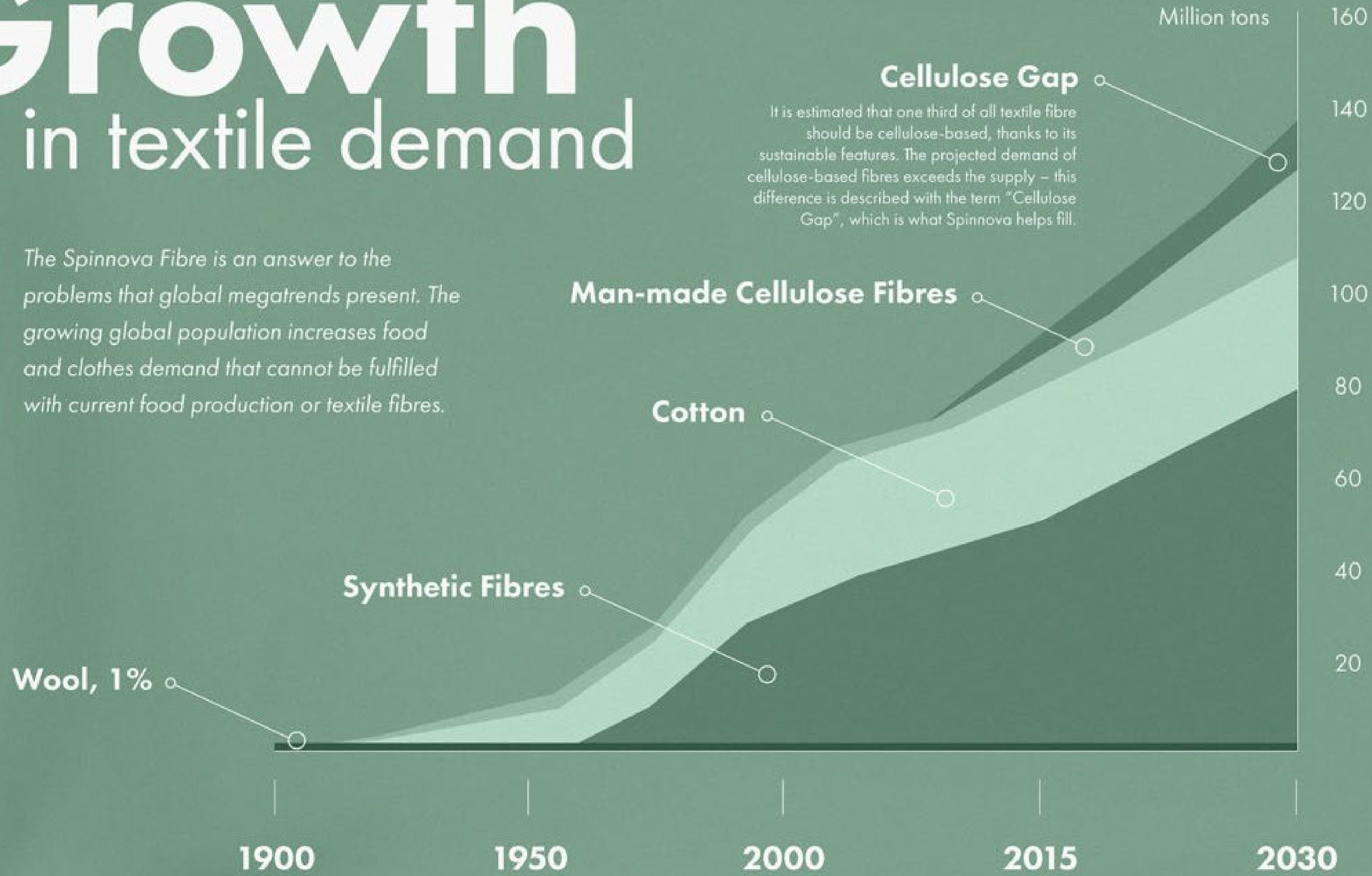
Polyamid

- filament: 5.2 Mt

Carbon fiber 0.1 Mt

Growth
in textile demand

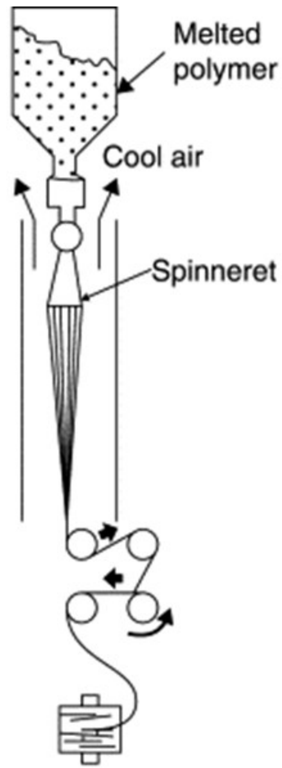
The Spinnova Fibre is an answer to the problems that global megatrends present. The growing global population increases food and clothes demand that cannot be fulfilled with current food production or textile fibres.



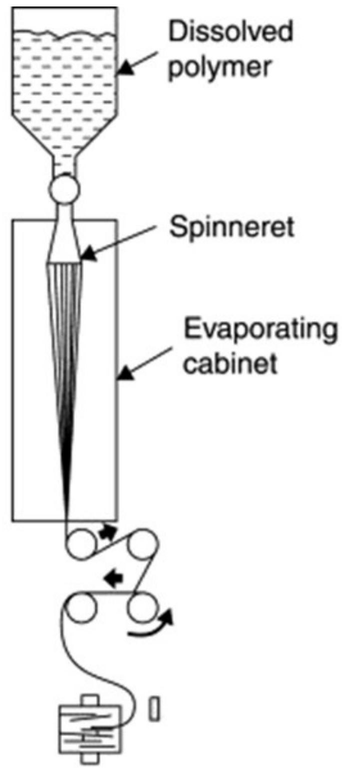
Spinnova
The Sustainable Fibre Company

https://spinnova.com/us/megatrends/

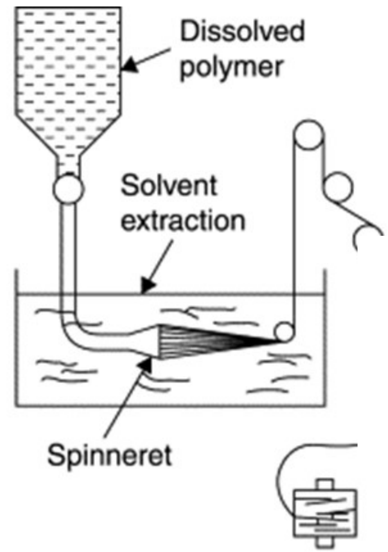
Spinning technologies



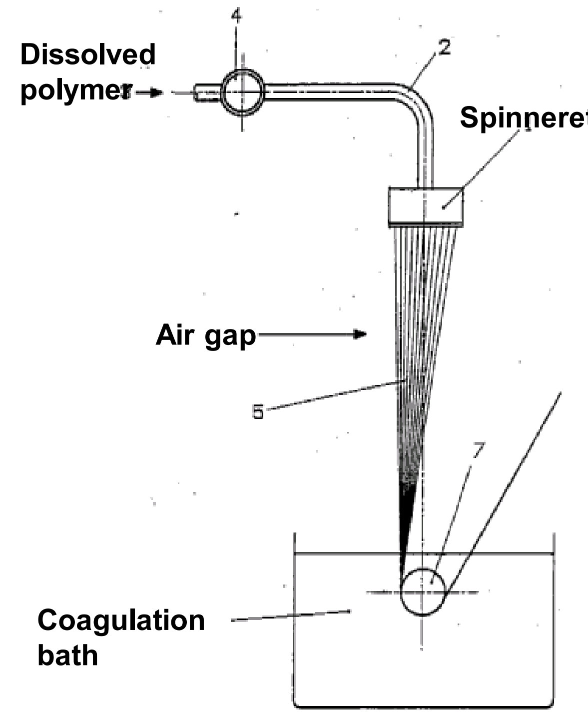
Melt spinning



Dry spinning



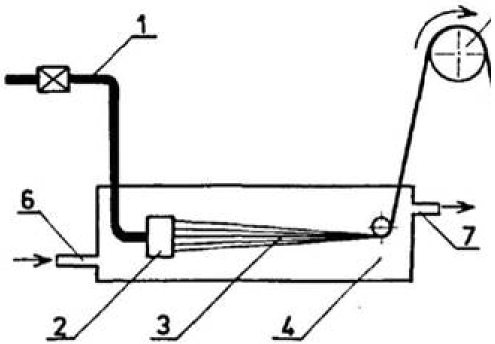
Wet spinning



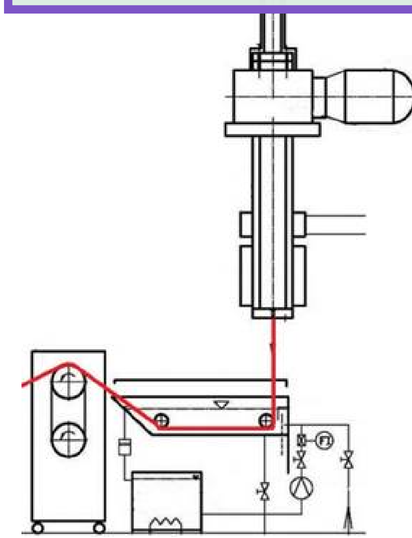
Dry-jet wet spinning

Man-made cellulosic fibers

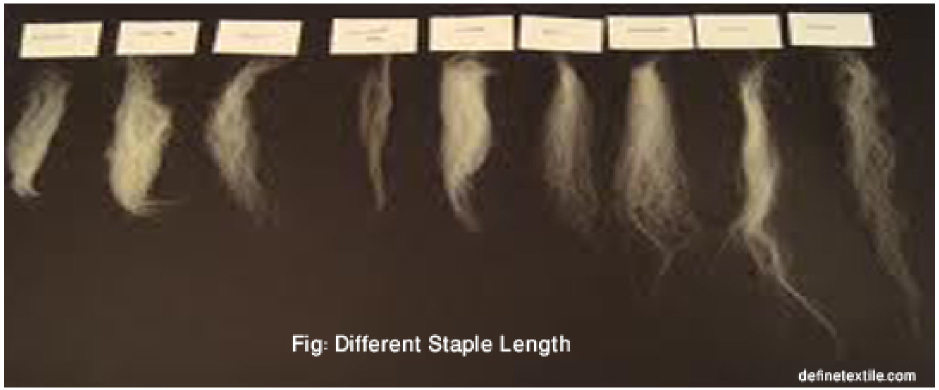
Wet spinning



Dry-wet spinning



Staple fibre vs. continuous filaments



short length fibres, which are twisted together (spun) to form a coherent yarn

The average length of a spinnable fiber is called *Staple Length*.

It influences:

- Spinning limit
- Yarn evenness
- Handle of the product
- Luster of the product
- Yarn hairiness
- Productivity

Staple fibre vs. continuous filaments

"endless" filament

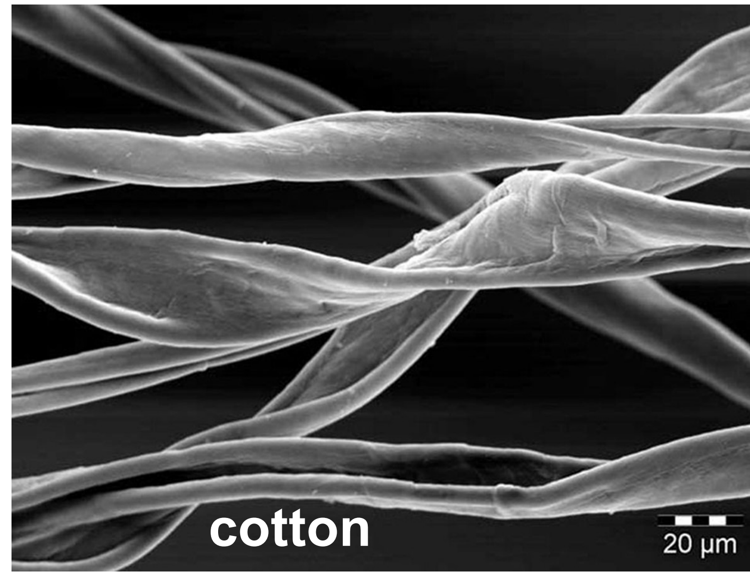
Multifilament consists of monofilaments

Filament number:
From 100 to a few 1000

Fiber thickness

Thickness is expresses as **Linear Density**
= Mass per length = **Titre**

Unit
1 tex = 1 g fiber / 1000m
1 dtex = 1 g fibre / 10000 m



Fiber thickness

Linear Density (fiber fineness)
Mass per unit length (= titre)
1 dtex = g fibre / 10000 m

Circular cross section
Area A is related to diameter D:
Linear density c:
c... tex
D...mm
ρ....g/cm³

$$A = \frac{\pi D^2}{4}$$

$$c = A\rho = \frac{\pi \rho D^2}{4}$$

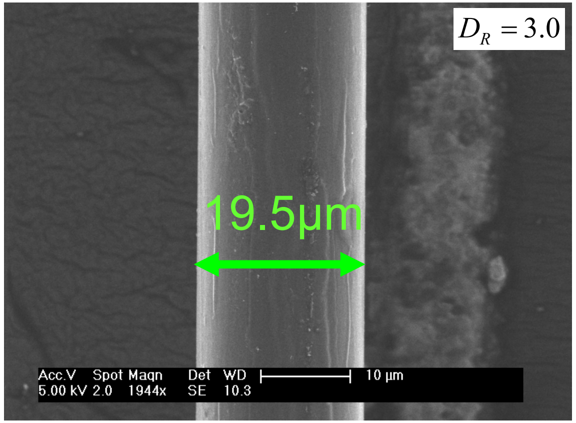
$$D = 2 \cdot \sqrt{\frac{c}{\pi \cdot \rho}}$$

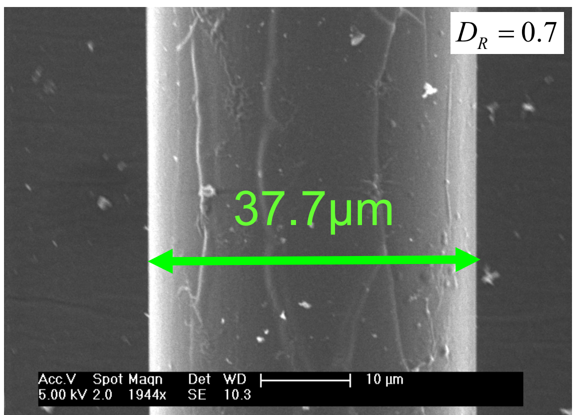
Diameter of a 1.3 dtex fibre?

