Theory and Practice of Wet Spinning of Cellulose Solutions

Doctoral Course, Part 8

Aalto University
School of Chemical
Engineering

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March 10 – 11, 2022

Outline

1. Introduction, history
2. Pulps as raw materials
3. Cellulose solvents
4. Theoretical aspects of cellulose dissolution
5. Rheology of cellulose solutions
6. Coagulation and regeneration of cellulose
7. Filament breaches during spinning
8. **Types and properties of MMCFs**

Schedule

L1	Introduction, Raw material	March 10	9:00 – 9:45
L2	Raw materials. Cellulose solvent	March 10	10:00-10:45
L3	Cellulose solvents	March 10	11:00-11:45
L4	Cellulose solvents	March 10	12:00-12:45
	Break		
L5	Cellulose dissolution	March 10	14:00-14:45
L6	Rheology	March 10	15:00-15:45
L7	Cellulose dissolution/ Coagulation and Regeneration	March 10	16:00-16:45
L8	Coagulation and Regeneration	March 11	9:00 – 9:45
L9	Coagulation and Regeneration	March 11	10:00-10:45
L10	Filament breaches	March 11	11:00-11:45
L11	Types and properties of MMCFs	March 11	12:00-12:45
L12	Q&A	March 11	13:00 -

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Types and Properties of MMCFs

- Commercial vs Selected Non-Commercial MMCFs
- Mechanical properties
- Optical properties
- Interaction with water

Classification of Fiber properties

Geometric

- **Length**
  - Average values
  - Distribution
- **Cross section**
  - Area
  - Shape
- **Crimp**
  - Frequency
  - Form

Physical

- **Density**
  - Linear
  - Bulk
- **Thermal**
  - Melting point
  - Transitions
  - Conductivity
  - Decomposition
- **Optical**
  - Birefringence
  - Refractive index
  - Luster and color
- **Electrical**
  - Resistivity
  - Dielectric constant
- **Surface**
  - Friction
  - Roughness
- **Mechanical**
  - Tension
  - Compression
  - Torsion
  - Bending
  - Shear

Chemical

- **Response to**
  - Acids
  - Alkalies
  - Oxidation
  - Reduction
  - Heat
- **Sorption**
  - Moisture
  - Dyes
  - Other chemicals
- **Swelling**
  - Anisotropy

Rebenfeld, L. Lenz Ber. (1989), 68, 14-18

Matrix of fibre properties investigated

Mechanical properties	**Stress-strain**	**Yield point**	**Toughness**
	Linear density	**Elastic limit**	**Prop. Limit**
	Höller Diagram	**Factor analysis**	
Cellulose structure	**X-Ray diffraction**	**WAXS**	**SAXS**
	Birefringence		
	Pore structure		
Cellulose-Water Interaction	**DVS**	**Hailwood-Horrobin model**	
Fiber Fibrillation	**Method**	**Cross-linking**	

Linear density calculation: Lyocell

TASK:

Linear density (titer, dtex) of an Ioncell fiber?

$Hole\ diameter, \quad d = 100\ \mu m$

$Number\ of\ holes, \quad n = 400$

$Density, \quad \rho = 1.139\ g/cm^3$

$Cellulose\ conc, \quad c = 0.13$

$Extr.vel, \quad v_{extr} = 5\frac{m}{min}$

$Take-up\ vel, \quad v_{tup} = 55\frac{m}{min}$

ANSWER:

$\boldsymbol{Dope\ flow, Q?}$

$$Q = \frac{v_{extr} \cdot n \cdot d^2 \cdot \pi}{4} = \frac{5\ m}{min} \cdot 400 \cdot \frac{1 \cdot 10^{-8} m^2}{4} \cdot \pi$$

$$= 15.71 \cdot 10^{-6}\ m^3/min = 15{,}71\ ml/min$$

$\boldsymbol{Titer\ calculation, T?}$

$$T = \frac{Q \cdot \rho \cdot c}{v_{tup} \cdot n}$$

$$= \frac{15.71 \cdot 10^{-6}\ m^3}{min} \cdot \frac{1139\ kg}{m^3} \cdot 0.13 \cdot \frac{min}{55\ m} \cdot \frac{1}{400}$$

$$= 1.06 \cdot 10^{-7}\ kg/m = 1.06 \frac{g}{10000} m = dtex$$

Linear density calculation: Lyocell

TASK:

Consideration of fiber shrinkage and moisture content:

At a shrinkage of 8%, the filament shrinks from 9000 m by 720 m. Thus

$$\boldsymbol{f = 1.08}$$

At a moisture content of 11%, a titer of 100 corresponds to an effective titer of 111. Thus,

$$\boldsymbol{h = \frac{111}{100} = 1.11}$$

ANSWER:

Effective $\boldsymbol{Titer\ calculation, T}$?

$$T = \frac{Q \cdot \rho \cdot c \cdot \boldsymbol{f} \cdot \boldsymbol{h}}{v_{tup} \cdot n} = 1.06 \cdot 1{,}08 \cdot 1{,}11$$

$$\boldsymbol{T_{eff} = 1.27\ dtex}$$

Linear density calculation: Viscose

TASK:

Linear density (titer, dtex) of a Viscose fiber?

$Hole\ diameter, \qquad d = 50\ \mu m$

$Number\ of\ holes, \qquad n = 100$

$Density, \qquad \rho = 1.4\ g/cm^3$

$Cellulose\ conc, \qquad c = 0.06$

$Extr.vel, \qquad v_{extr} = 20\,\frac{m}{min}$

$Take-up\ vel, \qquad v_{tup} = 22\,\frac{m}{min}$

ANSWER:

$\boldsymbol{Dope\ flow, Q?}$

$$Q = \frac{v_{extr}\cdot n\cdot d^2\cdot \pi}{4} = \frac{20\ m}{min}\cdot 100\cdot \frac{2.5\cdot 10^{-9} m^2}{4}\cdot \pi$$

$$= 3.93\cdot 10^{-6}\ m^3/min = 3{,}93\ ml/min$$

$\boldsymbol{Titer\ calculation, T?}$

$$T_{eff} = \frac{Q\cdot \rho\cdot c\cdot \boldsymbol{f}\cdot \boldsymbol{h}}{v_{tup}\cdot n} = 1.50\cdot 1{,}08\cdot 1{,}11$$

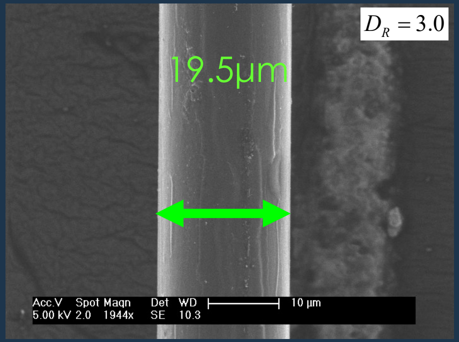
$$= \boldsymbol{1.80\ dtex}$$

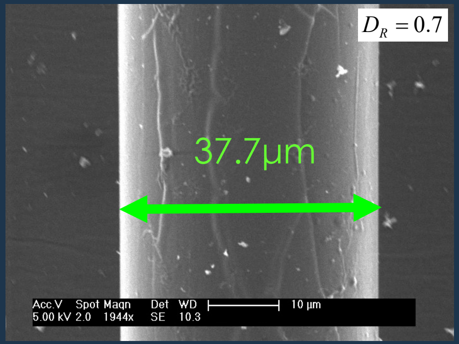
$$= \frac{3.93\cdot 10^{-6}\ m^3}{min}\cdot \frac{1400\ kg}{m^3}\cdot 0.06\cdot \frac{min}{22\ m}\cdot \frac{1}{100}$$

$$= 1.50\cdot 10^{-7}\ kg/m = 1.50\,\frac{g}{10000}\,m = dtex$$

LYCELL

- **Linear density**
- **Fiber diameter**





Linear density (titer, dtex)

- $Hole\ diameter,\quad d = 100\ \mu m$
- $Number\ of\ holes,\ n = 200$
- $Density,\quad \rho = 1.139\ g/cm^3$
- $Cellulose\ conc,\quad c = 0.13$
- $Extr.vel,\quad v_{extr} = 4\frac{m}{min}$
- $Take-up\ vel,\quad v_{tup} = 48\frac{m}{min}$

$$Q = \frac{v_{extr}\cdot n\cdot d^2\cdot\pi}{4} = 6.283\cdot 10^{-6}\ m^3/min$$

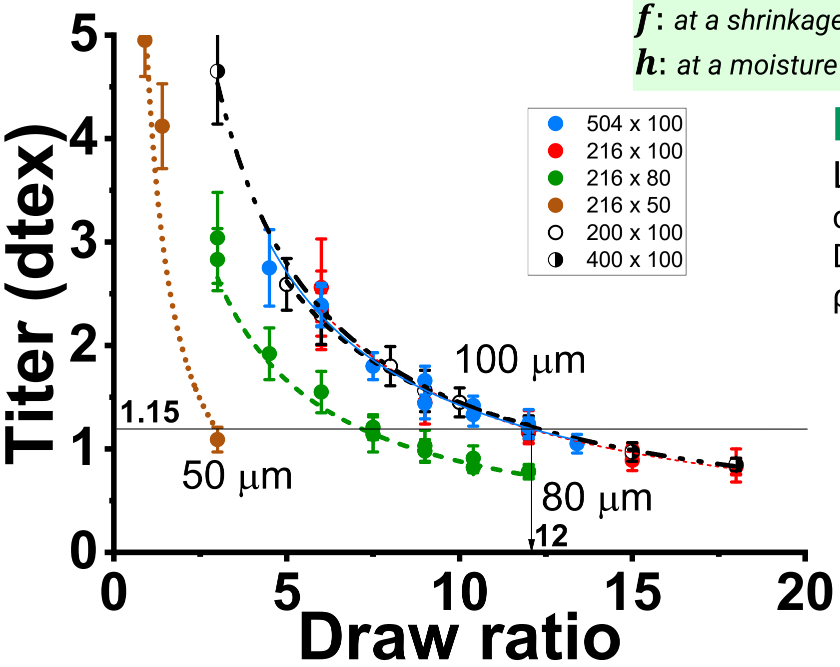
Titer calculation, T

$$T = \frac{Q\cdot\rho\cdot c}{v_{tup}\cdot n} = 9.7\cdot\frac{10^{-8}kg}{m} = 0.97\frac{g}{10000}m = dtex$$

$$T_{eff} = T\cdot f\cdot h = 0.97\cdot 1,05\cdot 1,11 = \mathbf{1.13\ dtex}$$

f: *at a shrinkage of 5%, the titer increases by a factor of 1.05*

h: *at a moisture of 11%, the titer increases by a factor of 1.11*



Fiber diameter

Linear density c:

c... Tex... g/1000 m

D...µm

ρ....g/cm³

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

$$D = 2\cdot\sqrt{\frac{c}{\pi\cdot\rho}} = 2\cdot\sqrt{\frac{1.13}{\pi\cdot 1.5}} = \mathbf{10.2\ \mu m}$$

Terms and Definitions

Linear Density (fiber fineness)

c, mass per unit length (= titre, linear density)
1 tex = g fibre / 1000 m

Circular cross section

Area A is related to Diameter D

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

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

Diameter of a 1.3 dtex fibre?

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

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

Mechanical Strength

Tenacity in cN/tex; Tensile Strength, stress in MPa

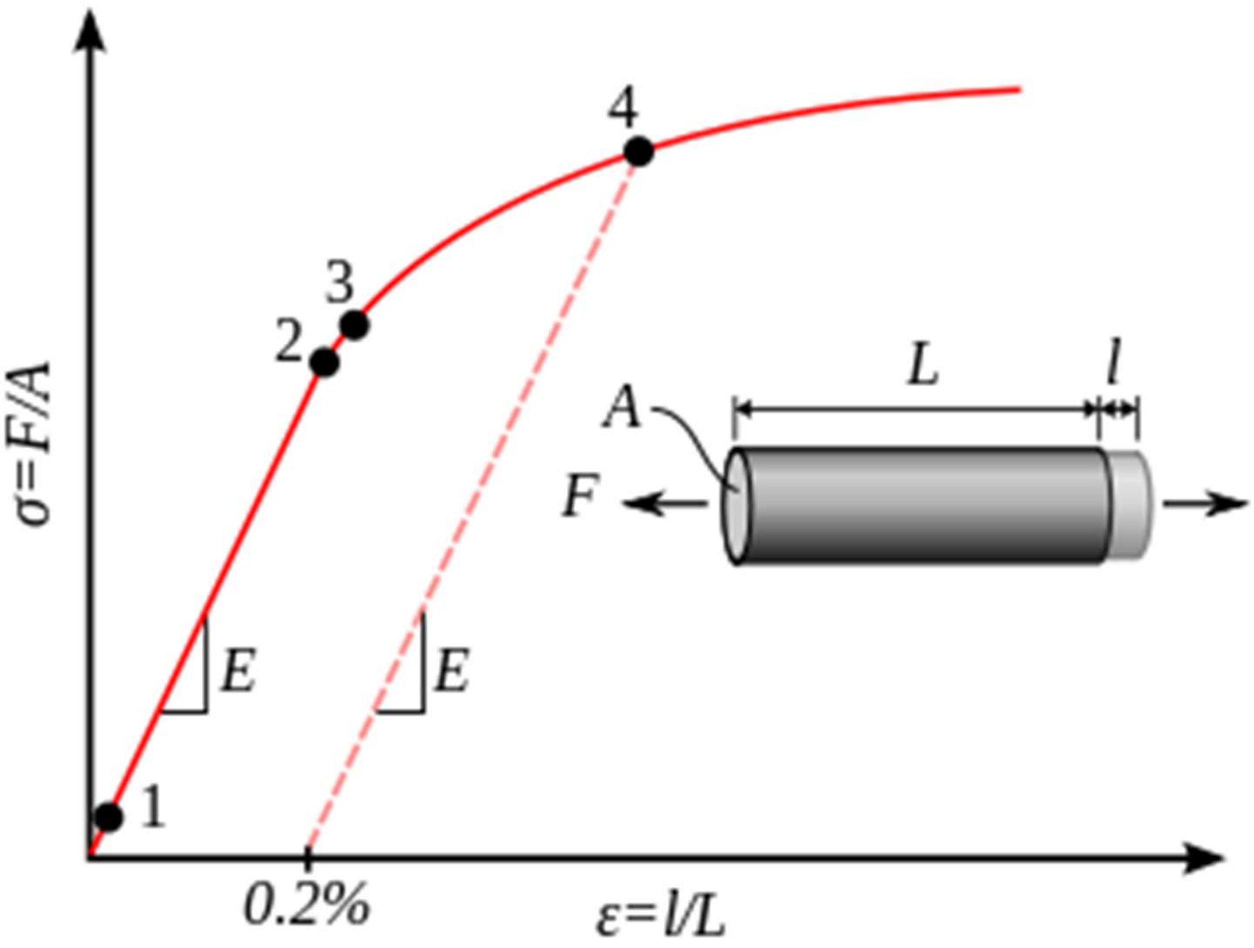
$$\frac{cN}{tex} = \frac{10^{-2} \cdot kg \cdot m \cdot s^2 \cdot 10^3 \cdot m}{s^2 \cdot kg \cdot m \cdot 9.81 \cdot 10^{-3}} \approx 10^3 m$$