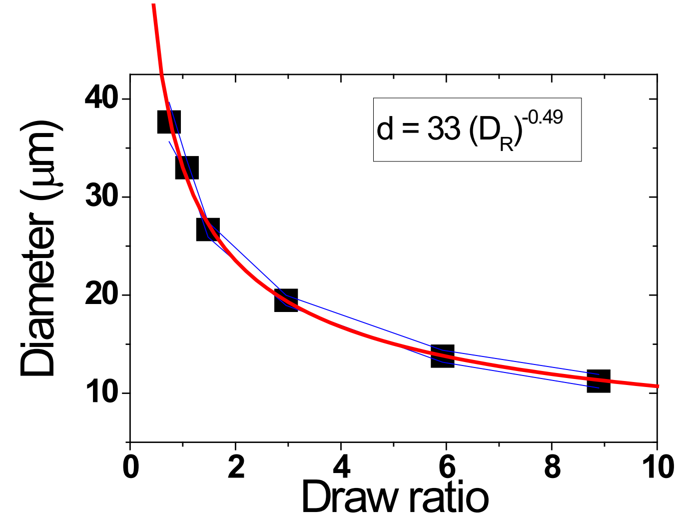
$$\left(\frac{0.13\ g}{1000\ m} \cdot \frac{1}{\pi} \cdot \frac{10^{-6} m^3}{1.53\ g}\right)^{0.5} \cdot 2 = 10.5 \cdot 10^{-6} m = 10.5\ \mu m$$

$$D\ [\mu m] = 11.3 \sqrt{\frac{c_{dtex}}{\rho}}$$

Effect of Draw ratio on Fibre Diameter





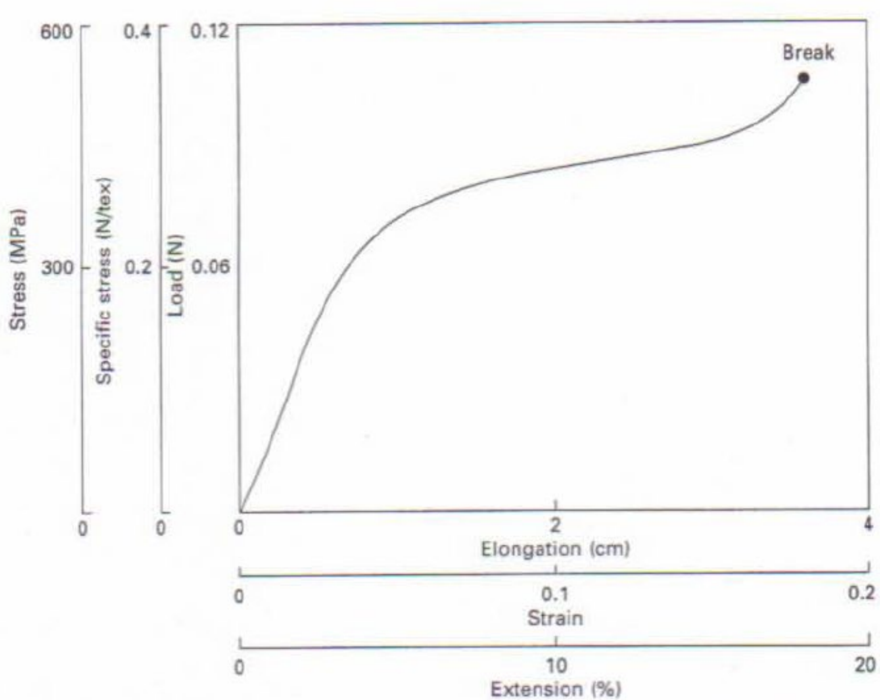


- Fibre diameter is strongly related to draw ratio

Mortimer, S. A and Péguy, A. A. (1996), Cell. Chem. Technol, 30, 117

S. J. Eichhorn, K. Kong. 229th ACS National meeting March 13 – 17, 2005

Stress-Strain Curves



$$Tensile\ strain = \frac{elongation}{initial\ length}$$

$$Stress = \frac{Load}{Area\ of\ cross-section}$$

SI units of stress is Pa (Nm^{-2}). In textile technology the stress is related to the linear density (mass per unit length)

$$Specific\ \ stress = \frac{Load}{Linear\ density}$$

Unit is Nm/kg or N/tex:

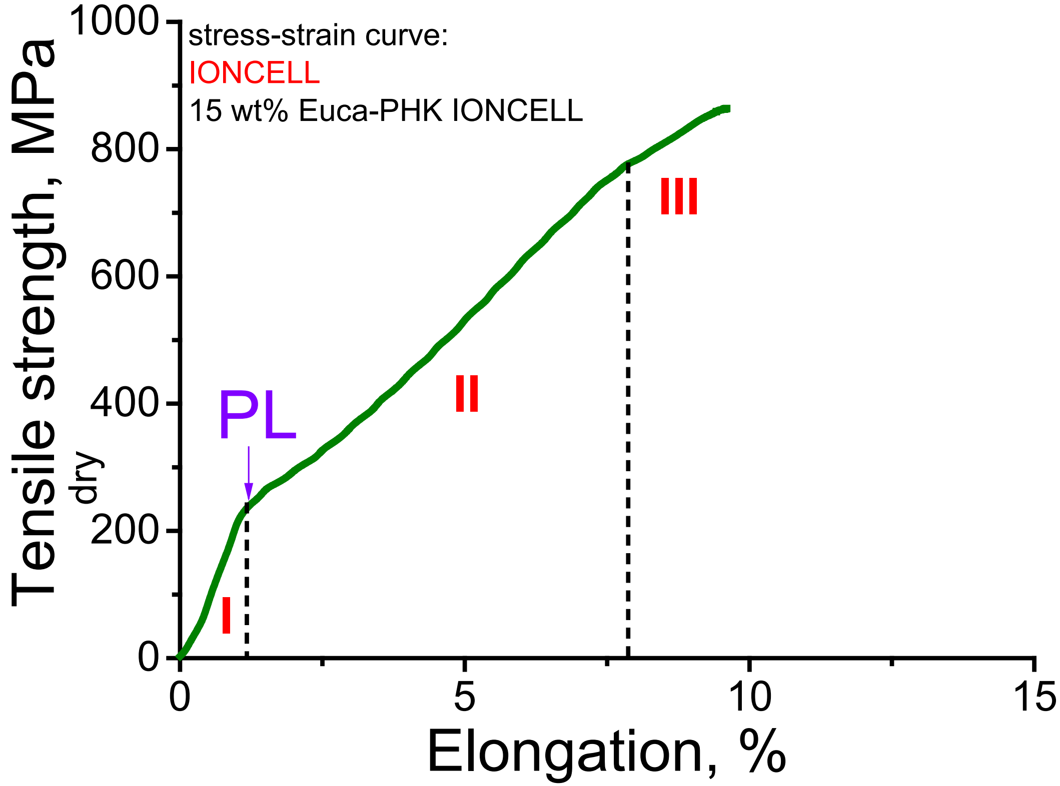
$10^6\ Nm/kg = N/tex$

Stress f (GPa), specific stress σ (N/tex), density ρ (g/cm^3):

$f = \sigma \cdot \rho$

Tenacity = Specific stress at break

Tensile deformation of dry cellulose fibres



Stage I:

Internal energy elasticity: Extension of fibrillar&molecular structure without disrupting H-bonds between fibrils.
Plastic deformation due to disruption of interfibrillar H-bonds close to PL

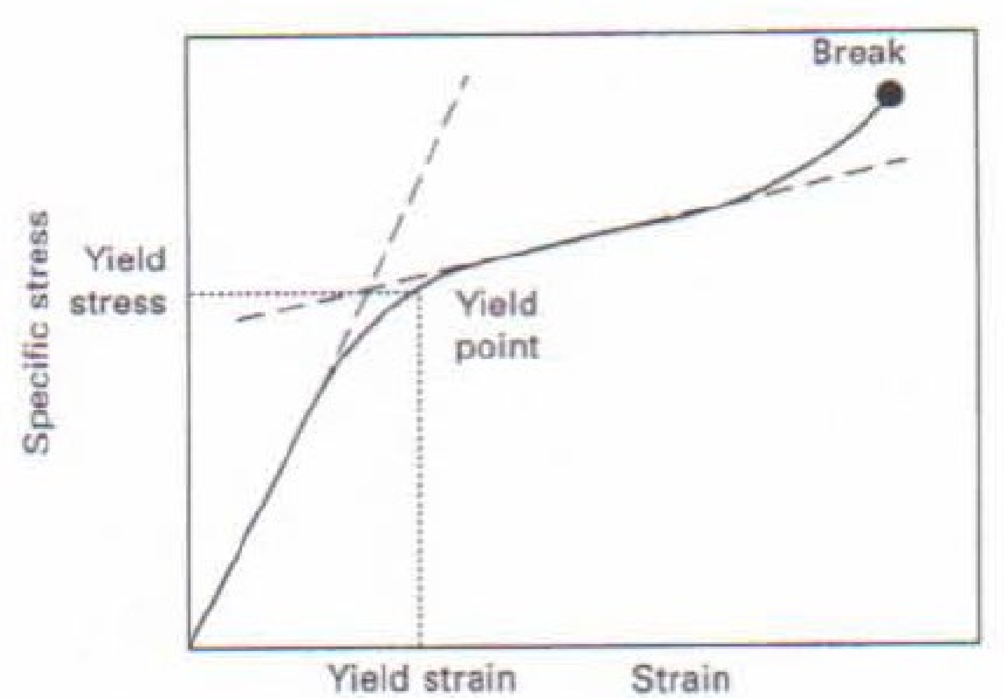
Stage II:

Orientation of fibrils unhindered by interconnecting H-bonds. Slower build-up of stress

Stage III:

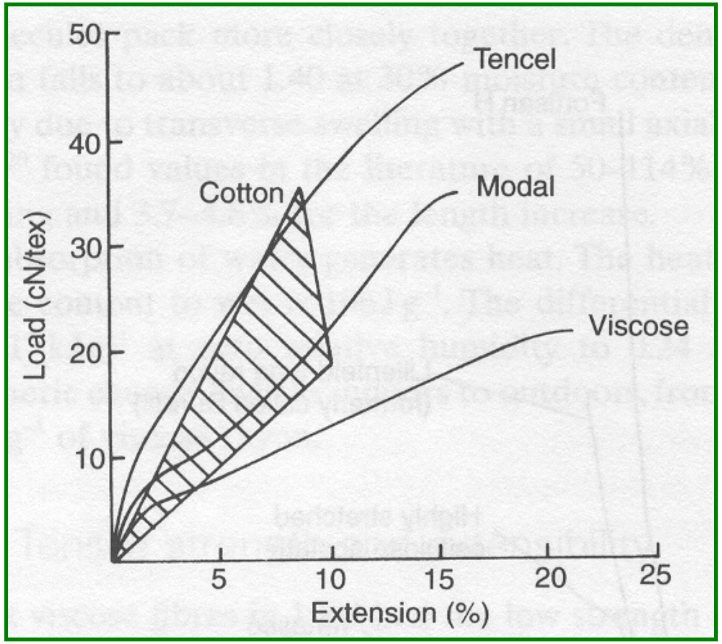
Chain slippage and chain rupture

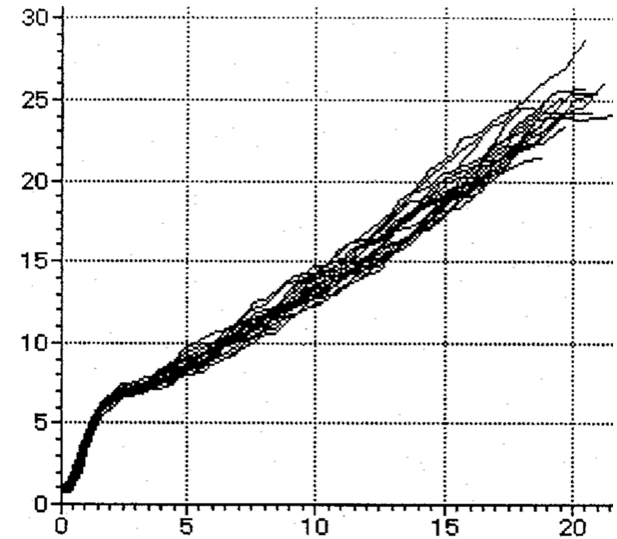
Yield Point



- Yield point as occuring at the stress given by the **intersection of the tangent at the origin with the tangent having the least slope.**
- At the yield point, elastic recovery becomes less complete for higher strains.
- **Point at which permanent deformation starts**

Tensile properties



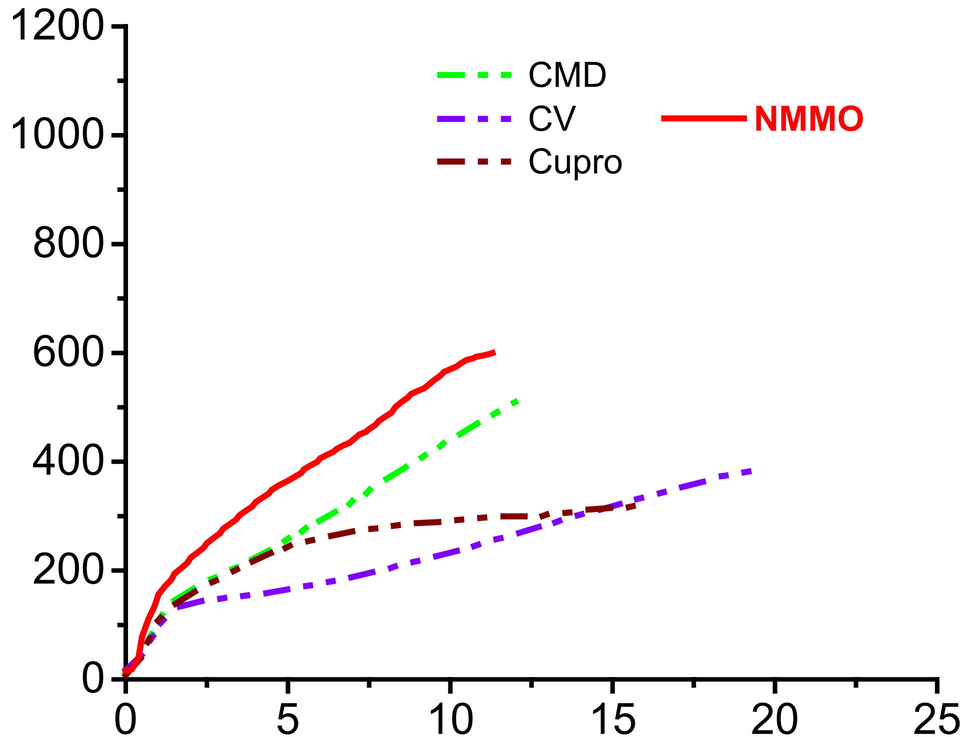


$$\frac{cN}{tex} = \frac{10^{-2} \cdot kg \cdot m \cdot s^2 \cdot 10^3 \cdot m}{s^2 \cdot kg \cdot m \cdot 9.81 \cdot 10^{-3}} \approx 10^3 m$$

$$R_m = \frac{cN}{tex} \cdot \rho \cdot g = 10^3 m \cdot \frac{1500\ kg \cdot 9.81 \cdot m \cdot s^{-2}}{s^2 \cdot kg \cdot m \cdot 9.81 \cdot 10^{-3}}$$

$$\approx \frac{1.5 \cdot 10^7 N}{m^2} = 15\ MPa = 0.015\ GPa$$

Stress-strain curves of Regenerated Cellulose Fibers

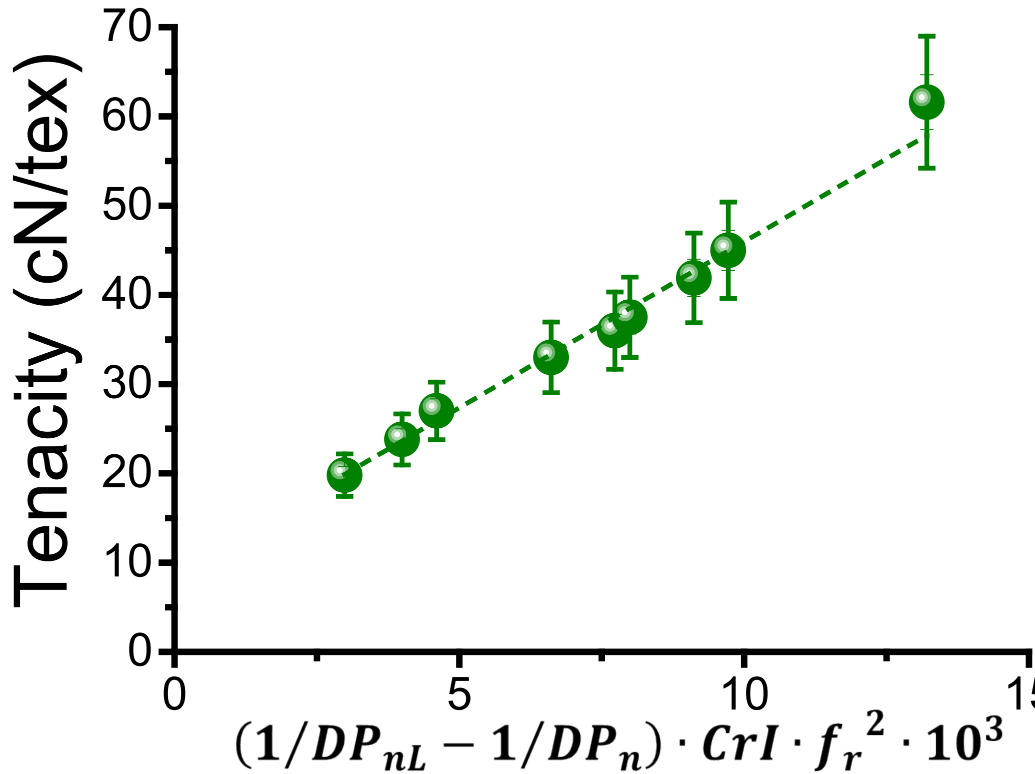


Structural vs. Mechanical Properties

- Mechanical properties such as fibre tenacity, $\mathbf{FF_c}$, are determined by
  - the $\mathbf{DP_n}$ in relation to the size of
  - the elementary crystallites $\mathbf{DP_{nL}}$
  - the degree of lateral order, $\mathbf{X_c}$, and
  - the degree of orientation, $\mathbf{f_c}$ and $\mathbf{f_{tot}}$.

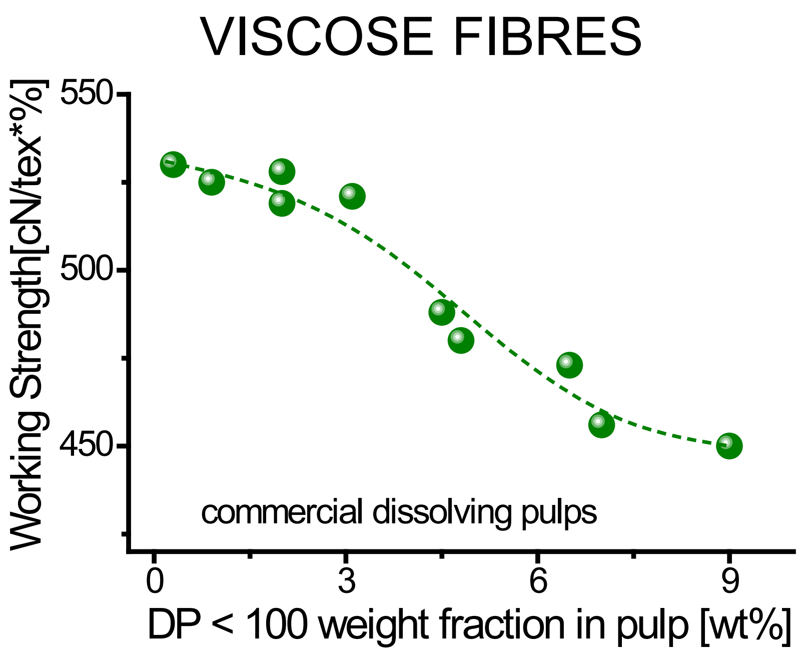
- Krässig has shown a linear relationship between $\mathbf{FF_c}$ and $(1/DP_{nL} - 1/DP_n) \cdot CrI \cdot {f_r}^2 \cdot 10^3$ valid for cellulose fibres including fortisan, polynosic and HWM.