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

$$\boldsymbol{1 \frac{cN}{tex} \approx \frac{1.5 \cdot 10^7 N}{m^2} = 15\ MPa = 0.015\ GPa}$$

$$\boldsymbol{1 GPa \approx 66.7 \frac{cN}{tex}}$$

Stress-strain

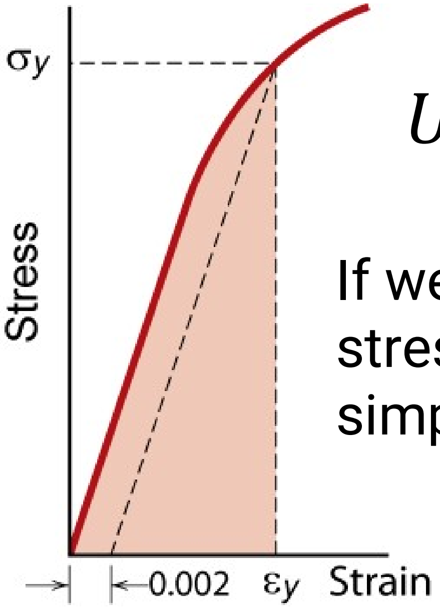


1. **True elastic limit**
2. **Proportionality limit (Hooke)**
3. **Elastic limit**: permanent deformation starts to occur
4. **Yield strength**: curve levels off. Plastic deformation begins

Adapted from Fig. 6.15, *Callister & Rethwisch 8e.*

Resilience, U_r

Ability of a material to store energy
Energy stored best in elastic region



$$U_r = \int_0^{\varepsilon_y} \sigma d\varepsilon$$

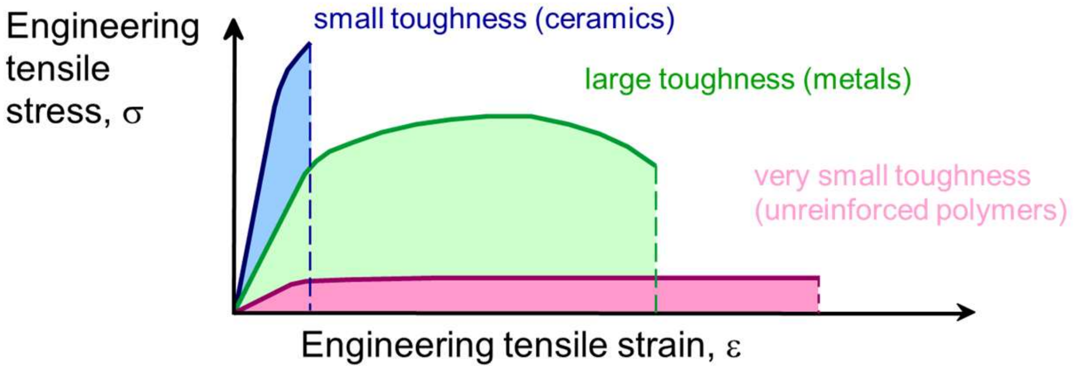
If we assume a linear stress-strain curve this simplifies to

$$U_r \cong \frac{1}{2}\sigma_y \varepsilon_y$$

Adapted from Fig. 6.15, *Callister & Rethwisch 8e.*

Toughness

Energy to break a unit volume of material
Approximate by area under the stress-strain curve.



Brittle fracture:	elastic energy
Ductile fracture:	elastic + plastic energy

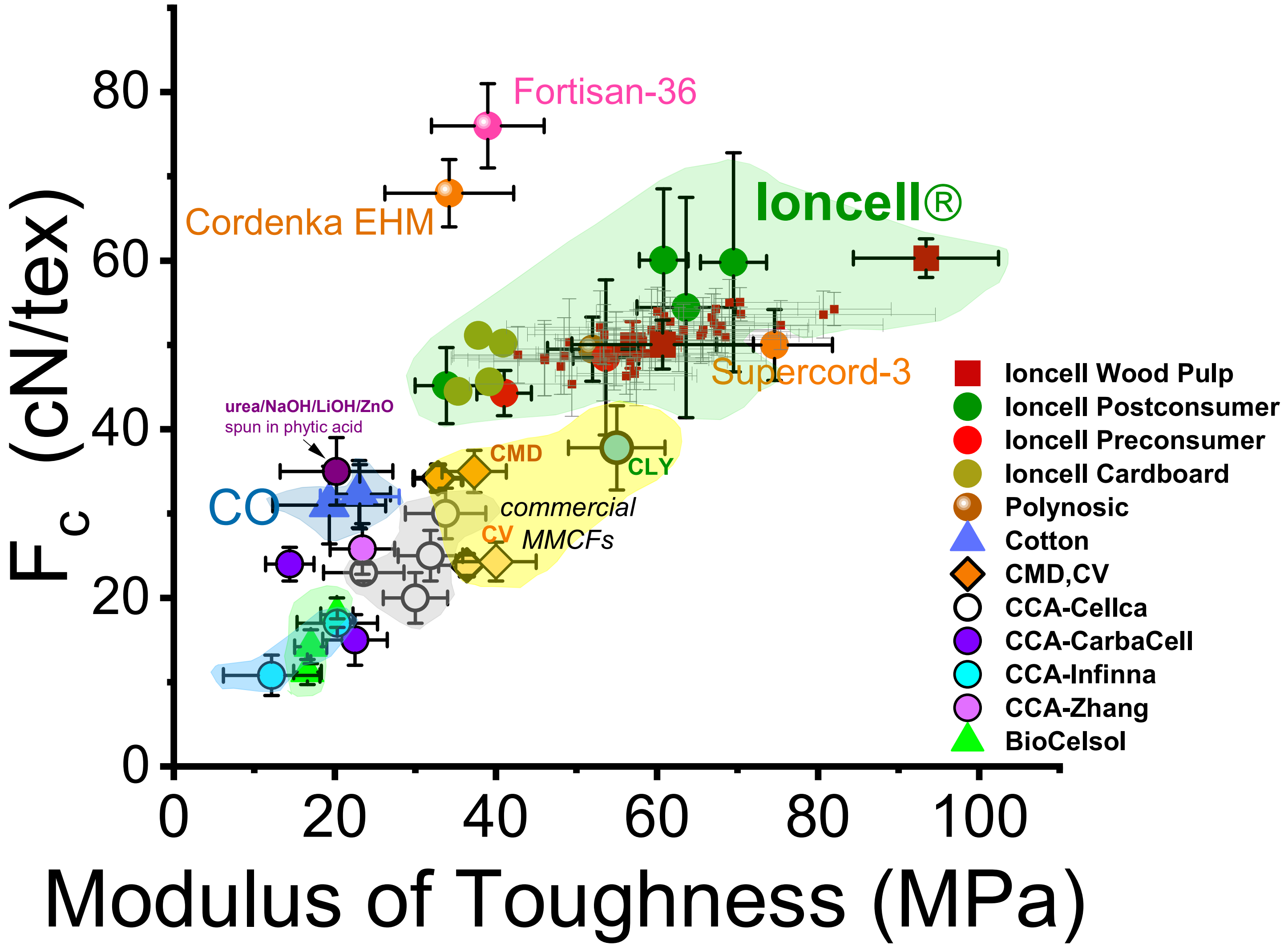
Unit: J/g or MPa

$$MPa \cong 1.5 \cdot \frac{J}{g}$$

Overview of MMCFs

	Production kt/a	Solvent	Regeneration	Tenacity cN/tex	Elong %	T-wet/dry	Toughn MPa	Source
Commercial MMCFs								
Viscose (CV)	6 900	Xanthate in NaOH$_{aq}$	H_2SO_4, Na_2SO_4, $ZnSO_4$, (organic modifier)	**24**	20	~ 0,50	**40**	
Modal (CMD)				**34**	13	~ 0,55	**35**	
Supercord-3				**50**	16	~ 0,60	**74**	
Lyocell (CLY)	> 300	NMMO.H_2O	H_2O/NMMO	**38**	16	~ 0,85	**55**	
Cupro	20	$Cu(NH_3)_4(OH)_2$	H_2O, H_2SO_4	**22**	12	~ 0,50	**20**	ISBN 185573459 1, p88f
Former MMCFs								
Fortisan-36		CTA, Acetone	Dry spin., sapon.	**76**	6		**39**	Moncrieff, R.W. (1953)
Polynosic		Viscose	low acid, no modif	**49**	12	~ 0,70	**52**	Tachikawa (1952)
Cordenka EHM		Viscose	Zn(II), modif; coag->reg	**68**	6		**34**	Northolt (1985)
MMCFs in development								
CARBAMATE								
Cellca		Urea, NaOH, ZnO	H_2SO_4, Na_2SO_4, $Al_2(SO_4)_3$	**25**	17		**32**	*Lenz. Ber. (1985), 59, 111-*
Carbacell		Urea/NaOH, ZnO	H_2SO_4, Na_2SO_4	**15**	20		**23**	US20090258227A1
Infinna		Urea, NaOH, H_2O_2, ZnO	H_2SO_4, Na_2SO_4, $Al_2(SO_4)_3$	**17**	16		**20**	Journal of Cleaner Produc
AQUEOUS NaOH								
Biocelsol		NaOH, ZnO	H_2SO_4, Na_2SO_4	**18**	15		**20**	Vehviläinen, M.^{a}, et al. Che
TreeToTextile		NaOH, ZnO	Na_2CO_3 (NaOH)	**19**	9		**13**	WO 2020 251463, WO202
Leena Zhang		Urea/thiourea, NaOH/LiOH, ZnO	Na_2SO_4, phytic acid (or H_2SO_4)	**35**	8		**20**	ACS Sustainable Chem En
IONCELL (CLY) ST		[Superbase] OAc	IL, water	**50**	13	0,90	**57**	
IONCELL (CLY) HT		[Superbase] OAc	IL, water	**62**	16	0,95	**93**	

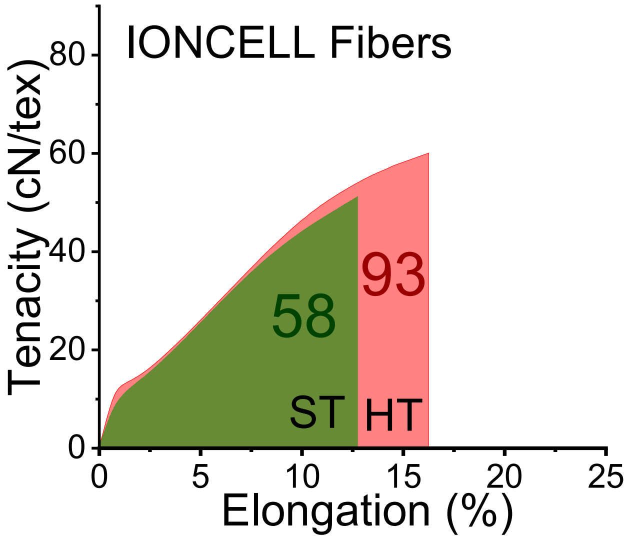
Tensile Strength vs Toughness

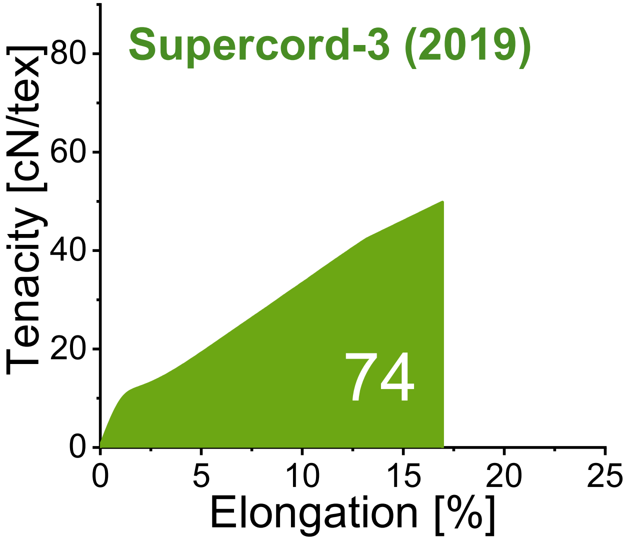


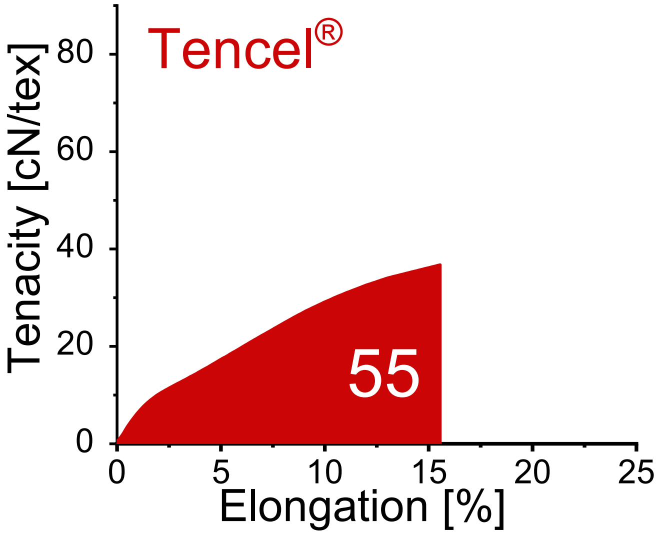
Series of toughness:

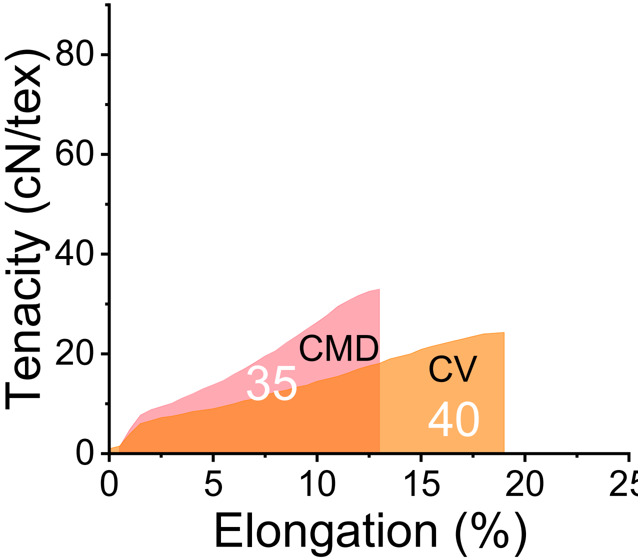
100% = 55 MPa = Lyocell Fiber

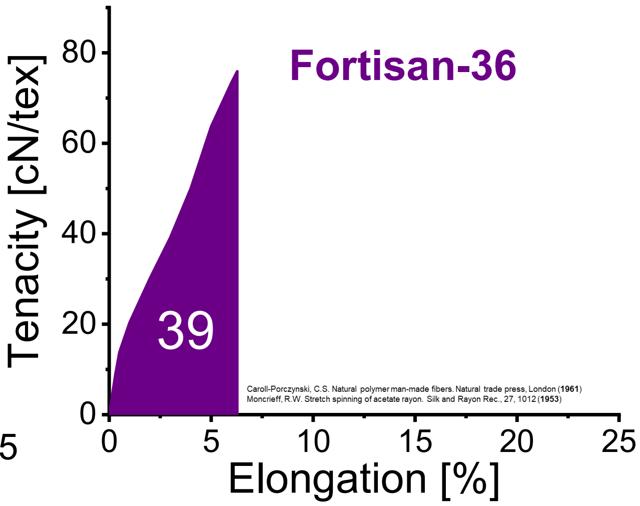
IONCELL-HT (**169**) > **Supercord-3 (135)** >
IONCELL-ST (**104**) > **Lyocell (100)** >
*Polynosic (**92**)* > **CV (73) >** *Fortisan-36 (**69**)* >
EHM (**62**) > **CMD (64)** > Cellca (**58**) >
Carbacell (**42**) > Infinna (**36**) =
Biocelsol (**36**) = Zhang-CCA (**36**) =
Cupro (**36**) > TTT (**24**)



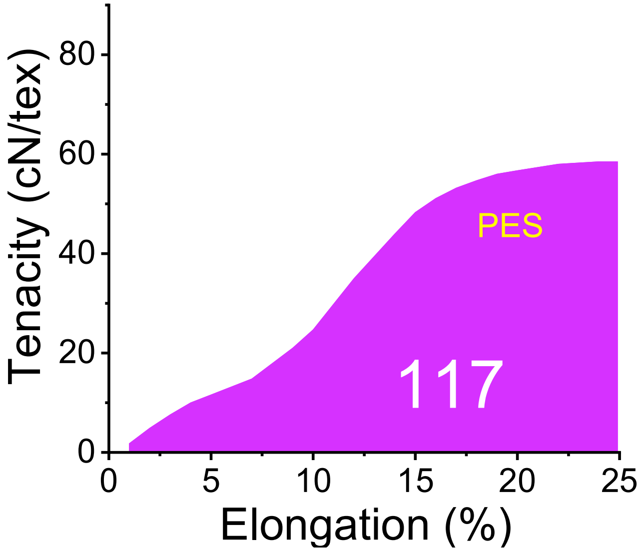




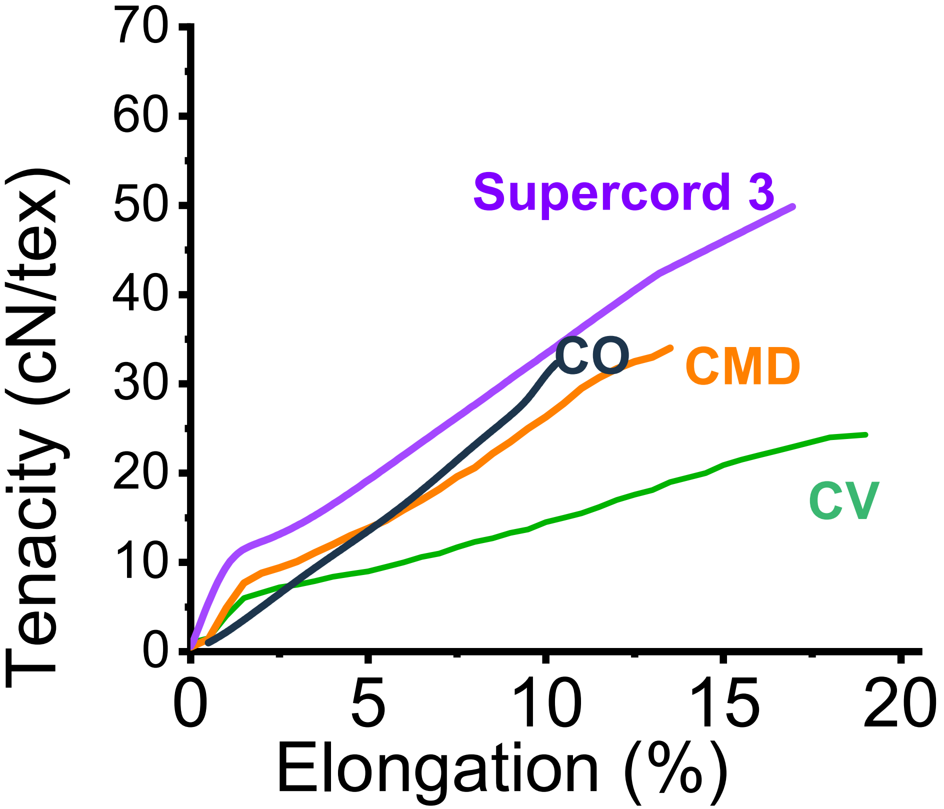


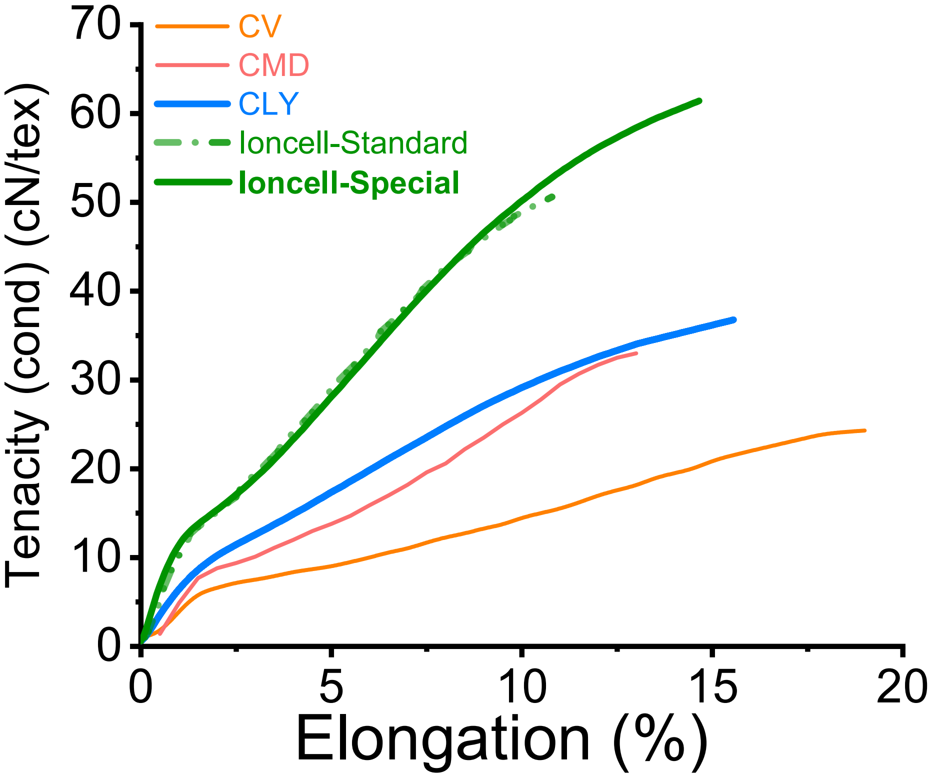


Caroll-Porczynski, C.S. Natural polymer man-made fibers. Natural trade press, London (**1961**)
Moncrieff, R.W. Stretch spinning of acetate rayon. Silk and Rayon Rec., 27, 1012 (**1953**)

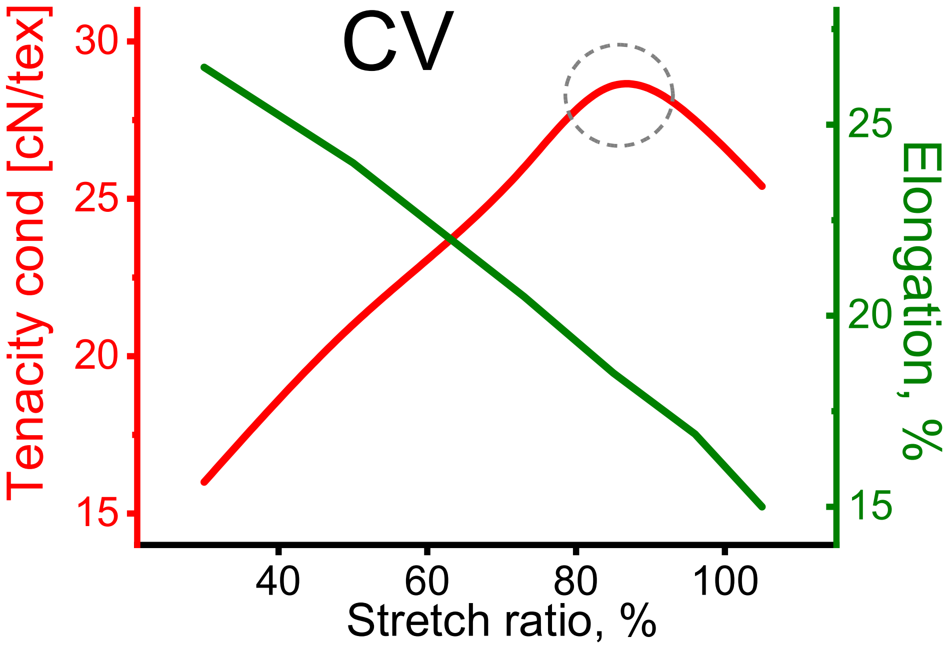


Stress-strain of MMCFs and CO

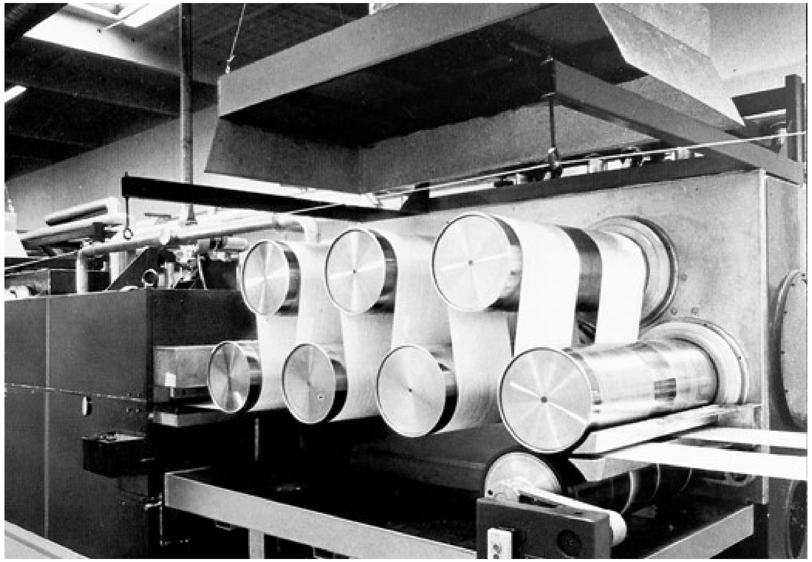


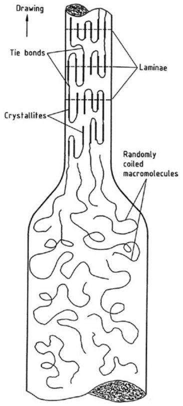


Overstretching of filaments



Maximum tenacity derived from stretching below the maximum.