Effect of molecular an structural characteristics



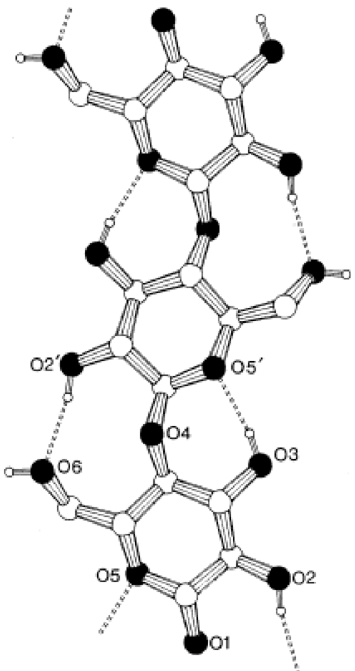
Hans Krässig: Cellulose (1993), p161

Short-chain molecules, DP < 100

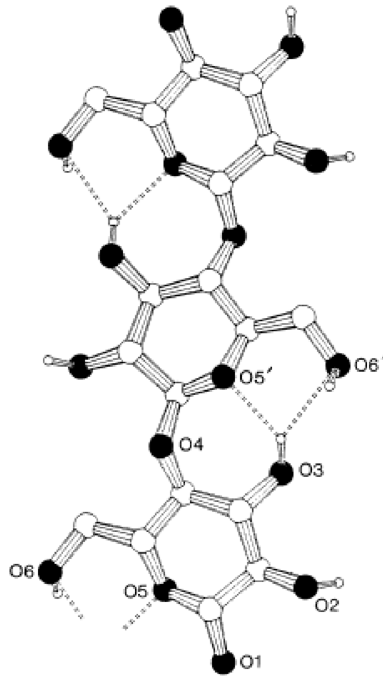


Maximum strength properties (tensile strength times elongation) of regular visose fibres dependend on the amount of DP<100 fraction.

Continuous chain model



CELL I
Chain modulus =
140 GPa



CELL II
Chain modulus =
90 GPa

- Chains are oriented parallel to the symmetry axis and the orientation angle of this axis ϕ with the fiber axis shows a distribution $\rho(\phi)$

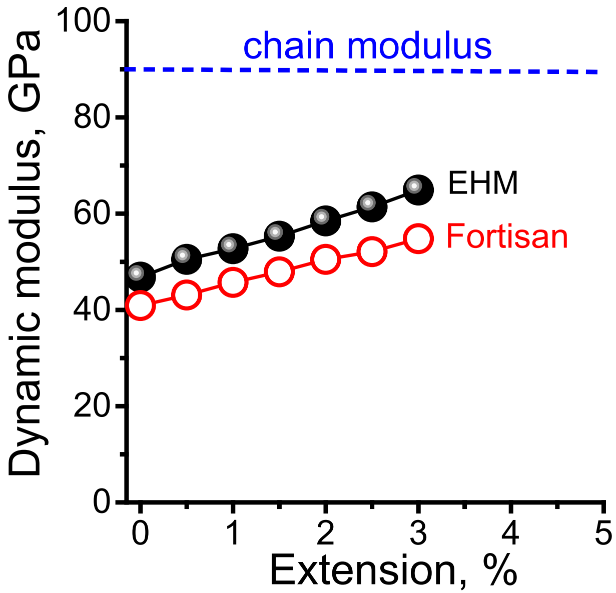
- Elastic tensile deformation is due to the chain elongation and the shear deformation.

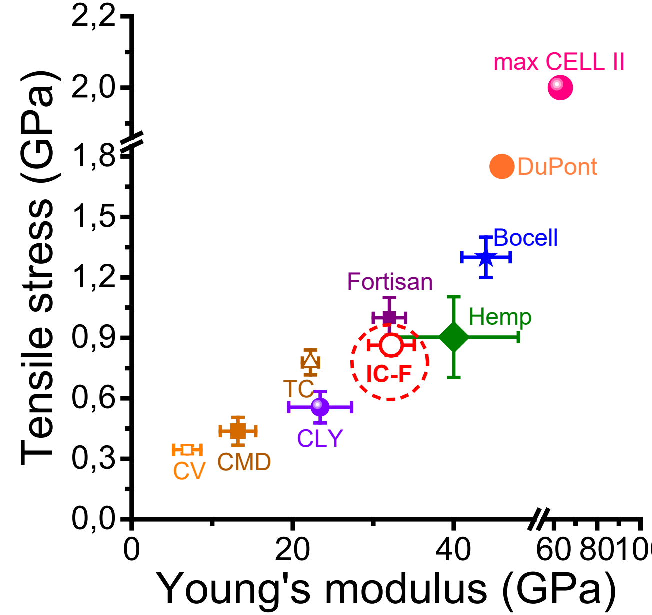
- Chain modulus, **e_c**, purely elastic, shear deformation, **g**, is determined by intermolecular H-bonding (time dependent) and denotes the shear between adjacent chains.

$$\frac{1}{E} = \frac{1}{e_c} + \frac{\langle sin^2\phi \rangle_E}{2g}$$

$\langle sin^2\phi \rangle$	orientation parameter
E, e_c, g	elastic, chain, shear moduli
σ	tensile stress

Ultimate strength of cellulose fibers





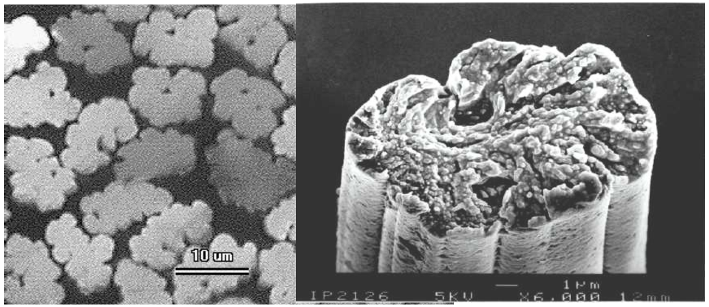
Dynamic modulus depends only on the extension: **E as a f (ε)** for well-oriented regenerated cellulose fibers: **second loading cycle.**

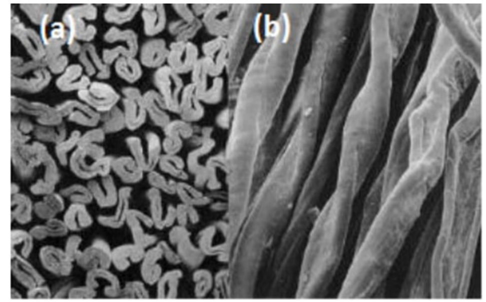
E_{max}: ~ 60 GPa (IC-F: 35)

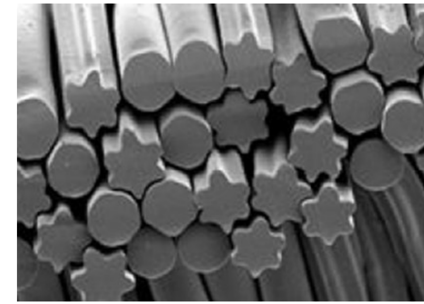
σ_{max}: ~ 1.8 GPa (IC-F: 0.9)

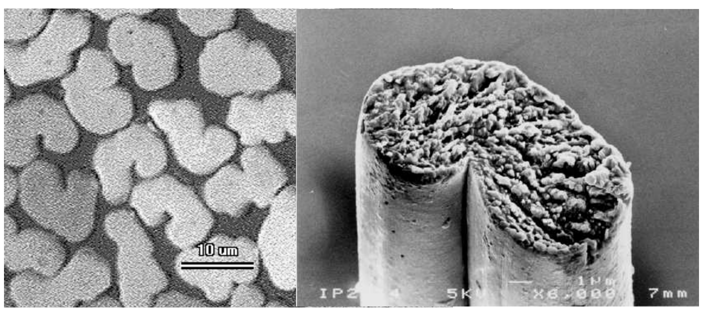
Northolt, M.G. Lenzinger Berichte, (**1985**), 59, 71-79. De Vries. Appl. Sci. Res. A3, 111 (**1952**).

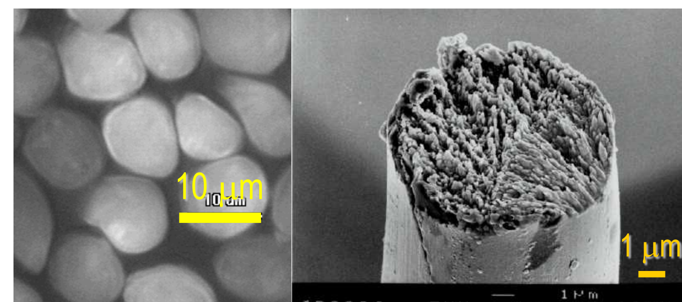
Cross section











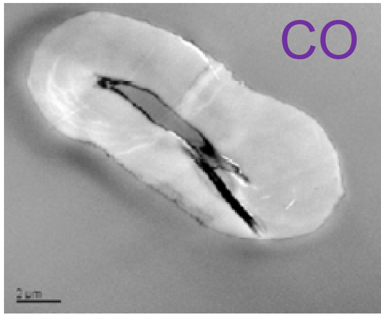
Structure and Mechanical Properties

Fiber	Mechanical properties			Structural properties			
	σ_C	ε_C	F_w	DP_v	X_c	f_C	f_{tot}
	GPa	%			%		
Viscose	0.38	20	0.50	430	28	0.62	0.41
Modal	0.51	13	0.57	650	29	0.66	0.47
Tencel™	0.60	15	0.90	900	41	0.85	0.59
Ioncell™	0.85	10	0.92	900		0.96*	0.81*
Bocell	1.30	7	0.85	650	59		

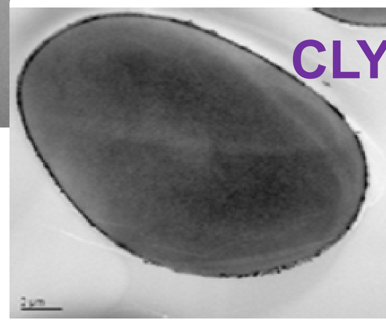
F_w ratio wet-to-dry strength
x_c WAXS degree of crystallinity
f_c crystalline orientation parameter (Hermans, 1946)
f_{tot} total orientation parameter
* different method

$$f_a = \frac{f_t - (x_C \cdot f_C)}{(1 - x_C) \cdot 0.91}$$

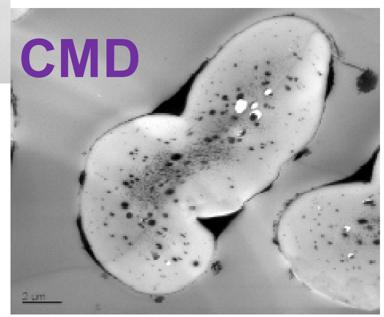
T. Röder, P. Zipper (2003), Lenzing AG
*H-P Fink (2014)



Cotton absorbs only little water

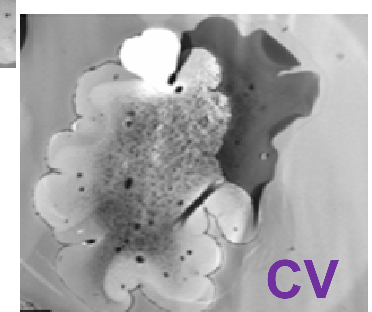


Tencel shows uniform water absorption over the whole fiber cross section



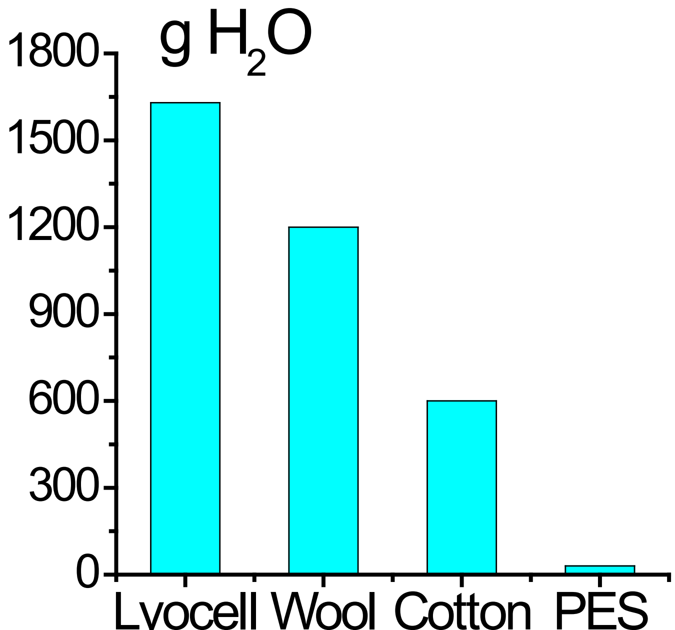
Crystalline skin of **Modal** contains less water than the core

Visualization of water:
Solvent exchange procedure followed by isoprene polymerization and OsO_4 staining in aqueous solution:
M. Abu-Rous et al. *Cellulose*, 13, 411-419 (2006)



Uneven water distribution in **viscose**

Water Vapour Sorption



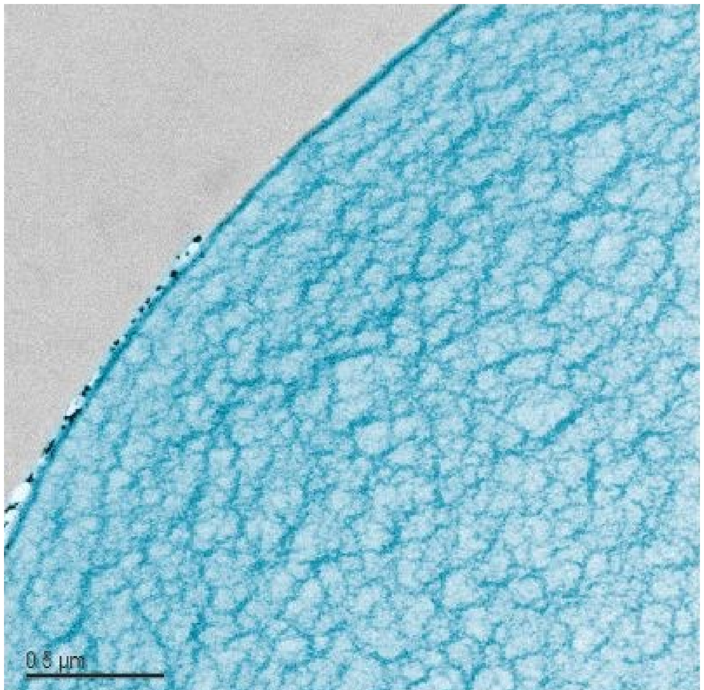
Absorption capacity of equivalent beds at 100 % RH

Lyocell beds helps to make a comfortable sleeping climate.