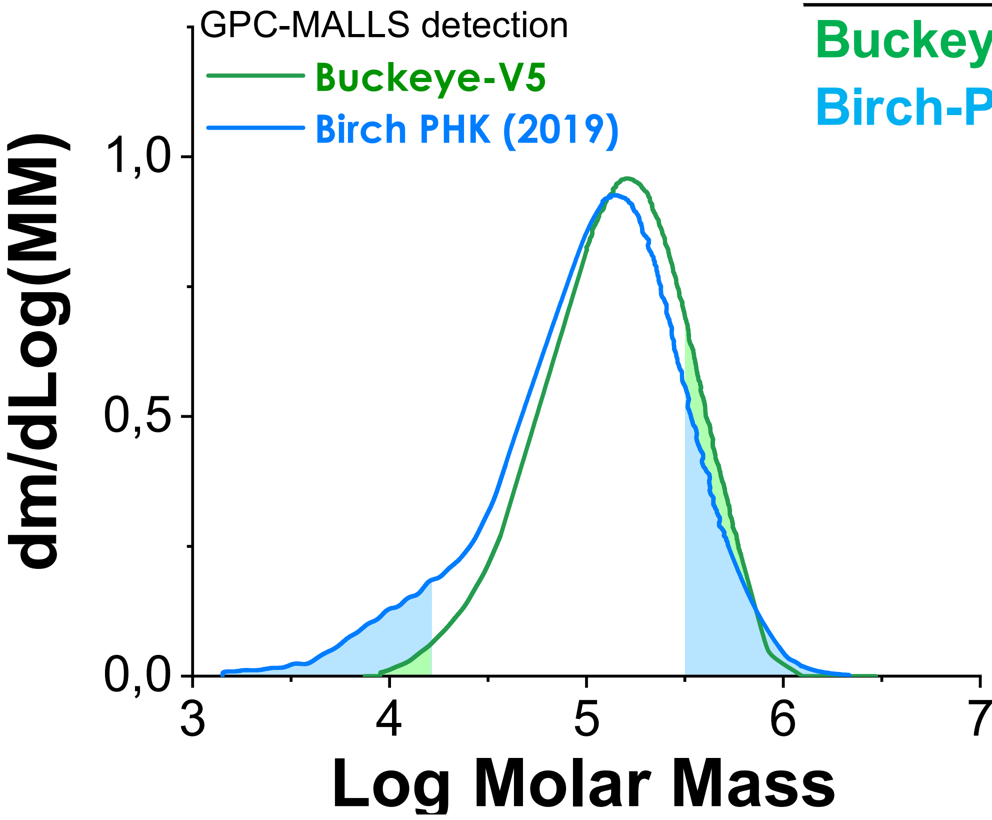
Stretching beyond the maximum leads to a breakage of the fiber bundle.

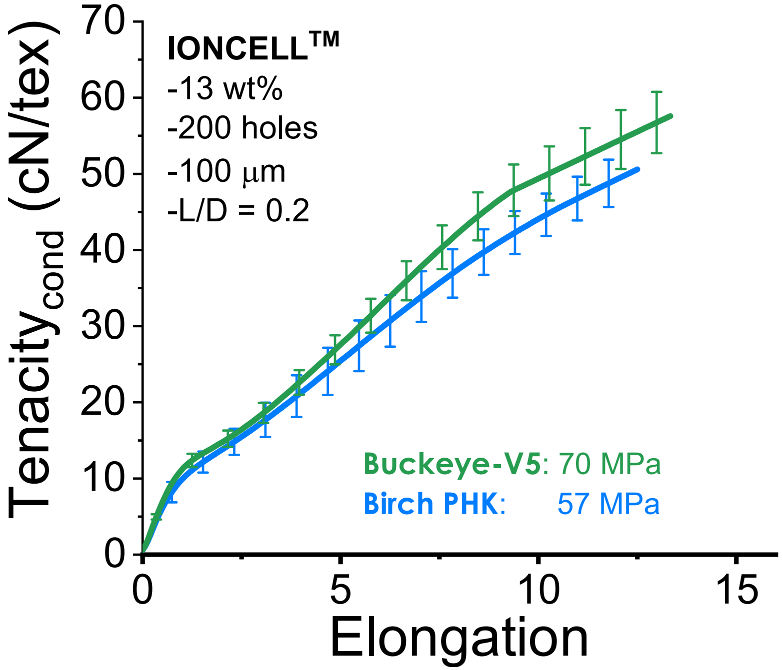
Fiber structure gets disruped and the fiber surface becomes rough.

Effect of pulp properties: IONCELL

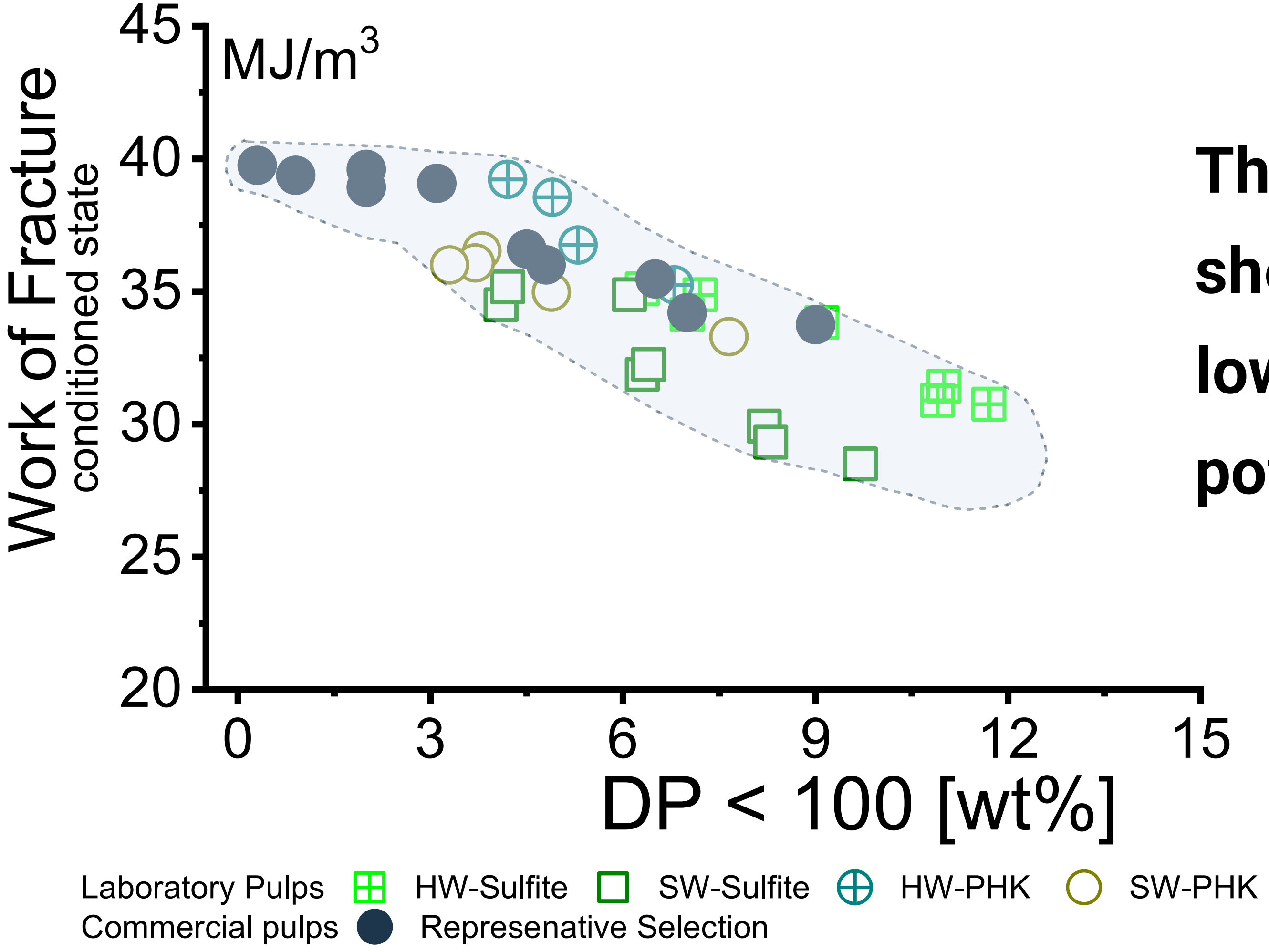
Pulp		Viscosity mL/g	Xylan % od	Mannan % od	DPw	DPn	DP<100 % od	DP>2000 % od
Pine PHK-CCE	Buckeye-V5	617	0,6	0,7	1240	570	0,8	16,4
Birch-PHK		502	7,0	1,2	1030	275	7,1	12,7

Fibers from Pulp	Ten_c	Elong_c	Ten_w	Elong_w
Buckeye-V5	57.6±4.1	13.4±2.5	57.5±4.0	14.3±1.6
Birch-PHK	49.9±4.4	12.5±2.0	47.3±4.5	14.2±2.1





Effect of MMD on Fiber Work Fracture



The higher the amount of short chains, DP < 100, the lower is the strength potential of viscose fibers.

H. Sixta et al., *Handbook of Pulp*, 2006

Classification of Fiber Properties

In an effort to understand the multitude of mechanical property parameters of fibres such as conditioned and wet strength (σ_c, σ_w), conditioned and wet elongation ($\varepsilon_c, \varepsilon_w$), wet modulus ($WM$), loop and knot strength (L_S, Kn) a factor analysis was carried out and the correlation of these parameters was summarized into two factors, F1 and F2.

Factor analysis: $\underline{\boldsymbol{Z}} = \underline{\boldsymbol{A}} \cdot \underline{\boldsymbol{F}} + \underline{\boldsymbol{E}}$

$\underline{\boldsymbol{Z}}$ matrix of standardized characteristics; $\underline{\boldsymbol{A}}$ matrix of factor loadings; $\underline{\boldsymbol{F}}$ matrix of common factors; $\underline{\boldsymbol{E}}$ matrix of feature-specific factors.

Factor analysis is a multivariate statistical method that makes it possible to reduce a group of m correlated characteristics to a small number of uncorrelated factors (linear correlation).

$$\boldsymbol{F_1 = -1.109 + 0.03992 * \sigma_c - 0.06502 * \varepsilon_c + 0.04634 * \sigma_w - 0.04048 * \varepsilon_c + 0.08936 * WM + 0.02748 * L_S + 0.02559 * Kn}$$

$$\boldsymbol{F_2 = -7.07 + 0.02771 * \sigma_c - 0.04335 * \varepsilon_c + 0.02541 * \sigma_w - 0.03885 * \varepsilon_c + 0.08936 * WM + 0.01542 * L_S + 0.02891 * Kn}$$

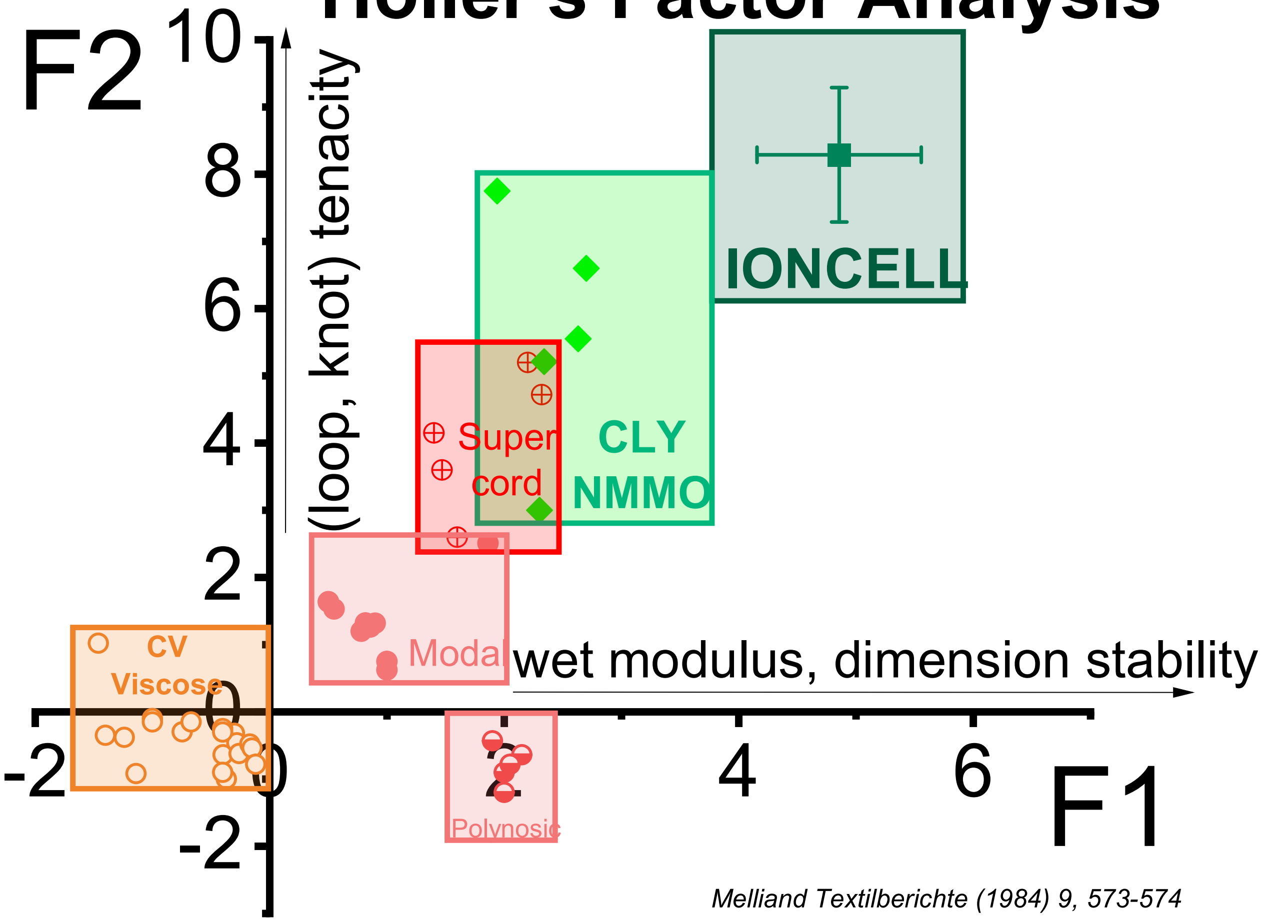
F1 characterizes mostly the modulus of the stress-strain both in dry and wet conditions

F2 characterizes the loop and knot strengths and the modulus of toughness

Lenz Ber (1985), 58, 94-100

Classification of Fiber Properties

Höller's Factor Analysis

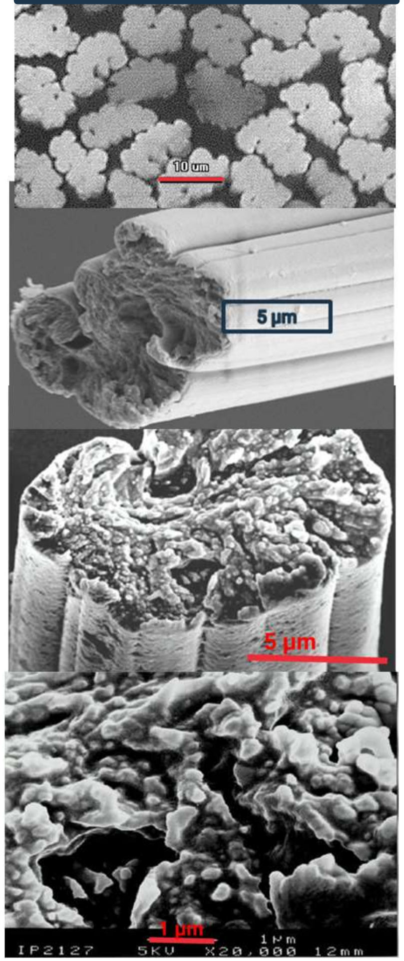


Melliand Textilberichte (1984) 9, 573-574
Lenz Ber. (1985), 58, 94-100

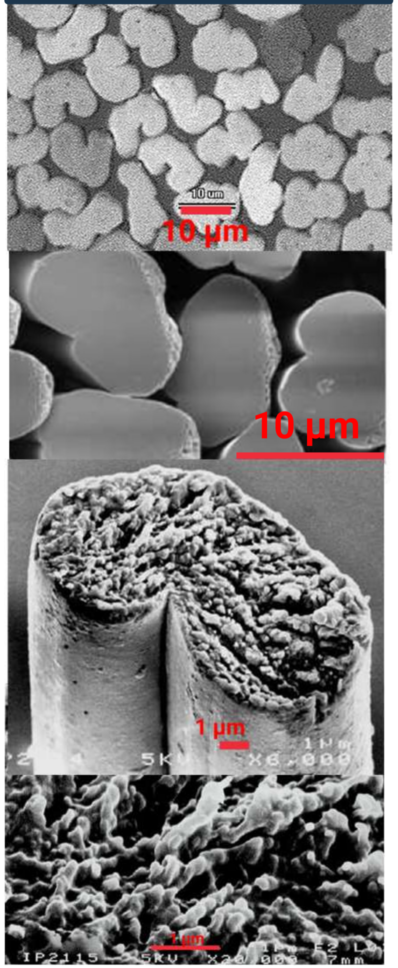
Lin. Density
Tenacity
Elongation
Elastic modulus
Modulus of toughness
Loop tenacity
Knot tenacity
Wet tenacity
Wet elongation

Fiber cross section

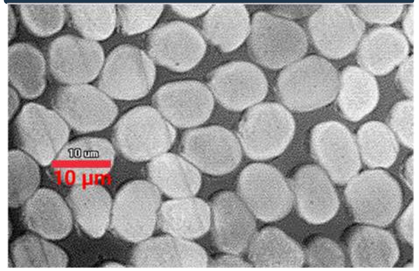
CV



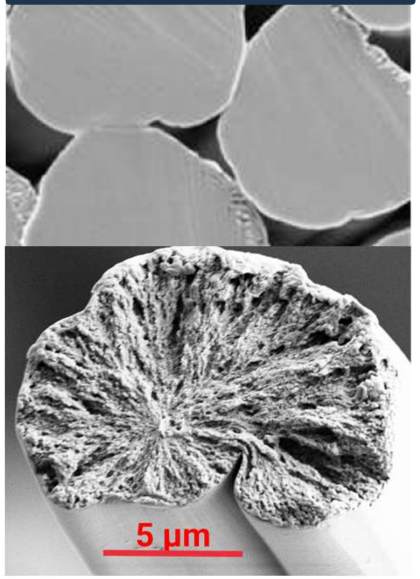
CMD



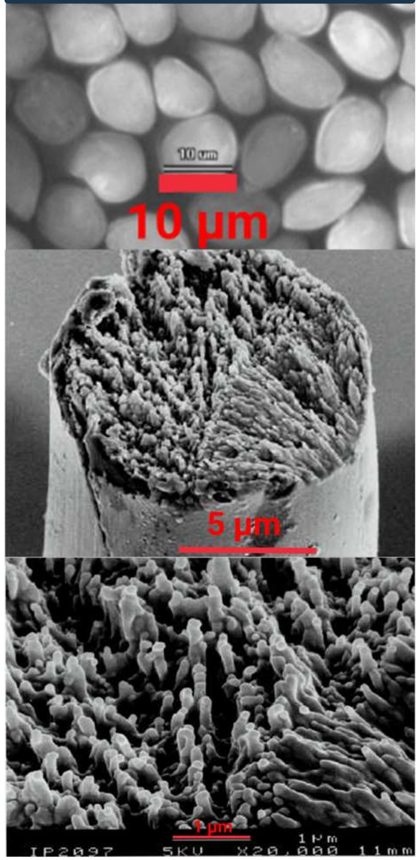
Polynosic



Supercord3



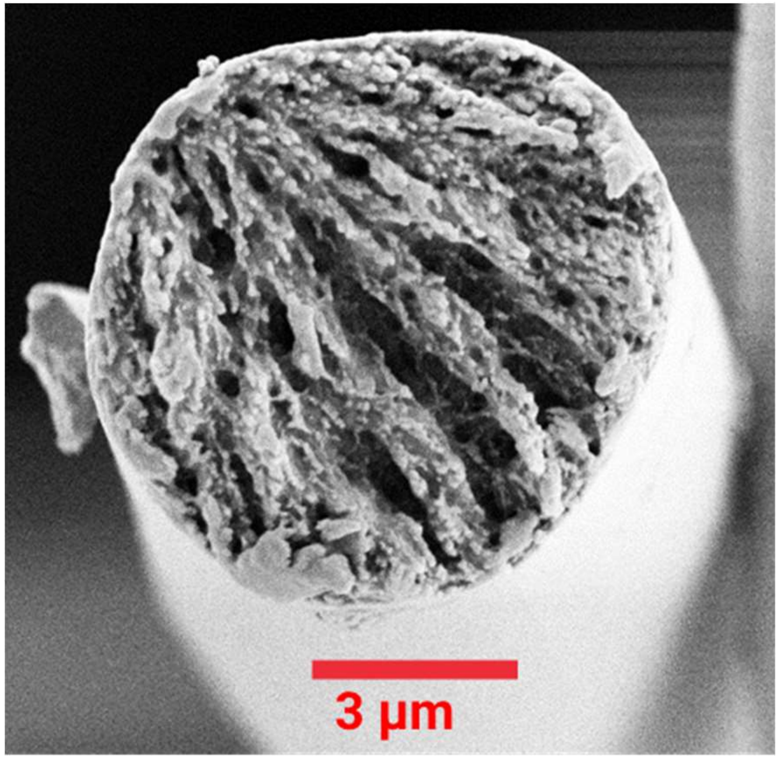
LYOCELL

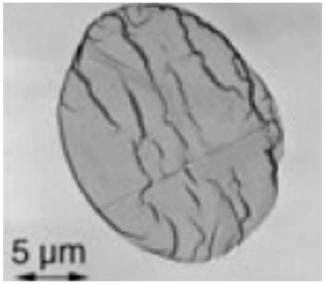


Röder, T. et al. Lenzinger Berichte 87 (2009) 98-105; CV, Tirecord birefringence measurement: Aalto; Cordenka EHM®: Boerstoel H. PhD thesis (1998)