Water absorption takes place in the capillaires between the fibrils only

H. Firgo et al., Dornbirn 2003

Nanofibrillar Structure of Lyocell Fibers

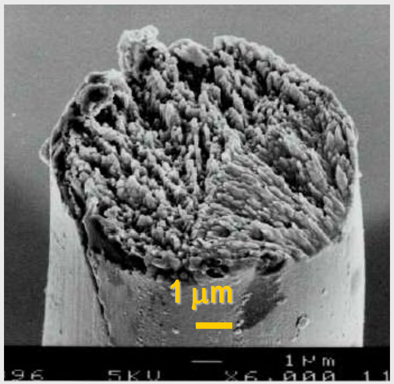


Nanofibrils act as a microscopic canal system that facilitates moisture absorption and transportation

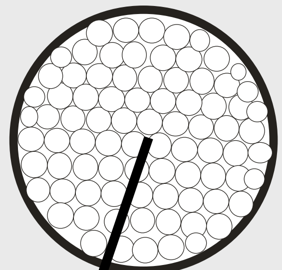
Courtesy to Lenzing AG

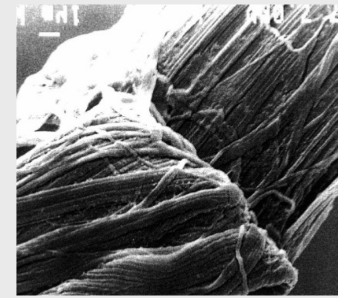
Lyocell Fiber – NanoMultifilament

- Nonswelling hydrophilic crystalline microfibrils
- Swelling amorphous regions and interfibril capillaries

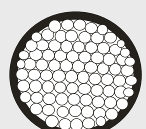


Fibre, diameter 8 - 30 µm



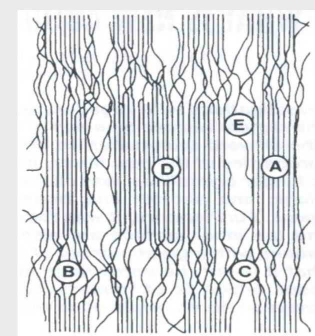


Skin, app. 100 nm dry, can swell widely in H_2O



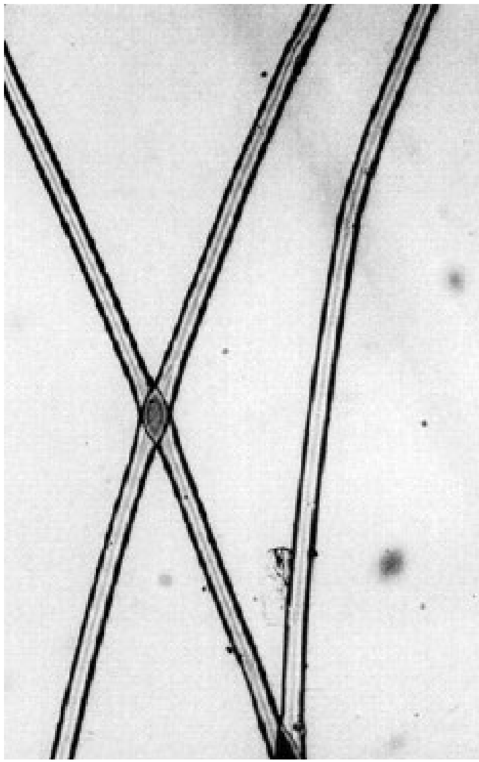
Macro-fibril (0,5 - 1µm), made up of micro-fibrils (10 - 100 nm)

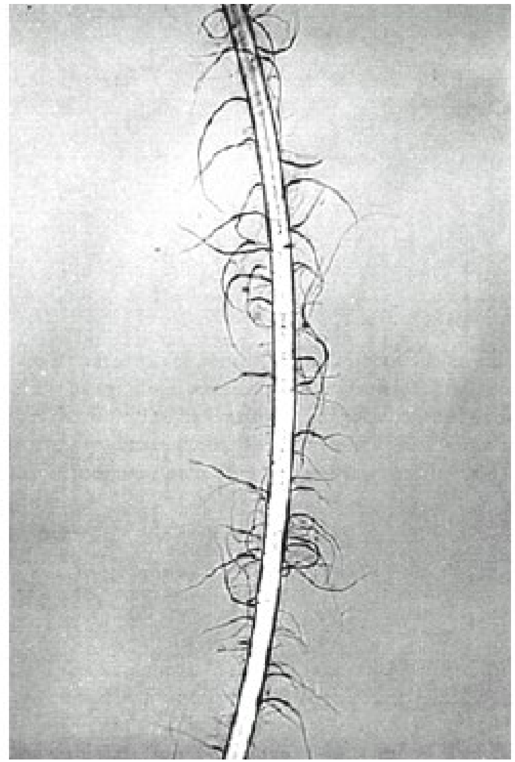
Microfibrils (D & A), non swelling

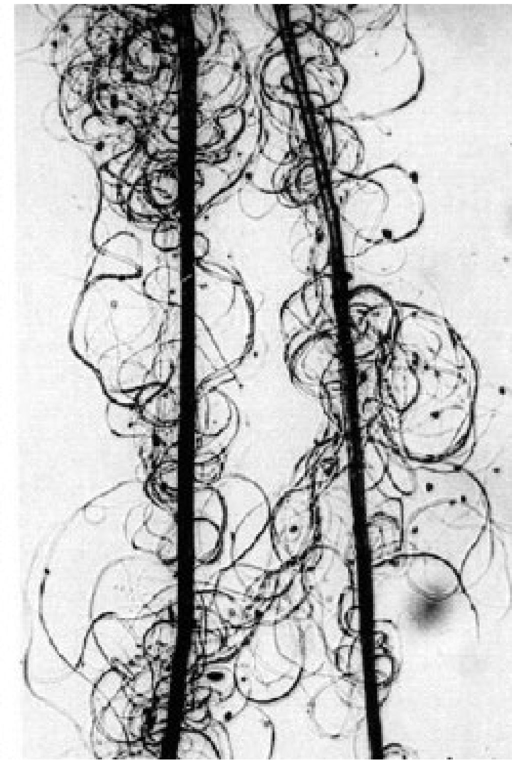


H. Firgo et al., Dornbirn 2003

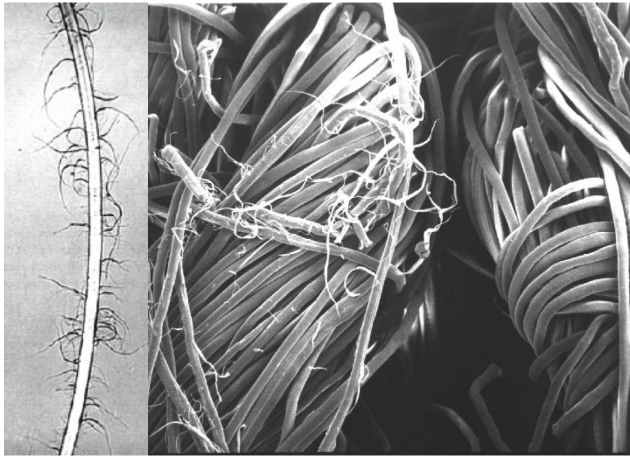
Fibrillation of Lyocell Fibres



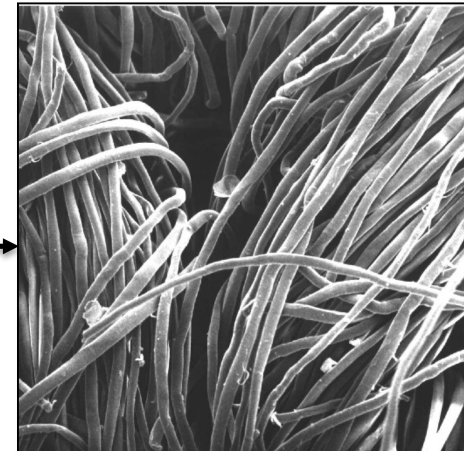




Tendency of Fibrillation



Cross-linking

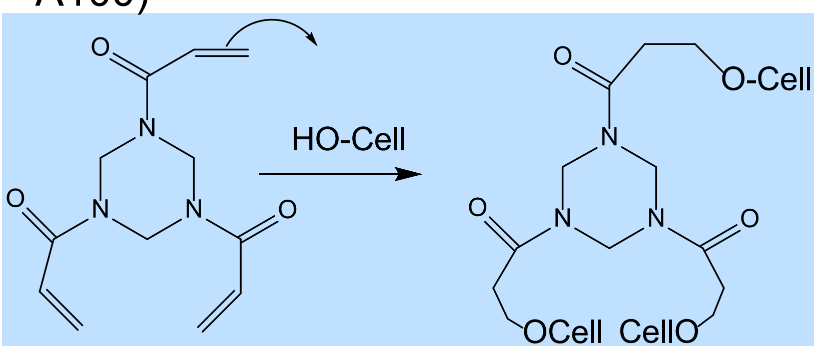


Mechanically treated

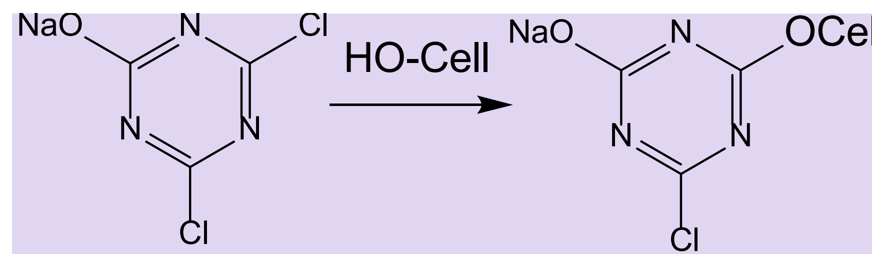
Lyocell

Lyocell LF

Triacrylamido-trihydrotriazin (Lenzing, A100)



2,4-Dichloro-6-hydroxy-1,3,5-triazin (Lenzing, Lyocell LF)



Crimp

The crimp of a fibre increases the covering power (capacity to cohere) and is the prerequisite for the further processing to yarn and fabric.

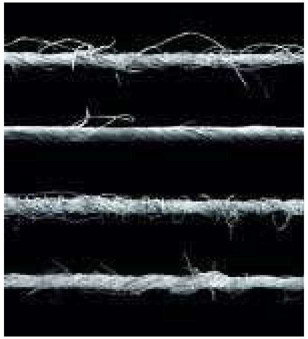
Viscose staple fibres receive a spontaneous crimp due to the skin-core structure

Summary questions

- What does the titer tell us and how is it connected to the thickness of a fiber?
- Which units are used for tensile strength?
- What is the chain modulus of cellulose?
- Lyocell has higher orientation than viscose type fibers. This affects which properties? Positive and negative examples

Yarn production

Yarn Spinning



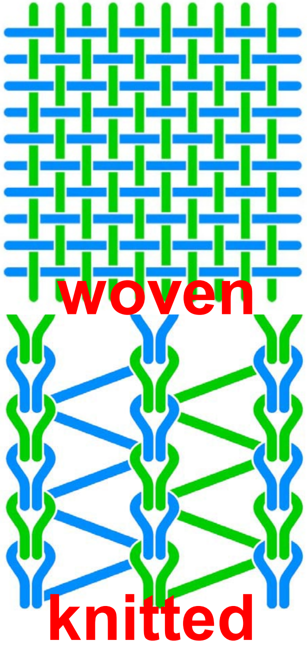
Ring: 20 m/min

Compact: 20 m/min

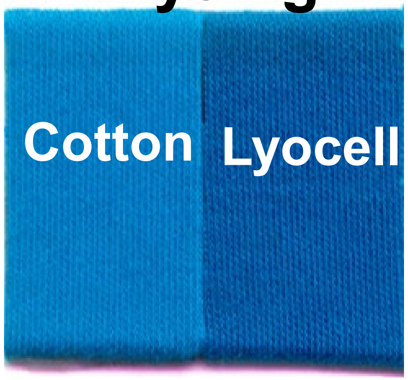
OE: 150 m/min

Air jet: 450 m/min

Weaving
Knitting



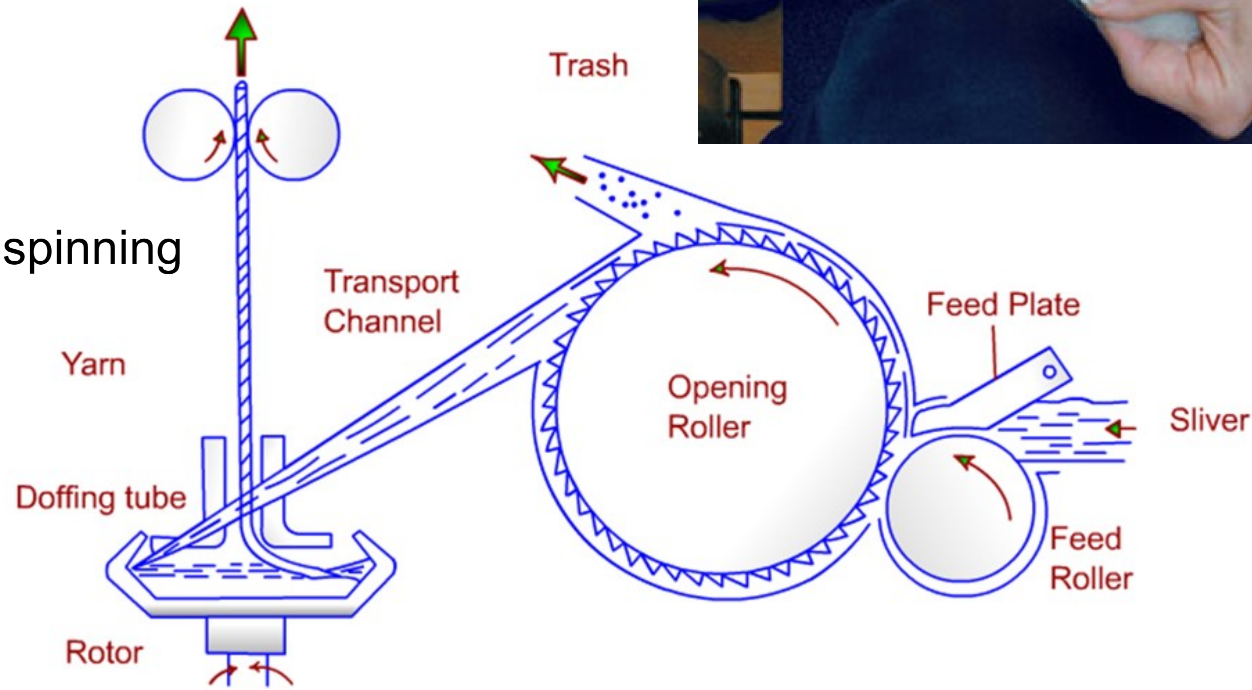
Dyeing



Yarn spinning techniques

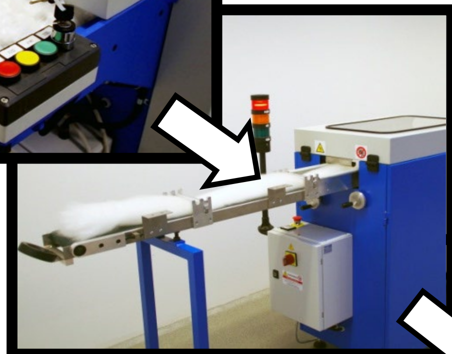
- Hand spinning
- Rotor spinning
- Ring spinning