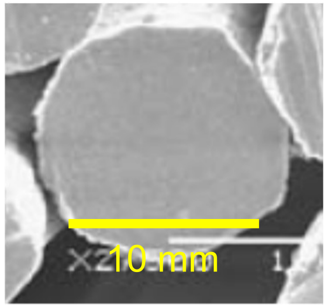
Fiber cross section

IONCELL

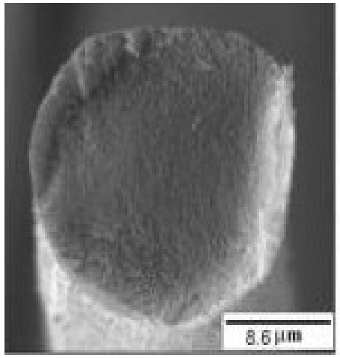




CarbaCell®
1.5 dtex



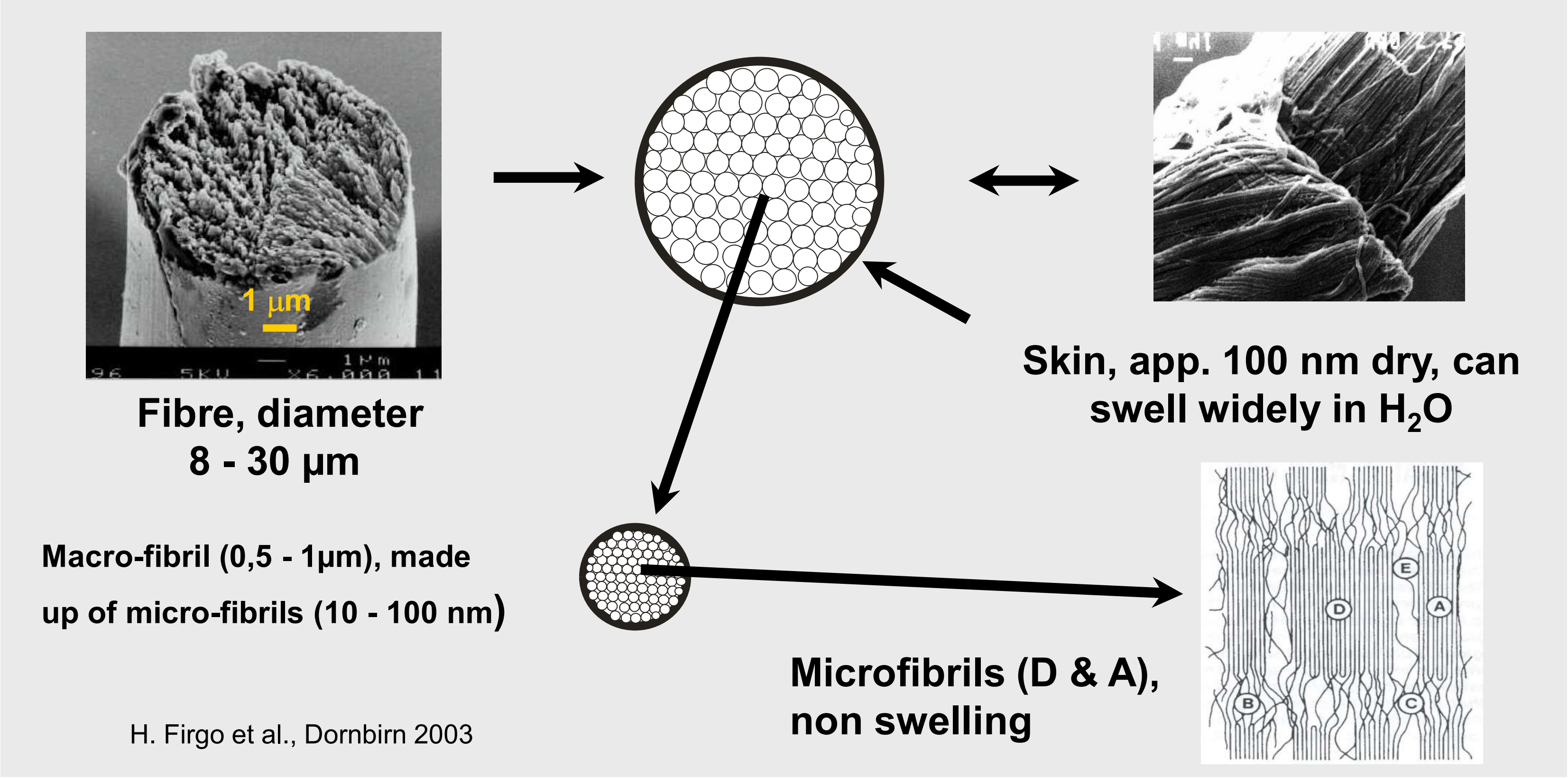
BioCelsol
2.1 dtex



NaOH/Urea
3.5 dtex

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

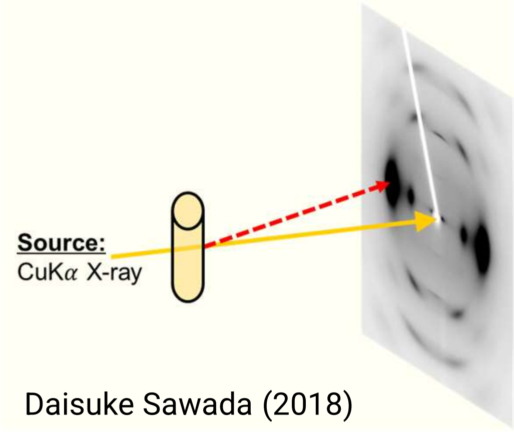
Macro-fibril (0,5 - 1µm), made up of micro-fibrils (10 - 100 nm)

Microfibrils (D & A), non swelling

H. Firgo et al., Dornbirn 2003

Estimation of structural parameters

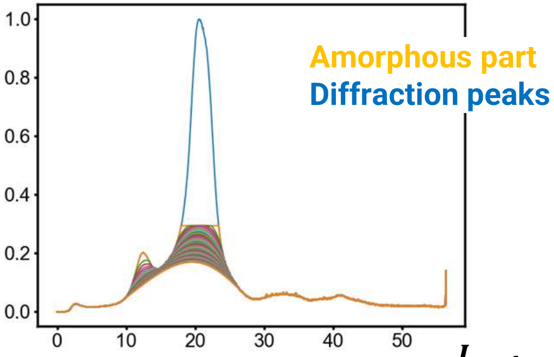
WAXS (0.1 – 20 nm)



Daisuke Sawada (2018)

Crystallinity index

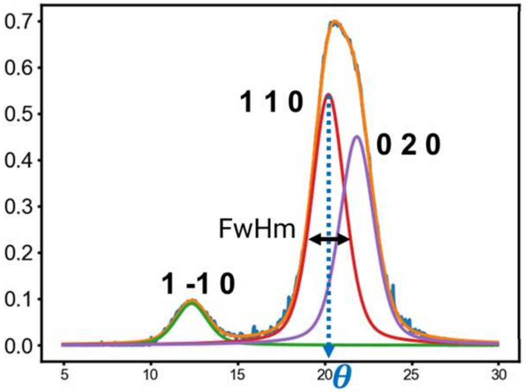
Background area vs peak area after background subtraction

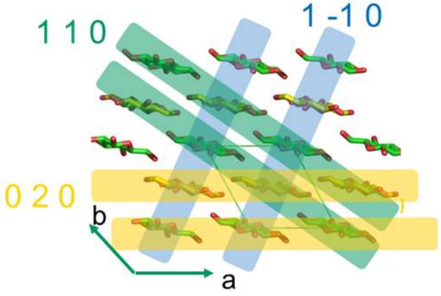


$$Crystallinity\ index = 100 \times \frac{I_{peak}}{I_{total}}$$

Crystal size

Estimated from Scherrer equation





Scherrer Equation

$$Crystal\ width = \frac{K\lambda}{FwHm \cdot cos\theta}$$

Orientation index, Hermans parameter

Estimated from equatorial diffraction azimuthal profile

$$f_c = \frac{3\langle cos^2\phi\rangle}{2}$$

Fiber axis vs. crystallographic axis - (020) lattice plane of cellulose II at 21.9° 2θ

Total, amorphous orientation

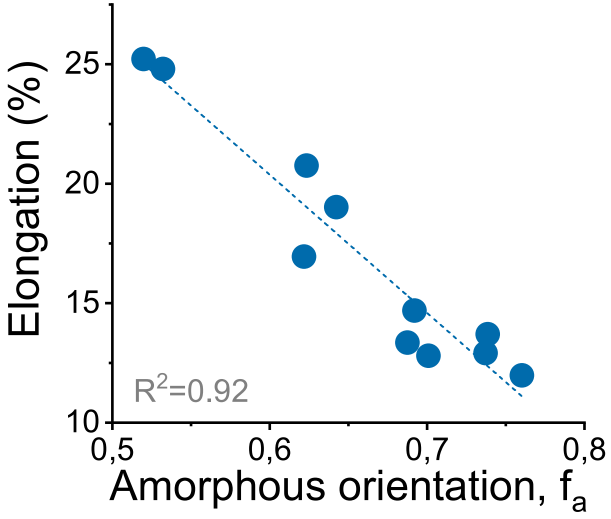
Determined by birefringence measurement using polarized light microscope with a 5 λBerek compensator.
Δn obtained by dividing the retardation of the polarized light by fiber thickness
Amorphous orientation f_a

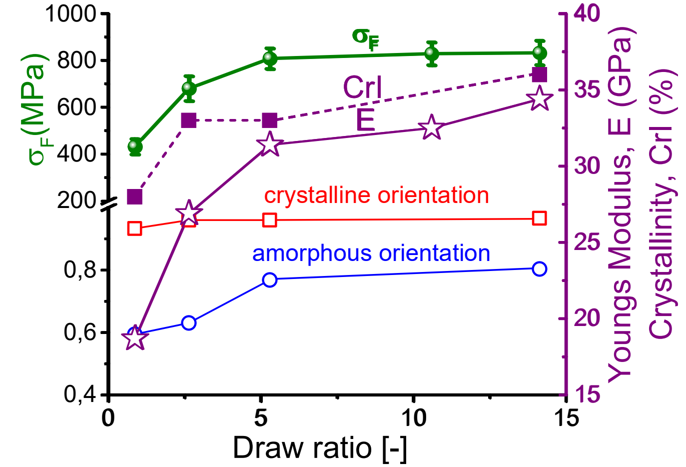
$$f_a = \frac{f_t - (X_c \cdot f_c)}{(1 - X_C) \cdot 0.91}$$

Daisuke Sawada (2018); Brückner, S. *J. Appl. Crystallogr.* **33**, 977–979 (2000).

Structural characterization

	Ioncell®			Tencel	Supercord3	Modal	Viscose
f_c	0,84	0,96	0,83	**0.79**	**0,83**	**0,75**	0,62
f_{tot}	0,71	0,82	0,68	**0,66**	**0,63**	**0,47**	0,41
f_{amorph}	0,71	0,81	0,64	0,60	0,62	0,35	0,27
CrI	33	36	37	**38**	**23**	**29**	28
Crystal size							
020 Å	34				**20**	**31**	
average Å	33				**23**	**33**	
Comment		1	2				





Ioncell-F: E-PHK pulp in 17 wt% IL

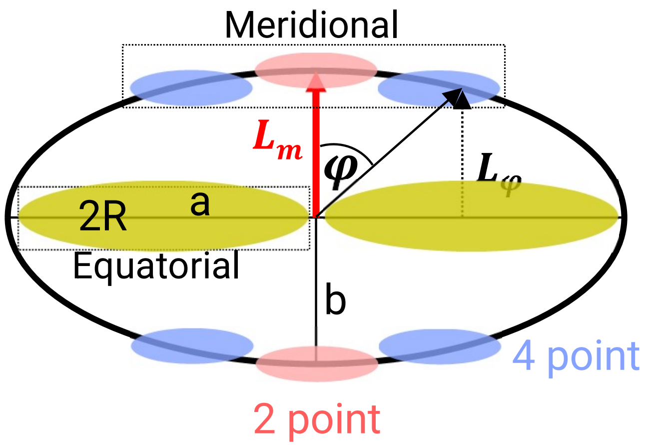
T. Röder, P. Zipper (2003), Lenzing AG

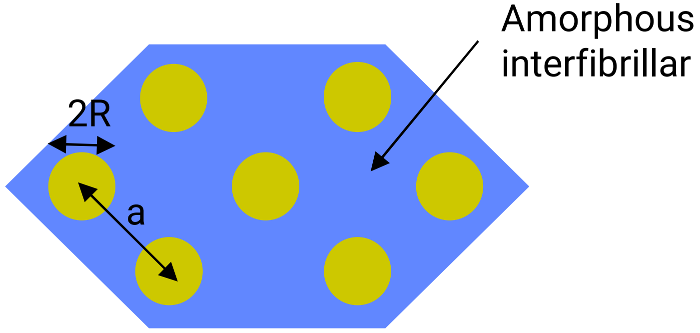
[1]NPPRJ (2015)

[2]Polymer 218 (2021), 123510

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

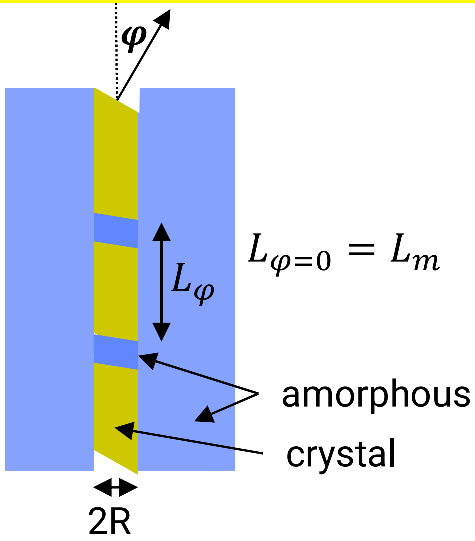
Small angle scattering pattern of fibrous polymer





Cross-section
of a hexagonally packed cylinder

Model of repeating unit in an elementary fibril constructed from the meriodional Bragg peak



Tilt angle φ indicates a higher level of interlinks between crystalline &amorphous regions in the elementary fibril

SANS measurements in the Q-range of 0.1-0.45Å^{-1}.
Elliptical shape of the meridional Bragg peak.

Meridional Bragg peak of SANS pattern to be attributed to the periodic structures, the

LONG PERIOD, L_φ, present in cellulose elementary fibrils.

Sawada Daisuke, et al. Polymer 218 (2021) 123510

Internal structure of elementary fibril

SANS measurements

Studying the meriodional Bragg peak for the quantification of the dimensions of the crystalline and amorphous phase in MMCFs

The larger Long Periods, the higher the tenacity.

An increase in the tilt angle improves the toughness

Sample	Tenacity_c cN/tex	Toughness MPa	L_m $Å^{-1}$	φ-max °
Ioncell STG pulp, DR 12	44	50	210	51
Lyocell-NMMO	38	54	198	45
Viscose	20	33	166	
Ioncell HPG pulp, DR 12	58	70	364	75

Kaniz Moriam et al. Cellulose (2021) 28: 9547-9566
Sawada Daisuke, et al. Polymer 218 (2021) 123510

Single-Phase Structure

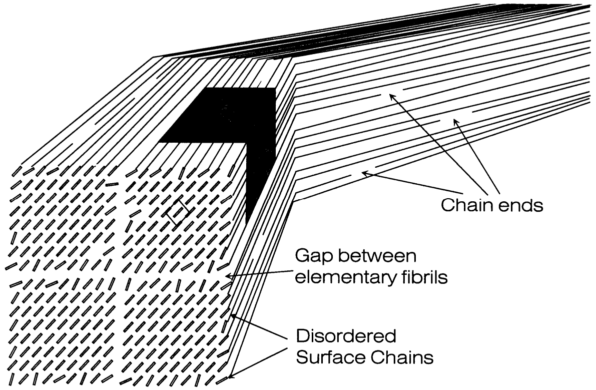
Continuous chain modulus: serial arrangement of crystallites (SAXS patterns do not show meridional reflexes)