Rotor spinning

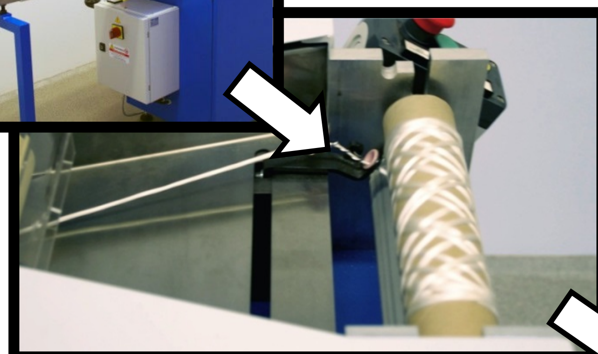


Ring spinning steps

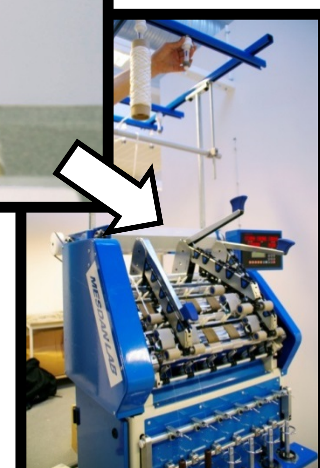
carding of fibers

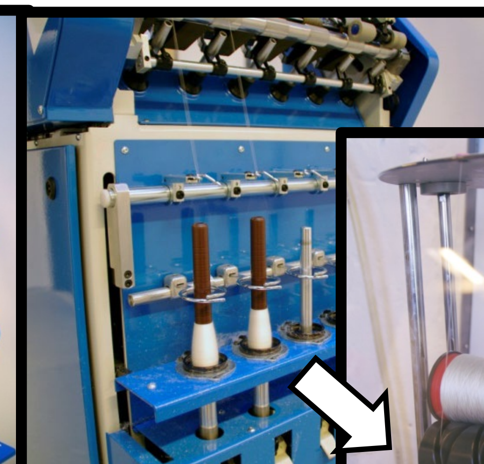


sliver fed to the drafting machine

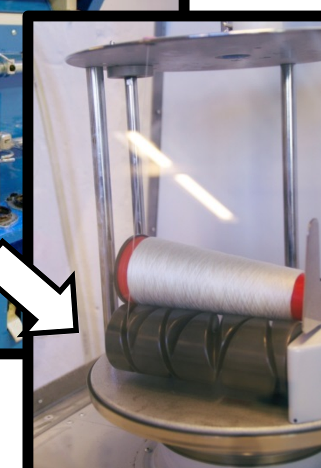


preparing of roving



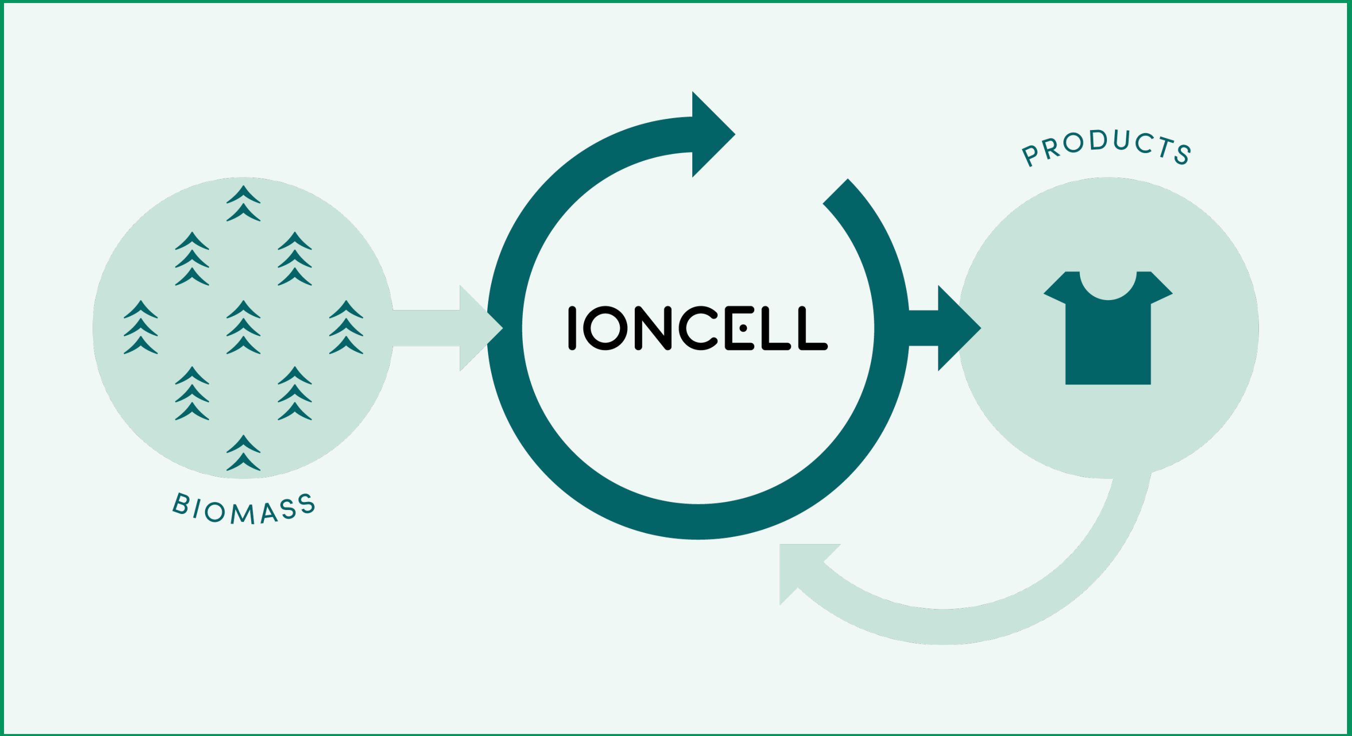


ring spinning



yarn plying

Ionic liquids



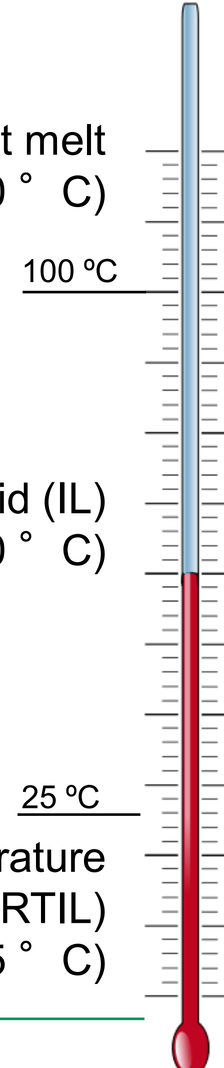
Ionic liquids (ILs)

- …is a salt in its liquid state
- …liquid that consists exclusively of ions
- …fused salts with a melting point below 100 °C

conventional salt melt
(> 100 ° C)

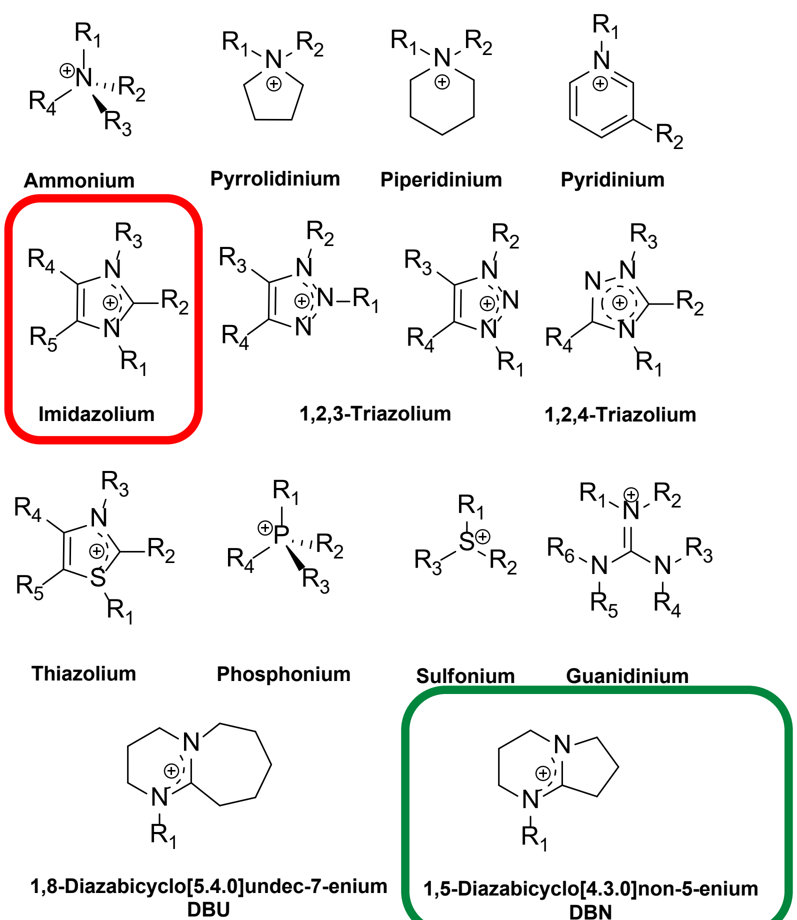
Ionic Liquid (IL)
(< 100 ° C)

Subclass: Room Temperature
Ionic Liquid (RTIL)
(< 25 ° C)



ILs as alternative cellulose solvents?

Cations



Anions

$Cl^{\ominus}$ $Br^{\ominus}$ $TsO^{\ominus}$ $BF_4^{\ominus}$ $PF_6^{\ominus}$

$CN^{\ominus}$ $SCN^{\ominus}$ $TfO^{\ominus}$ $Tf_2N^{\ominus}$ $(CN)_2N^{\ominus}$

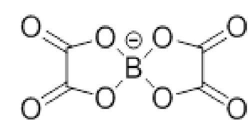
$CH_3CO_2^{\ominus}$ $CF_3CO_2^{\ominus}$ $NO_3^{\ominus}$ $ClO_4^{\ominus}$

$FeCl_4^{\ominus}$ $AlCl_4^{\ominus}$ $Al_2Cl_7^{\ominus}$ $HSO_4^{\ominus}$

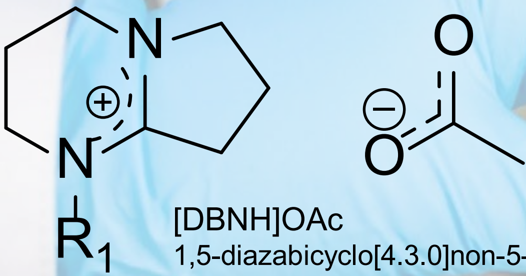
$Alkyl^FBF_3^{\ominus}$ $(Alkyl^F)_3PF_3^{\ominus}$

$(MeO)SO_3^{\ominus}$ $(MeO)SO_2^{\ominus}$

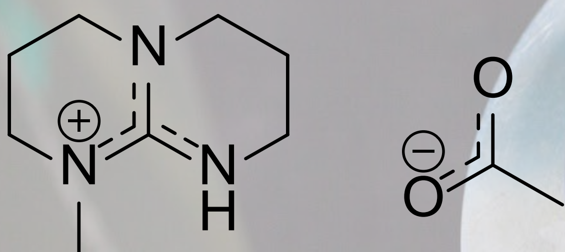
$(MeO)_2PO_2^{\ominus}$ $(MeO)_2PO^{\ominus}$



Technology based on Ionic liquids

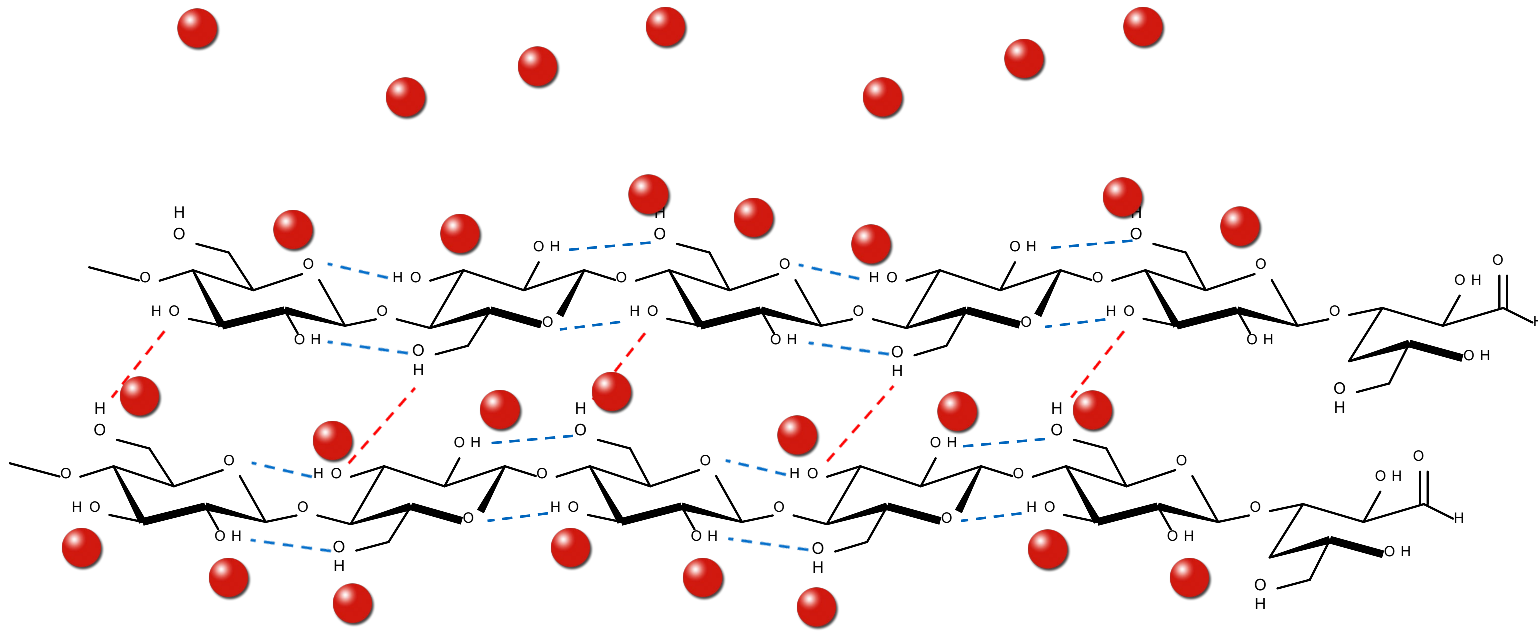


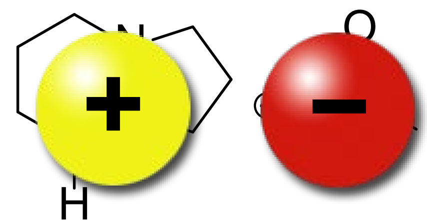
[DBNH]OAc
1,5-diazabicyclo[4.3.0]non-5-enium acetate

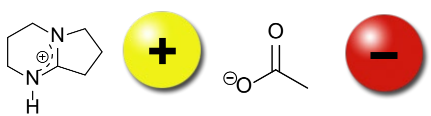


[MTBH]OAc
7-methyl-1,5,7-triazabicyclo[4.4.0]dec-5-enium acetate

UNIVERSITY OF HELSINKI







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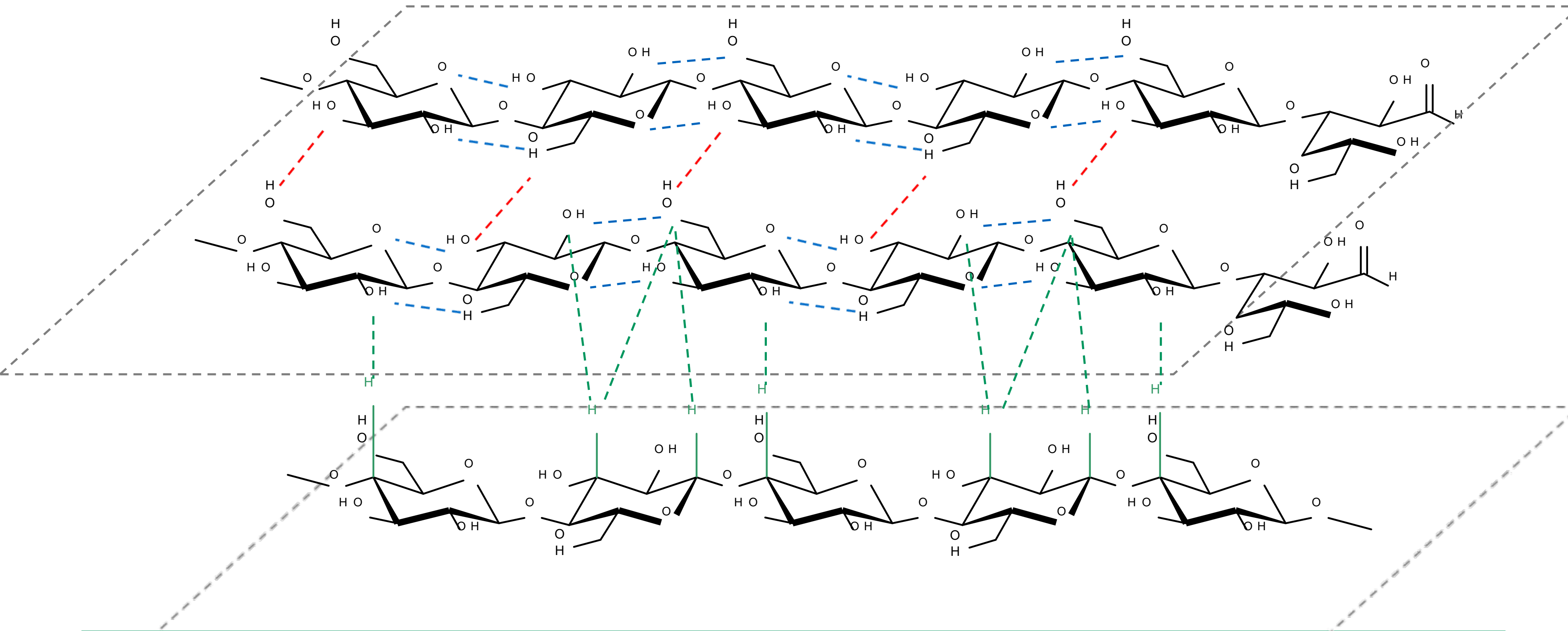
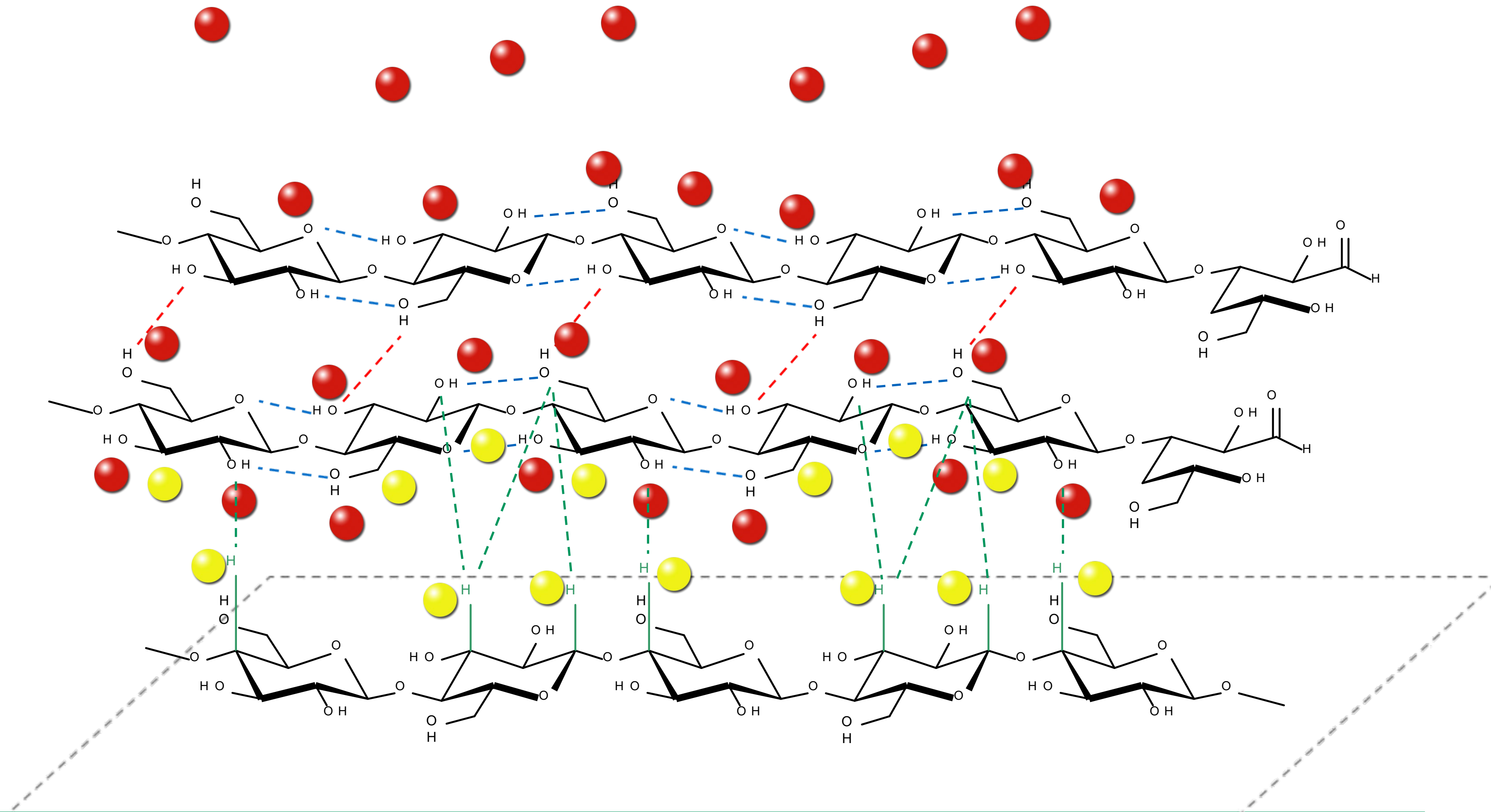
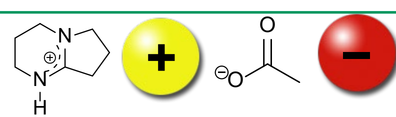
O3-H-O5 intrachain
O2-H-O6 intrachain
O6-H-O3 interchain



Aalto University
School of Chemical
Engineering

O3-H-O5 intrachain
O2-H-O6 intrachain
O6-H-O3 interchain
intersheet H-bond

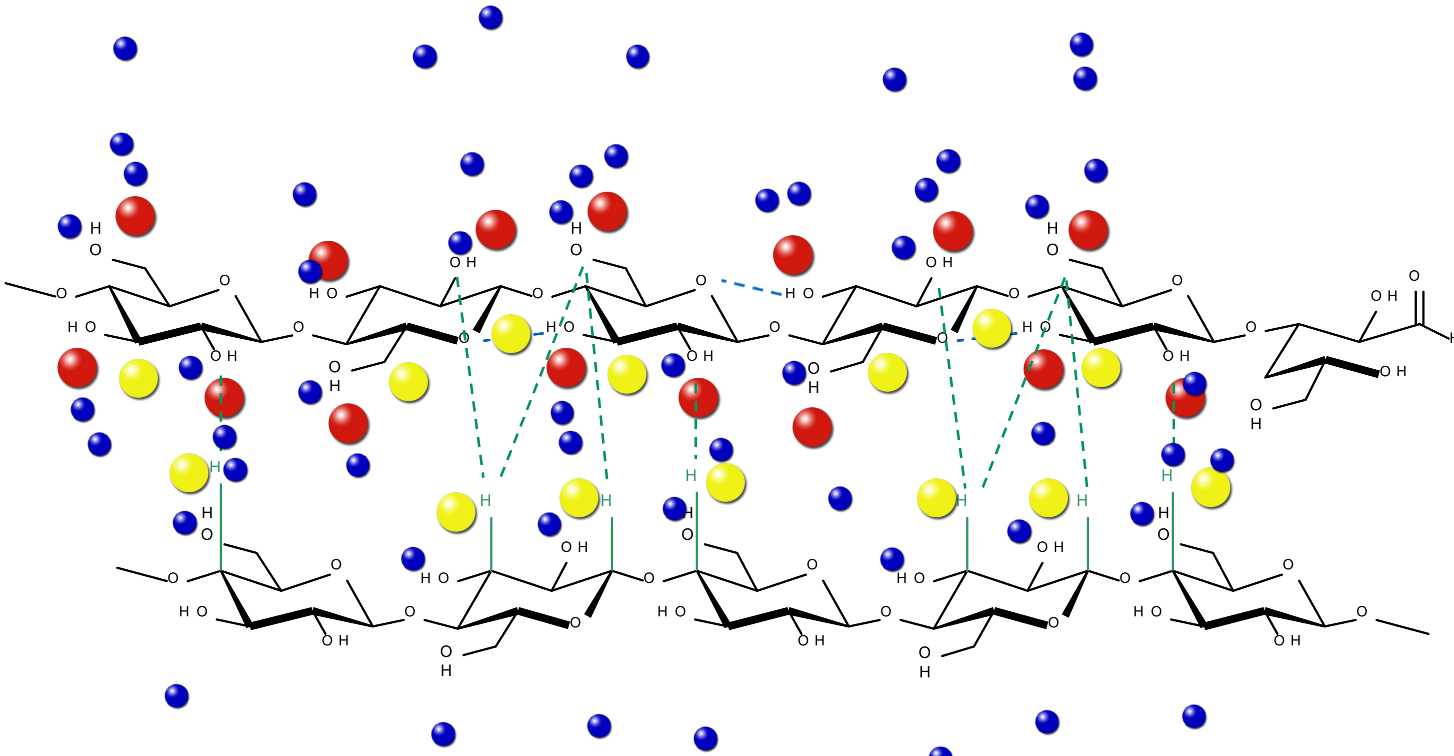


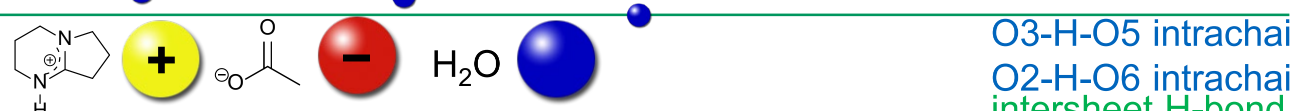


O3-H-O5 intrachain
O2-H-O6 intrachain
O6-H-O3 interchain
intersheet H-bond

Aalto University
School of Chemical Engineering

Cho, H.M.; Gross, A; Chu J.-W. *J. Am. Chem. Soc.* **2011,** doi 10.1021/ja2046155.





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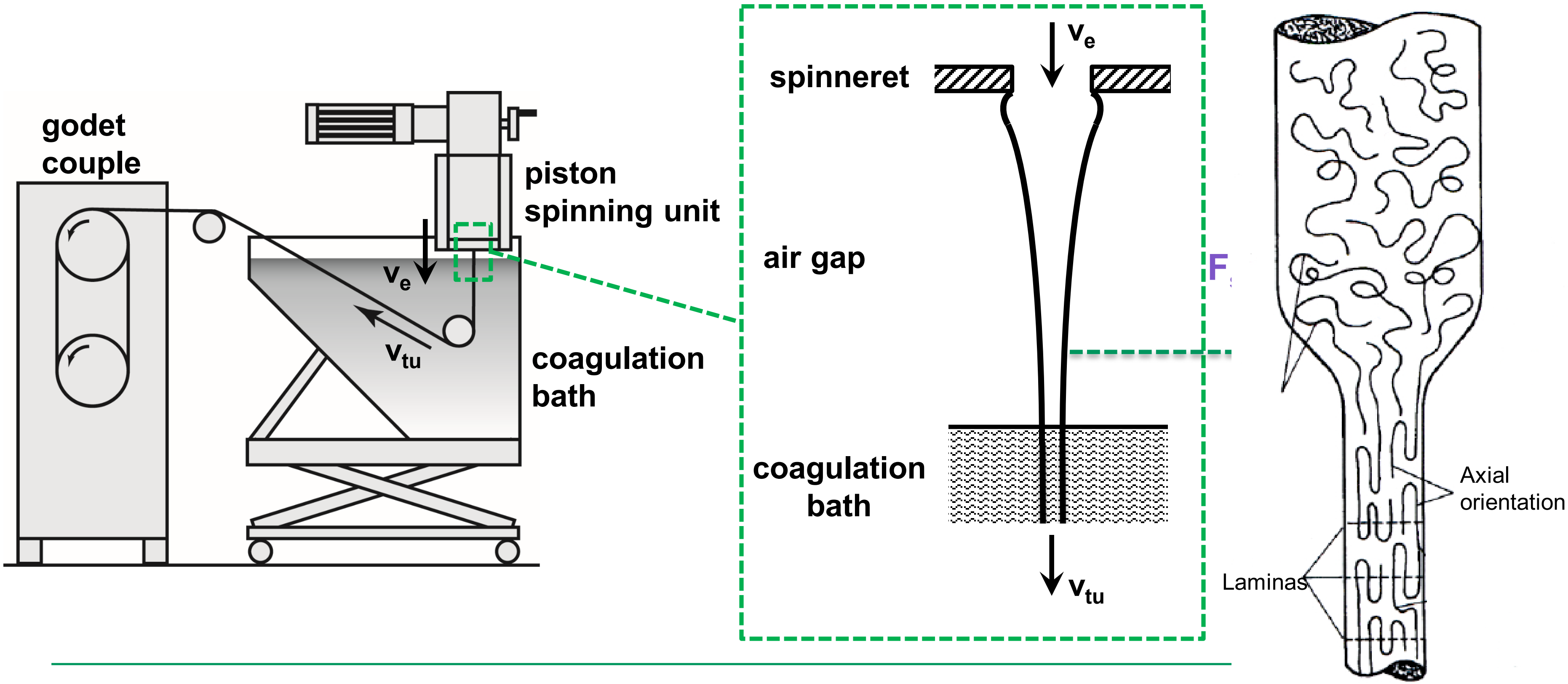
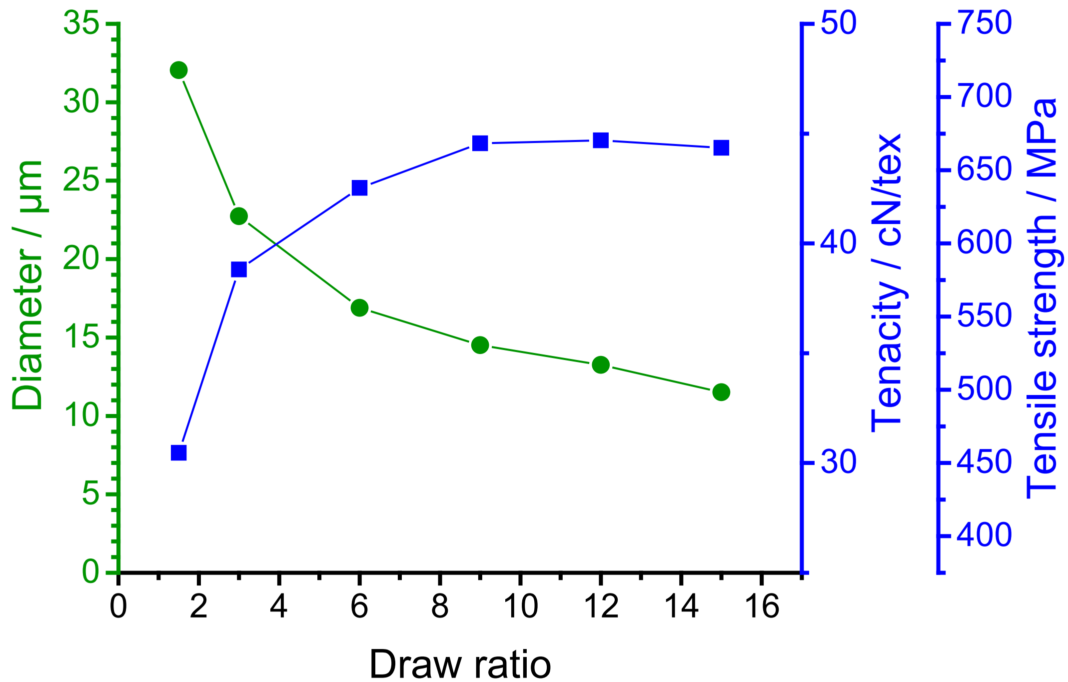
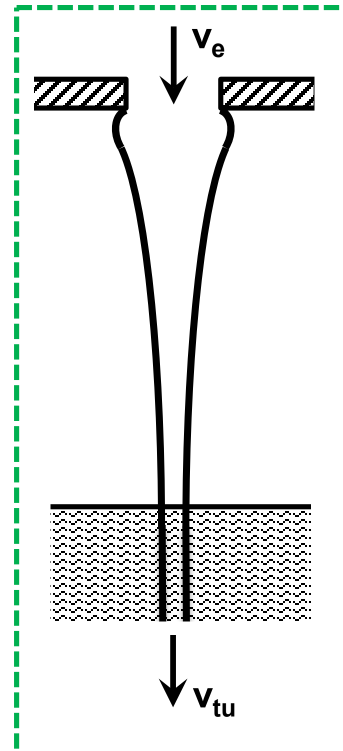
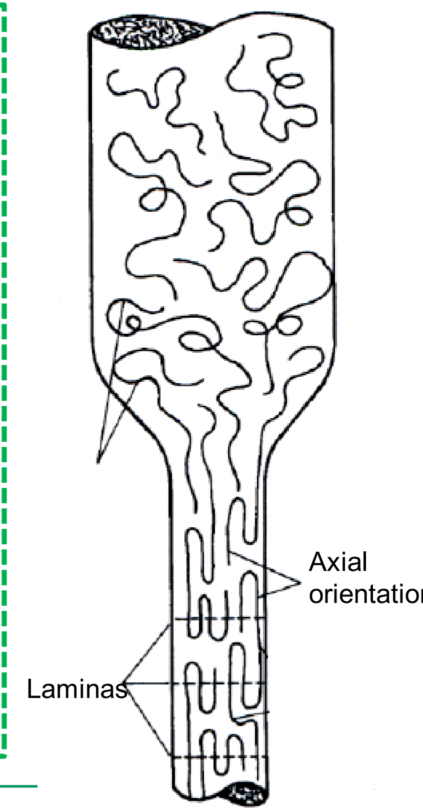
Liu, H.; Sale, K.L.; Simmons, B.A.; Singh, S. *Phys. Chem. B* **2011,** 115, 10251–10258.



Draw ratio: $D_R = \frac{v_{take-up}}{v_{extrusion}}$







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Draw ratio: $D_R = \frac{v_{take-up}}{v_{extrusion}}$

stable extrusion

Capillary breach

Melt fracture

Ionic liquid recycling

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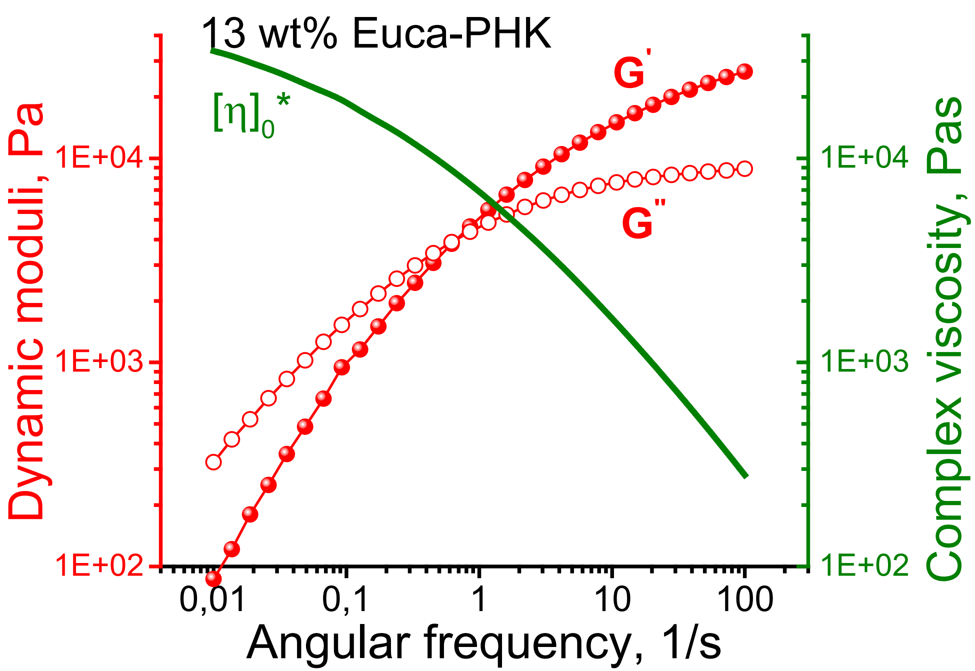
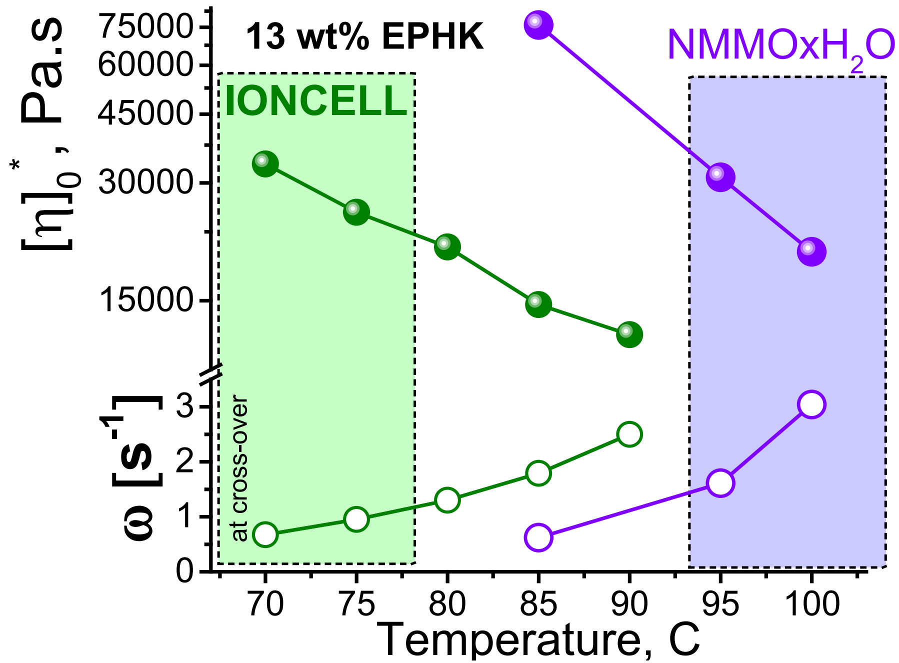
Standard spinning conditions