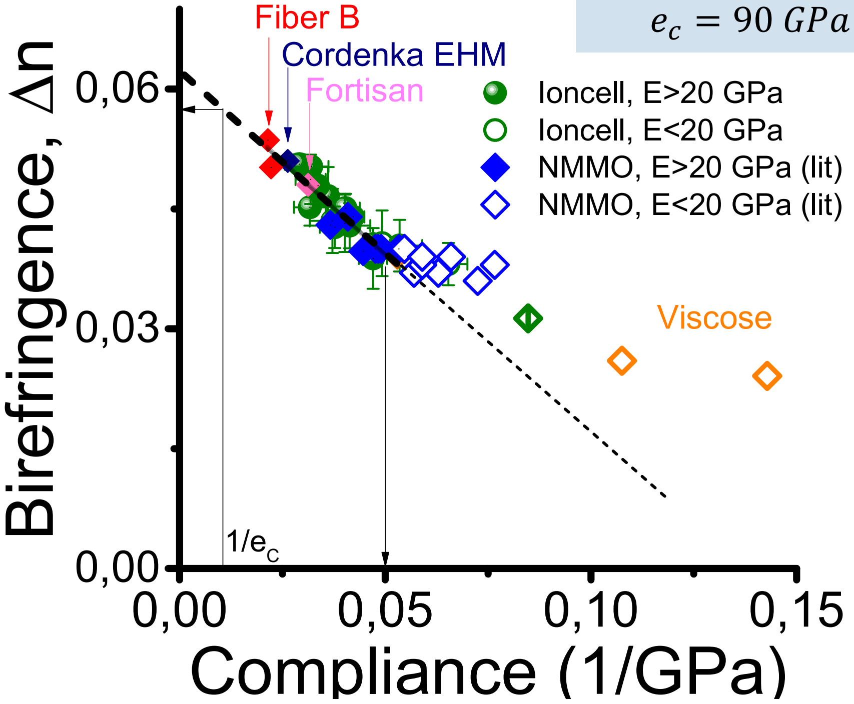
$$\frac{1}{E} = \frac{1}{e_c} + \frac{\langle sin^2\phi \rangle_E}{2g}$$

$$\Delta n = \Delta n_{max}\left(1 + \frac{3g}{e_c}\right) - \frac{3g\Delta n_{max}}{E}$$

$$\left.\frac{slope}{intercept} = \frac{3g}{1 + \frac{3g}{e_c}}\right\} \quad \begin{aligned} g &= 3.7\ GPa \\ \Delta n_{max} &= 0.068 \end{aligned}$$

$$e_c = 90\ GPa\ (II)$$





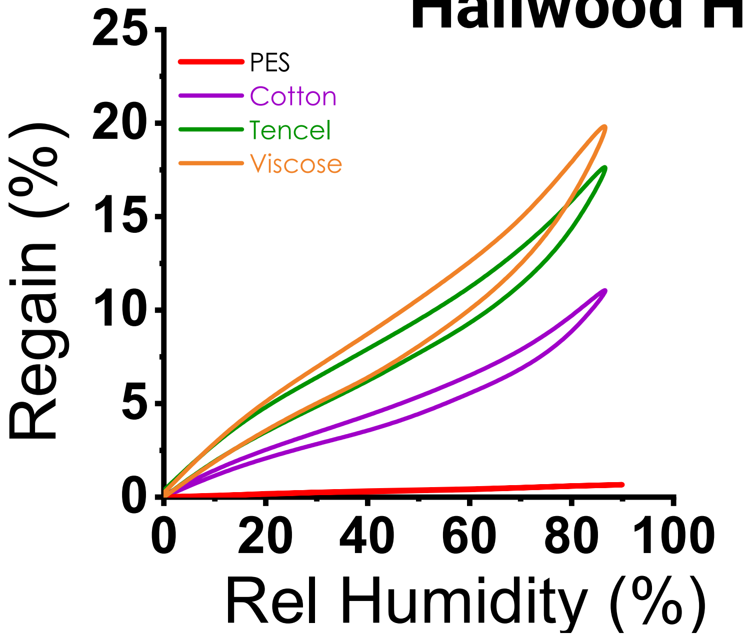
E, e_c, g elastic, chain, shear moduli

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

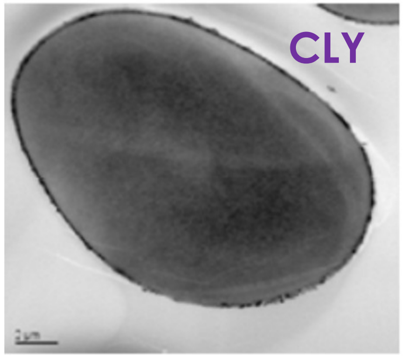
LYCELL

Fiber-Water Interaction

Hailwood Horrobin Model

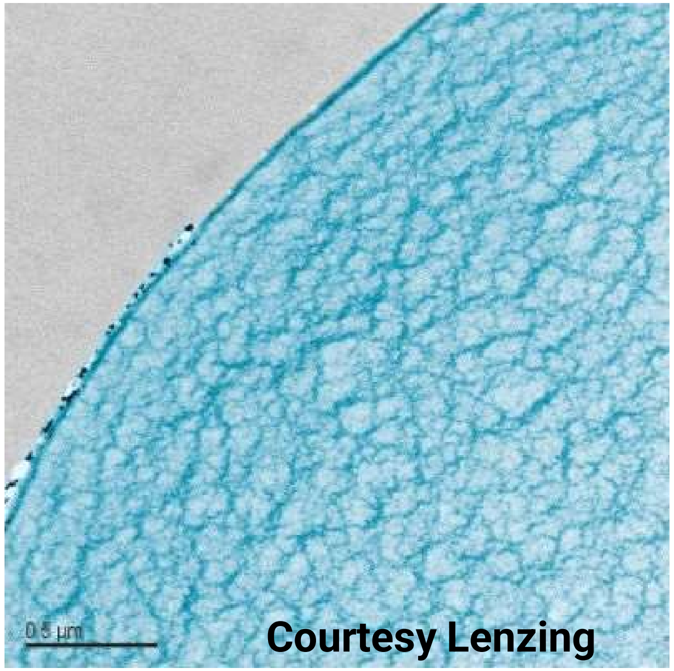


Sample	Sorption	Desorption	Hysteresis*
	Monolayer water		
	(mg/g)	(mg/g)	%
Cotton fibers	33	43	33
PES fibers	4	4	0
Tencel	**60**	**78**	**29**
Viscose	65	92	42



Solvent exchange followed by isoprene polymerization and OsO_4 staining

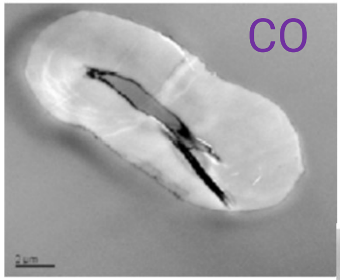
Nanofibrils act as a microscopic canal system facilitating moisture absorption and transportation



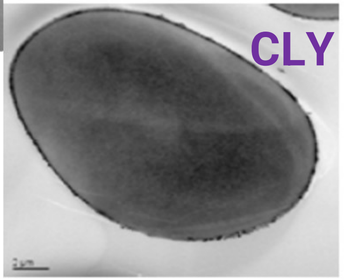
Courtesy Lenzing

M. Abu-Rous et al. Cellulose, 13, 411-419 (2006)

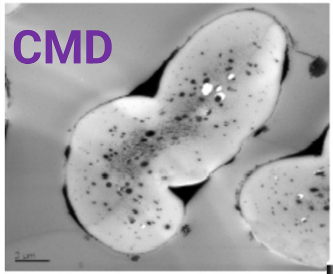
Absorbed Water in Cellulose Fibers



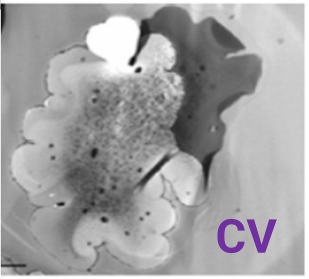
Cotton absorbs only little water



Tencel shows uniform water absorption over the whole fiber cross section



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

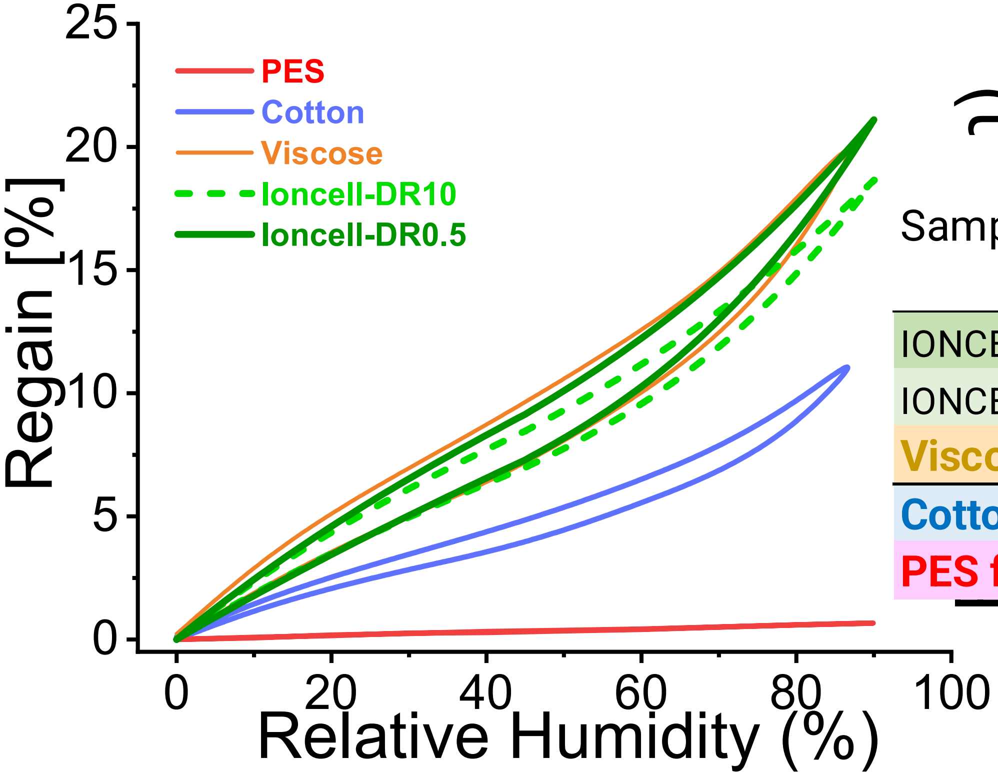


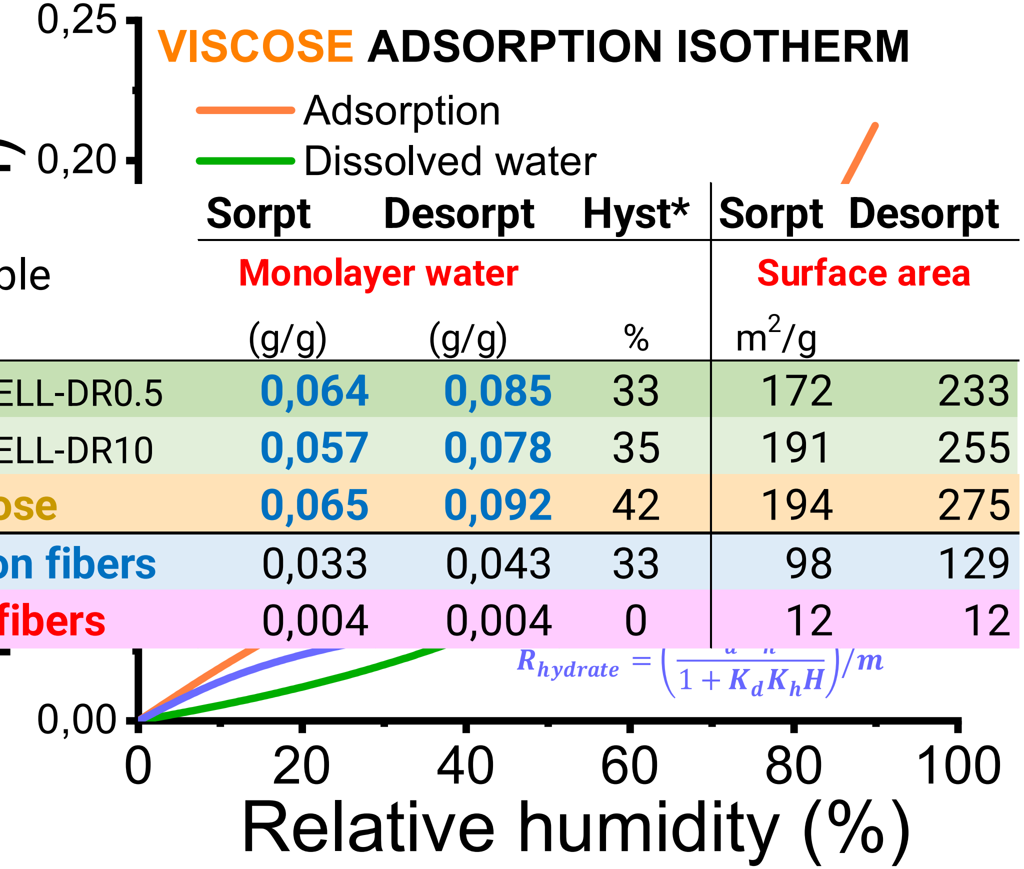
Uneven water distribution in **viscose**

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)

Interaction of fibers with water

Hailwood-Horrobin model





Sample	**Sorpt**	**Desorpt**	**Hyst***	**Sorpt**	**Desorpt**
	Monolayer water			**Surface area**	
	(g/g)	(g/g)	%	m^2/g	
IONCELL-DR0.5	**0,064**	**0,085**	33	172	233
IONCELL-DR10	**0,057**	**0,078**	35	191	255
Viscose	**0,065**	**0,092**	42	194	275
Cotton fibers	0,033	0,043	33	98	129
PES fibers	0,004	0,004	0	12	12

Hailwood, A.J. and S. Horrobin, *Trans. Faraday Soc.*, 1946. **42B:** p. 84-92, discussion 94-102