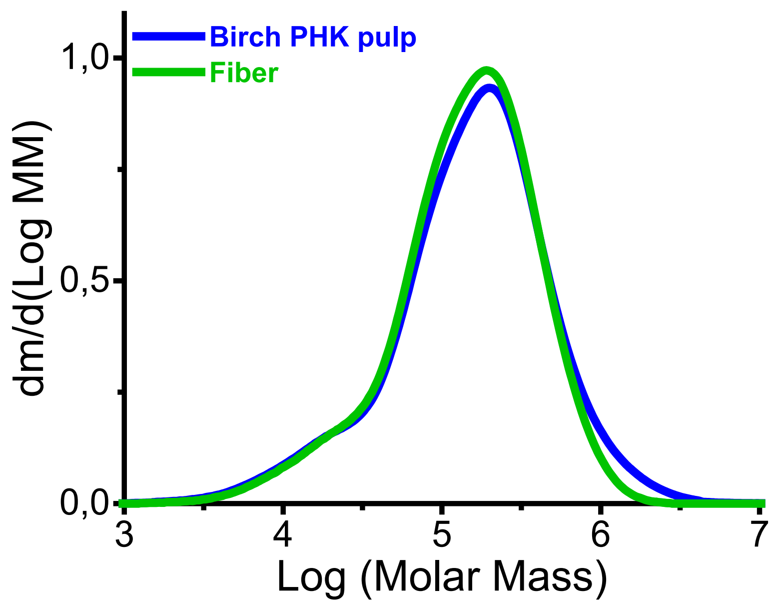


Dope from **novel cellulose solvent** shows stable spinning conditions at **much lower temperature** than dope from **NMMO.**

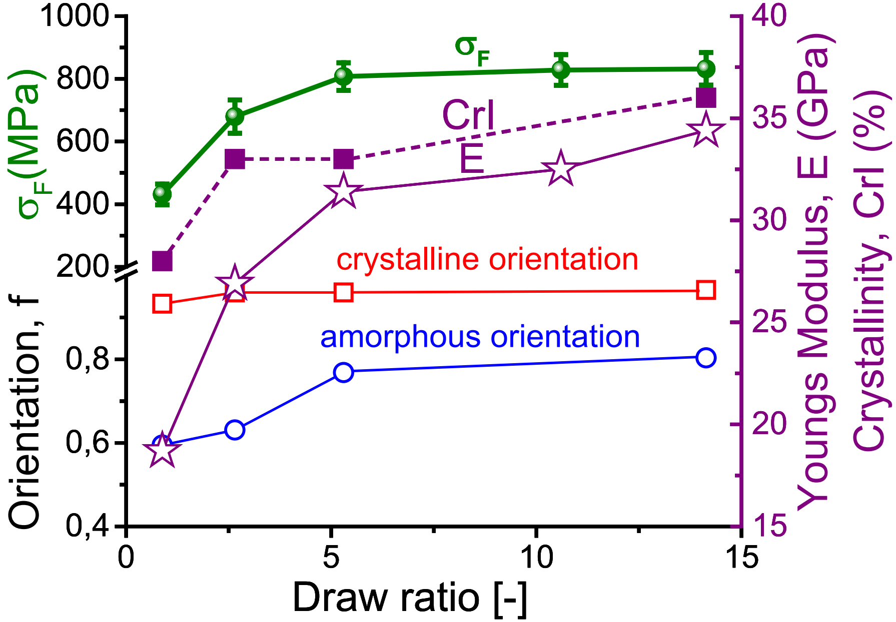
Standard spinning conditions

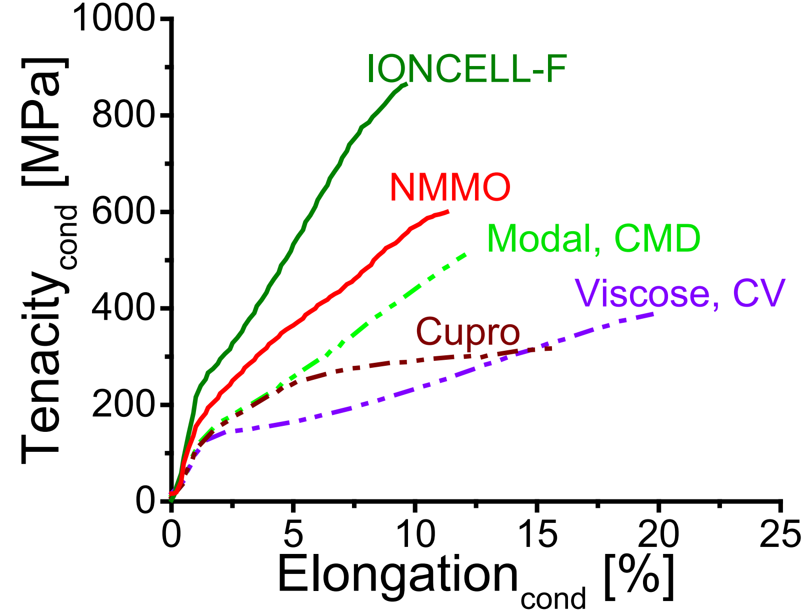
Molar Mass Distribution

Substrate	Viscosity (mL/g)	DP<100 wt%	DP>2000 wt%	PDI
Birch PHK	476	4,7	24,2	4,1
Fiber	447	4,3	20,5	3,2



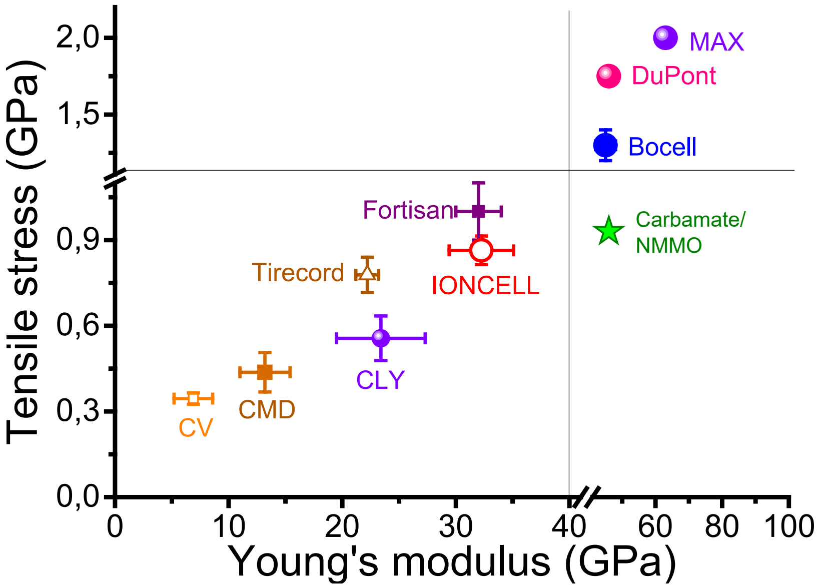
Mechanical vs. structural properties





Sixta, H. et al. *NPPRJ*, 30(1), **2015**, 43-57

Mechanical vs. structural properties



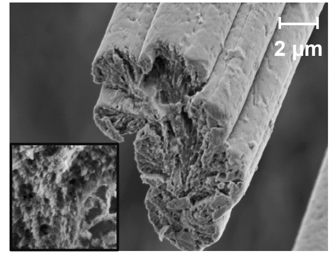
Spinning of **anisotropic solutions** to exploit the full strength potential of **cellulose II**:

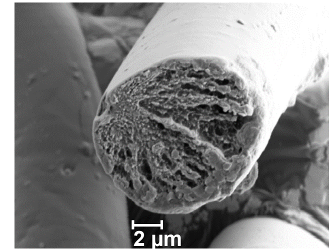
E_{max}: ~ 60 GPa (IC-F: 35)

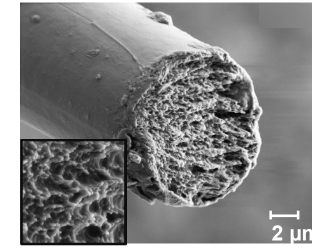
σ_{max}: ~ 2.1 GPa (IC-F: 0.9)

Sixta, H. et al. *NPPRJ*, 30(1), **2015**, 43-57
Northolt, M.G. Lenzinger Berichte, (**1985**), 59, 71-79.
De Vries. Appl. Sci. Res. A3, 111 (**1952**).

Fiber properties







	Viscose	Lyocell	Ioncell
Titre [dtex]	1.4 (ca. 10 µm)	1.3	1.3
Tenacity cond. [cN/tex]	23.9 (ca. 360 MPa)	40.2 (ca. 600 MPa)	51 (ca. 765 MPa)
Elongation cond. [%]	20.1	13.0	13.0
Tenacity wet [cN/tex]	12.5 (ca. 187 MPa)	37.5 (ca. 560 MPa)	48.0 (ca. 720 MPa)
Elongation wet [%]	22.0	18.4	15.0
Hermans' orientation factor	ca.0.40	ca.0.70	Ca. 0.71

Röder *et al. Lenzinger Berichte,* **2009,** 87, 98-105;
Gindl *et al. Polymer,* **2008,** 49, 792-799.

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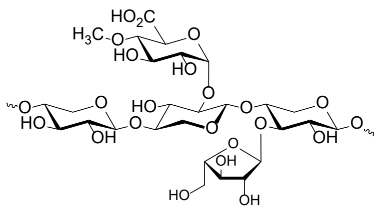
Pure cellulose

- Pre-hydrolysis kraft pulp (birch, eucalyptus)
- Old cotton textiles



Cellulose & hemicellulose

- Added xylan
- Kraft pulp
- Office waste paper
- Kraft cooked cardboard

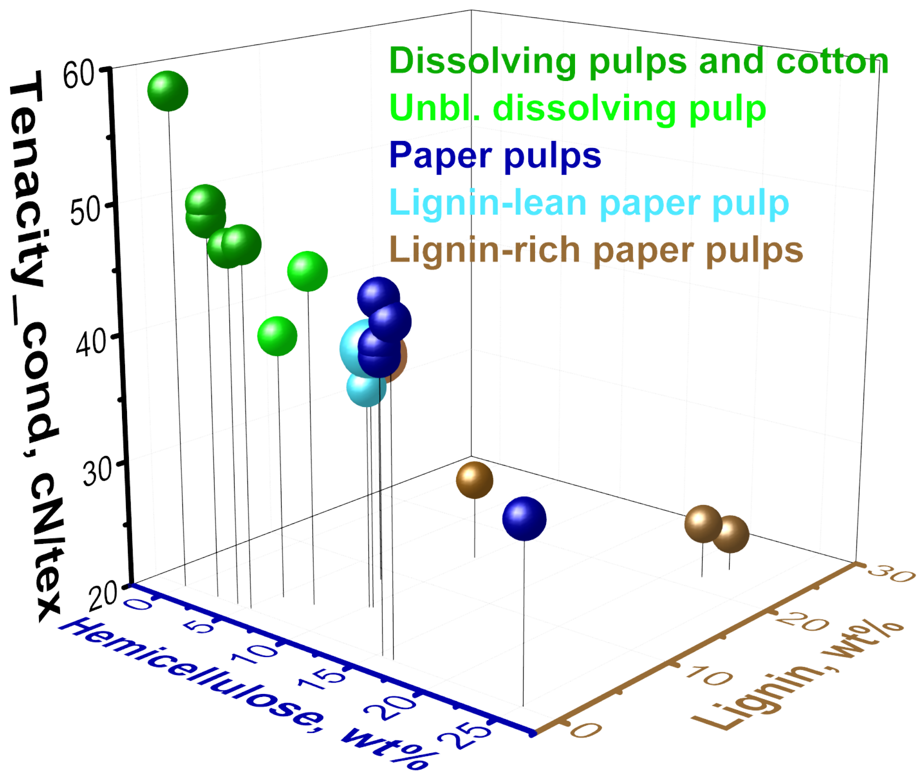
Cellulose & lignin

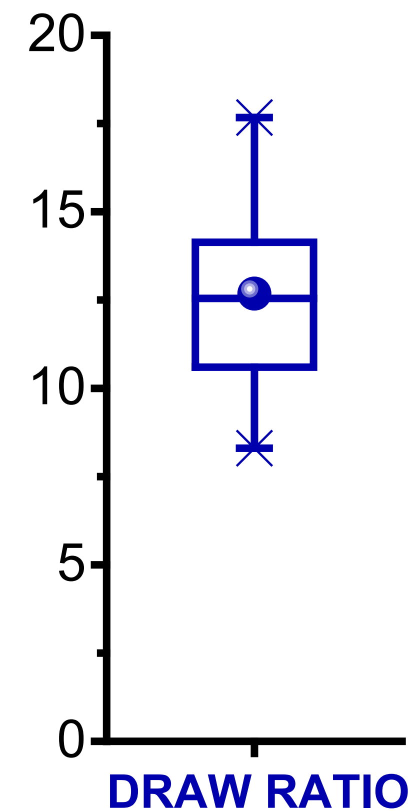
- Added organosolv lignin

Cellulose & hemicellulose & lignin

- Added xylan and lignin
- Cardboard
- Kraft pulp with low intensity cooking

Non-cellulosic consitutents





Yarns from lignin containing fibers

		Draw ratio	Titer (dtex)	Elongation (%)	Tenacity (cN/tex)
fibers	board B2	12.7	1.50	8.99	39.66
	pulp+ 15 wt% lignin	12.4	1.69	10.35	40.56
yarn	board B2		50.7	5.98	20.55
	pulp+ 15 wt% lignin		66.7	7.01	17.73

Ma *et al. Green Chem.* **2015,** 18, 858-866

Fabrics from lignin containing yarns

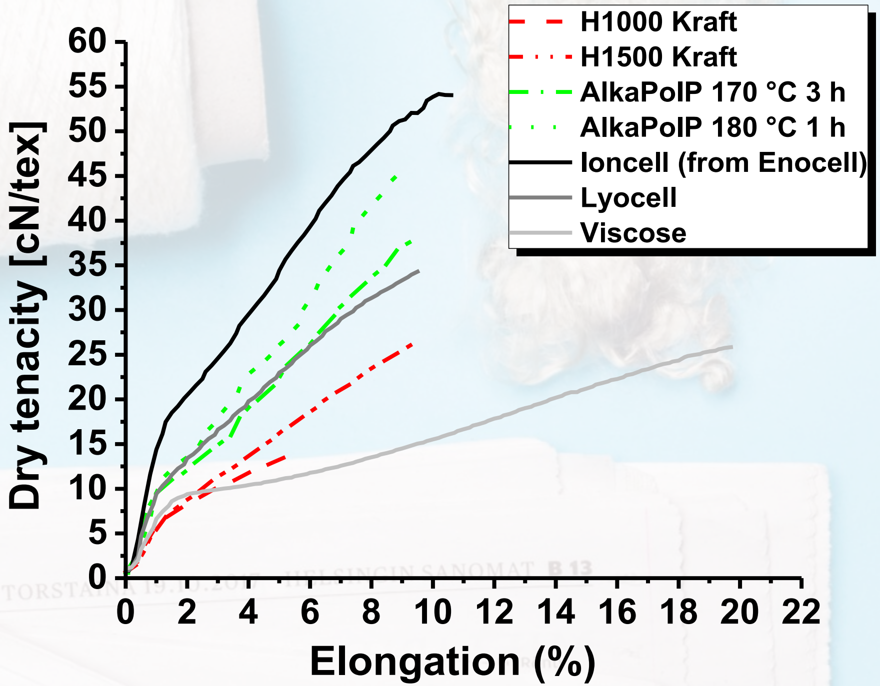
- The yarns were knitted. The natural color of the fibers were used to create patterns.
- Further, the fibers showed good dyeability, allowing for the production of colorful garments without any bleaching step.

Waste Newsprint →Textile fiber for special design

Deinked Newsprint → **Mild Pretreatment** → **Spinning** → **Staple fiber** → **Yarn**

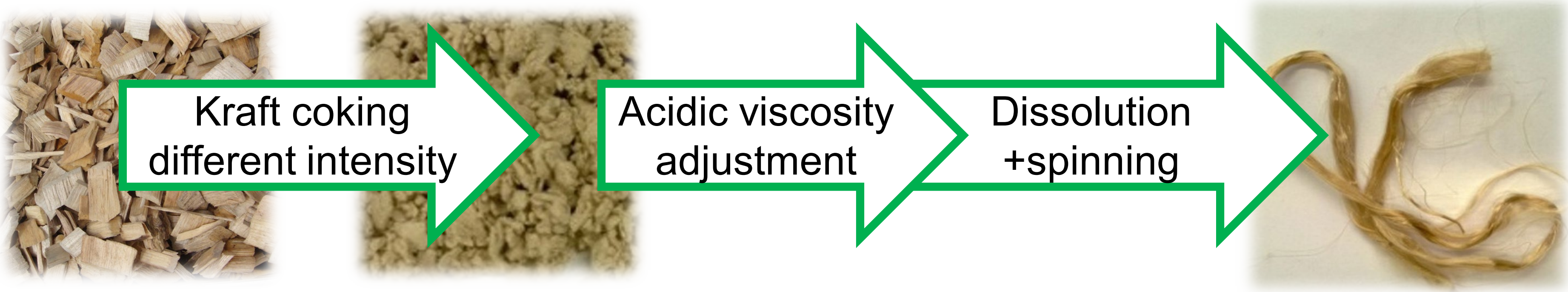
Ma Y. *et al. Green Chem.* 2018, 20, 160-169

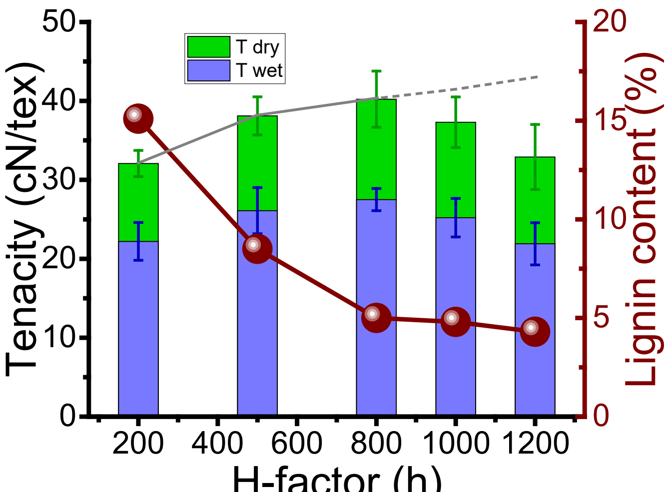
Textile fibers from waste paper and cardboard

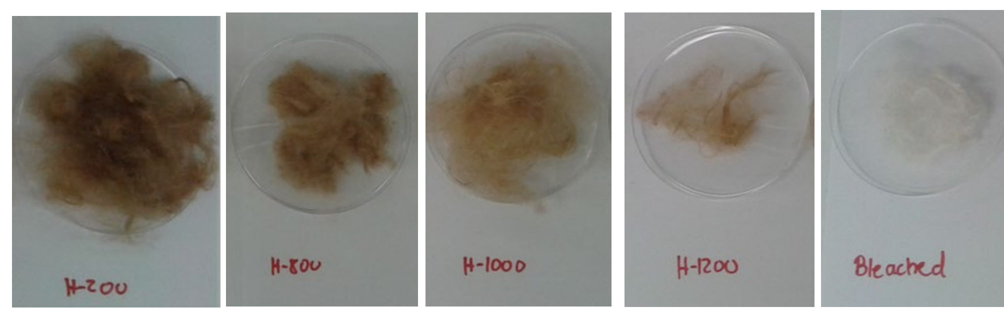


Ma *et al. Green Chem.* **2018,** 20, 160-169

Unbleached wood pulp







Ma, Y. *et al. Carbohydr. Polym.* 2018, 179, 145-151

Textile fibers from cotton waste

The global apparel market is valued at 3 trillion dollars (=2% of world's GDP).

Almost 75% of the world's fashion market is concentrated in Europe, USA, China and Japan.

Over 70% of the world's population use second hand clothes.

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Photo source: flickr.com. Ciarademp: Clothes market

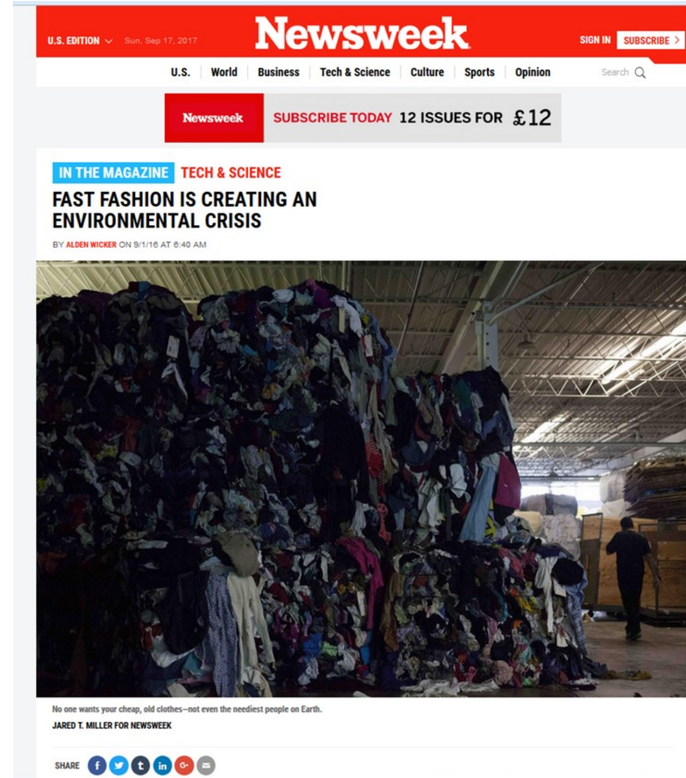
Waste statistics

The clothing and textile industry is the second largest polluter in the world

Textile waste: USA: 15.1 million tons,
EU 5.8 million tons

Around 30 – 40 kg per person each year

Recycling rate 15 – 25%

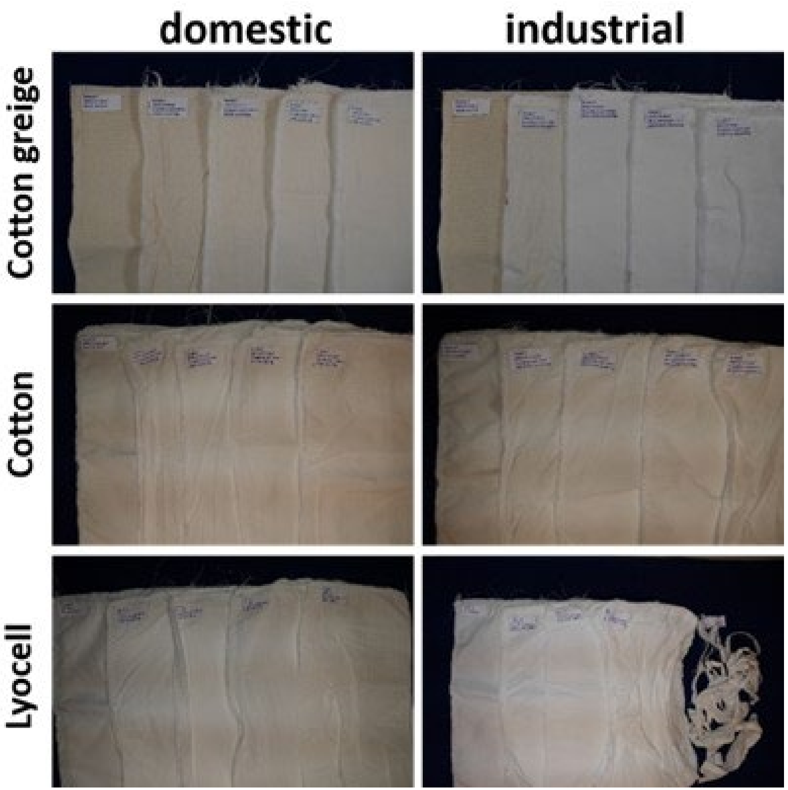


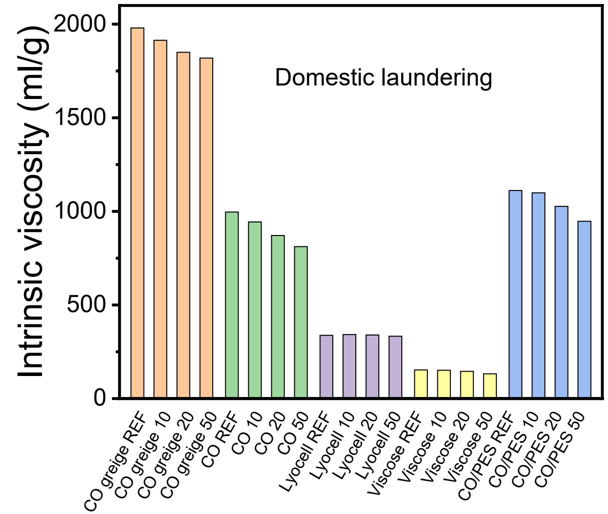
http://www.newsweek.com/2016/09/09/old-clothes-fashion-waste-crisis-494824.html

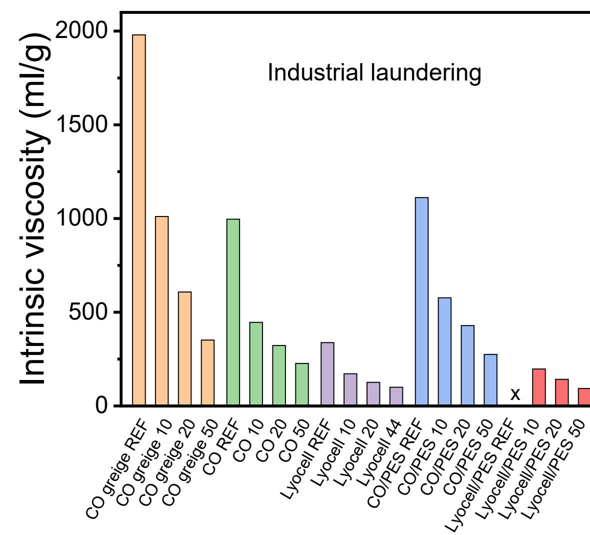

Global Change Award
AN INNOVATION CHALLENGE BY H&M CONSCIOUS FOUNDATION
photo: Essi Karell
Aalto University
School of Chemical
Engineering


TRASH
2
CASH
VTT

Cotton degradation





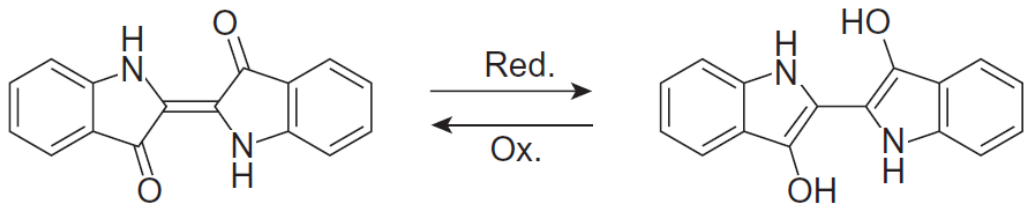


Wedin et al. *Text. Res. J.* 2019, 89, 5067-5075

Color Translation of Cotton Waste

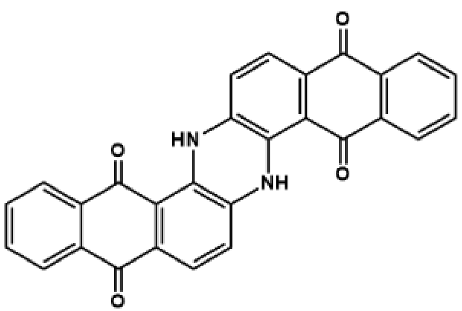
Kirsi Niinimäki
photo: Eeva Suorlahti

Textile colors – VAT dyes

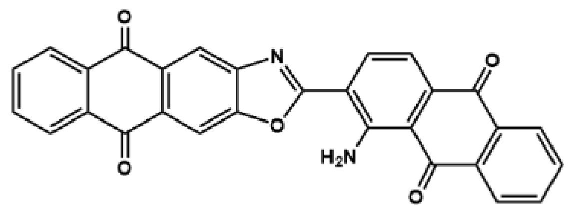


Indigo

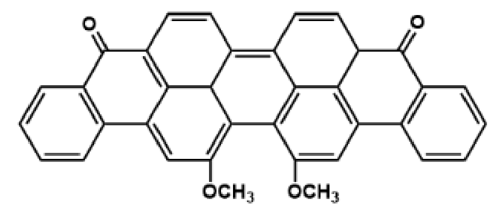
Leuco indigo



Indanthren Blue BC 3%



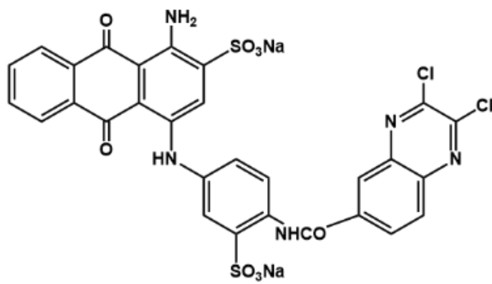
Indanthren Red FBB coll



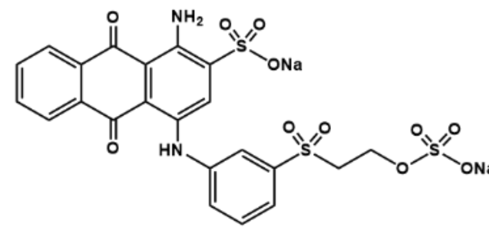
Indanthren Brilliant Green FBB coll

Chavan, R.B. Denim, Woodhead Publishing 2015, 37-67. DOI: 10.1016/B978-0-85709-843-6.00003-2
Haslinger S. *et al.* Green Chem. 2019, DOI: 10.1039/C9GC02776A

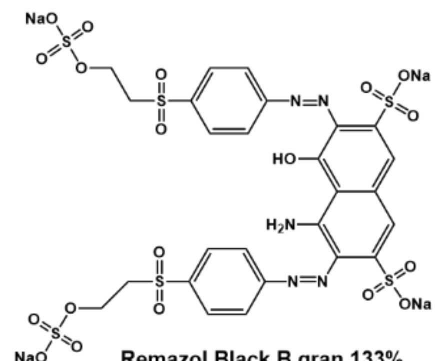
Textile colors – reactive dyes



Levafix Blue E-GRN gran



Remazol Brilliant Blue R spec



Remazol Black B gran 133%

Haslinger S. *et al.* Green Chem. 2019, DOI: 10.1039/C9GC02776A

Color translation

Samples	Waste fabric L*	a*	b*	Recycled regenerated fibers L*	a*	b*	ΔE
Indanthren Blue BC	69.0±0.3	-4.9±0.3	-22.2±1.1	56.6±1.1	-6.6±0.1	-14.0±0.3	14.9
Indanthren Red FBB	40.5±1	49.1±0.6	6.9±0.4	39.5±0.8	38.1±0.7	12.9±0.3	12.6
Indanthren Green FBB	37.0±0.5	-46.9±0.4	-1.4±0.1	34.5±0.4	-38.4±0.1	-0.9±0.1	8.8
Remazol Black	18.7±0.3	-5.0±0.1	-16.2±0.2	35.6±1.2	15.6±0.3	6.2±0.2	25.6
Remazol Blue	43.0±0.6	-1.8±0.1	-39.7±0.3	56.9±3.1	0.7±0.7	-20.7±0.4	23.6
Levafix Blue	37.5±0.9	-1.5±0.1	-31.97±0.3	35.3±1.4	-3.5±0.5	-23.3±0.6	9.2

CIELAB coordinates

$$\Delta E = \sqrt{(\Delta L *)^2 + (\Delta a *)^2 + (\Delta b *)^2}$$

Aalto University
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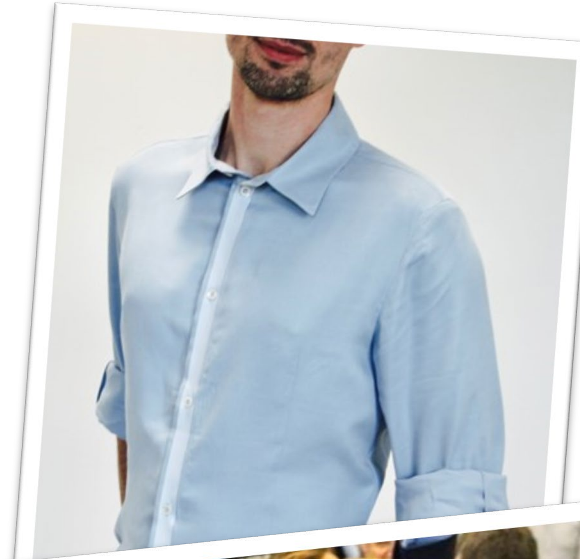

Summary questions

- Name 3 types of yarn spinning.
- What is an ionic liquid?
- What are the advantages of ionic liquids as fiber spinning solvent?
- What are the disadvantages of ionic liquids as fiber spinning solvent?
- What kind of fibers can be produced with the Ioncell™ process?