$* H = (ML_d - ML_a/ML_a)$

Water interaction

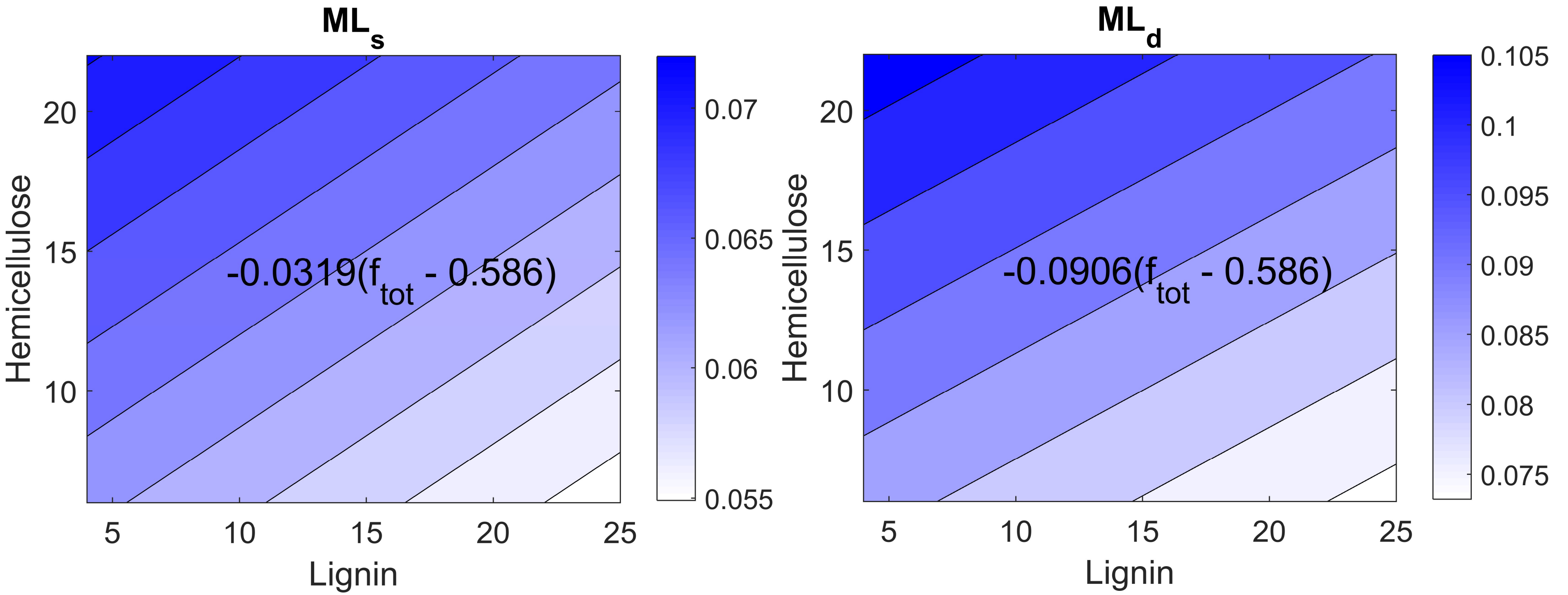
Cotton

Lyocell

Modal®

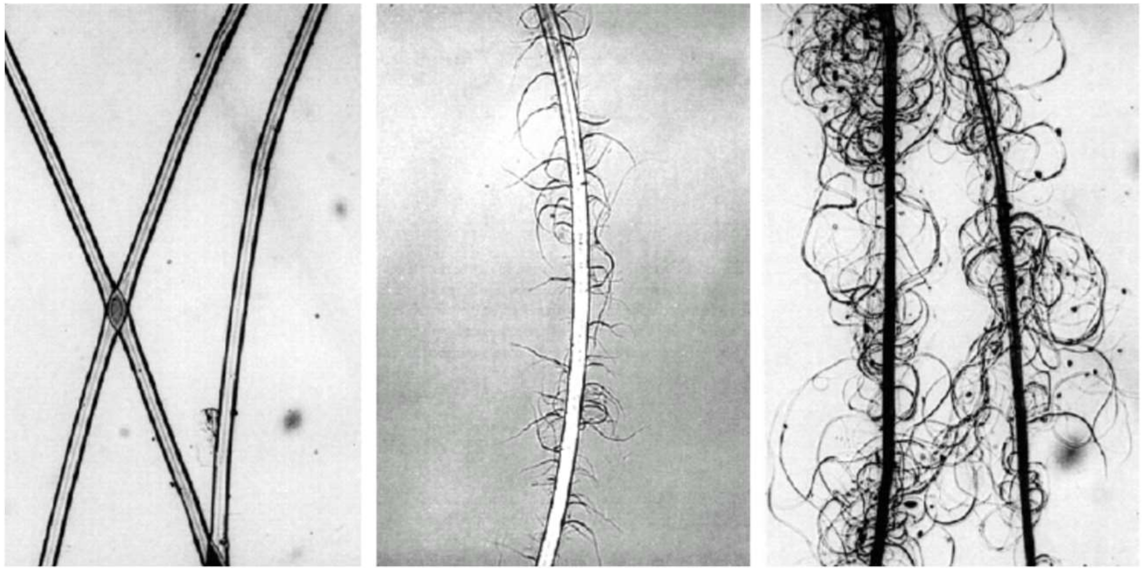
Schuster, K.C. et al. Lenzing AG

Interaction with Water- Effect of hemicellulose and lignin

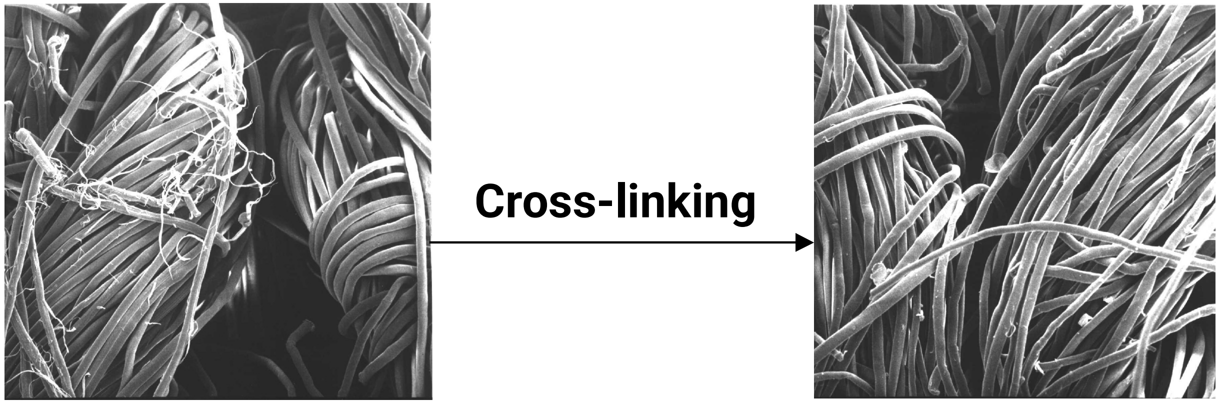


Fibrillation of Lyocell Fibres

- Weak lateral adhesion through high crystallinity and orientation
- Longitudinal splitting of fibrils from fibers
- By wet mechanical treatment (dyeing, washing, drying)
- Leads to the formation of pills, strips, hard surface,..



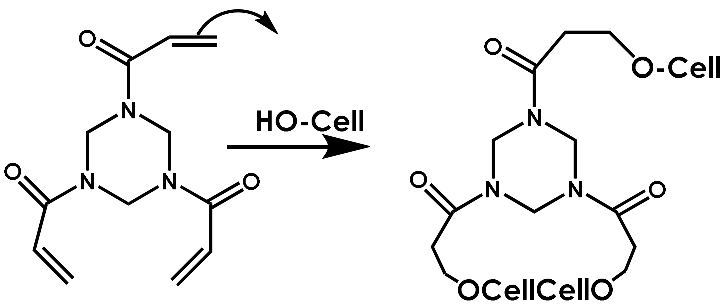
Cross-linking reduces Fibrillation



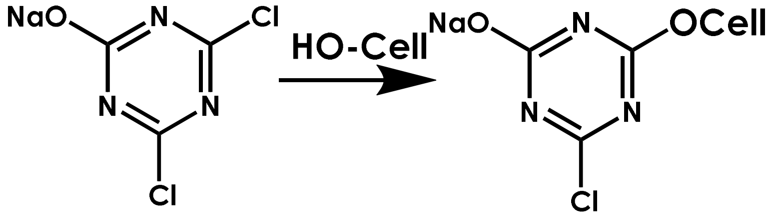
Lyocell

Lyocell LF

Triacrylamido-trihydrotriazin (Lenzing, A100).



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



Fibrillation in a blender

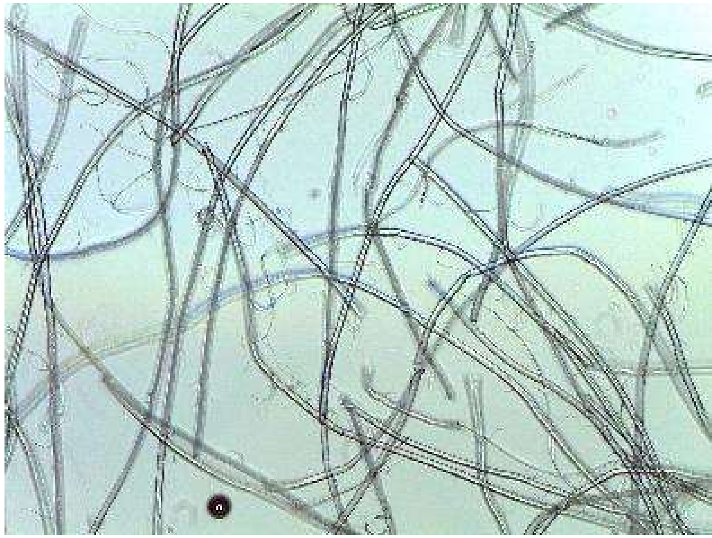
- 500 mg of air-dried fibers cut into 5 mm placed in the laboratory blender
- 500 ml water (or alkaline solution) added to the blender
- Mixing of the fiber suspension with high shear force
- Time and energy saving

Yibo Ma, Sixta H. et al. Cellulose (2021) 28:31–44

Assessment of Fibrillation index

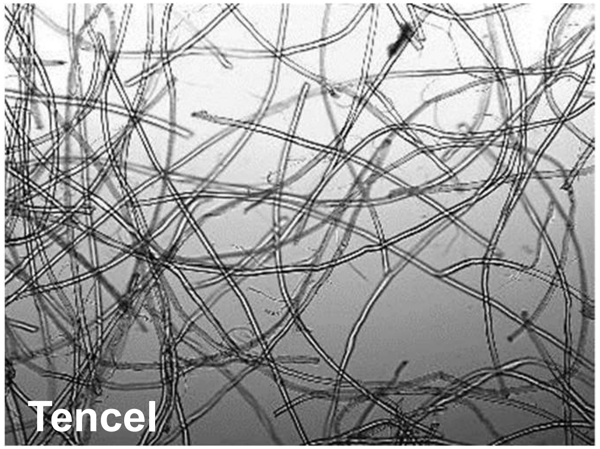
- **Blender treated fibers further cut to 2 mm diluted to 0.5-1.0 g/L suspension**
- **Suspension mixed 1:1 with 2% gelatin suspension (heating needed)**
- **2 drops of the suspension on objective glass with pipette tip that has been cut.**
- **Cover slide was placed before imaging with an optical microscope**
- **Fibrillation test using ImageJ software:**

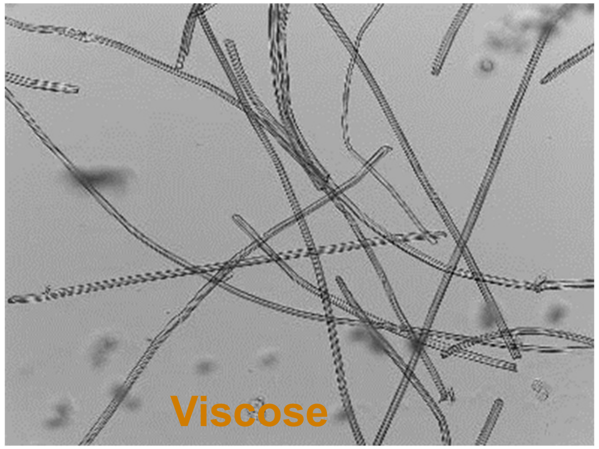
  $I_f = \frac{\sum_L l}{L}$ where I_f is the fibrillation index, l is the lengths of the fibril over the length of the fibre L

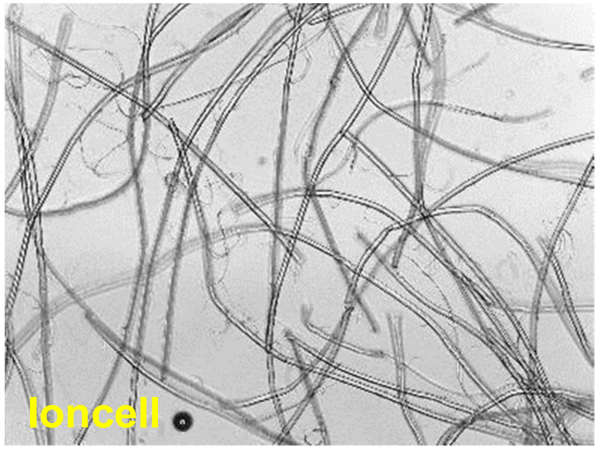


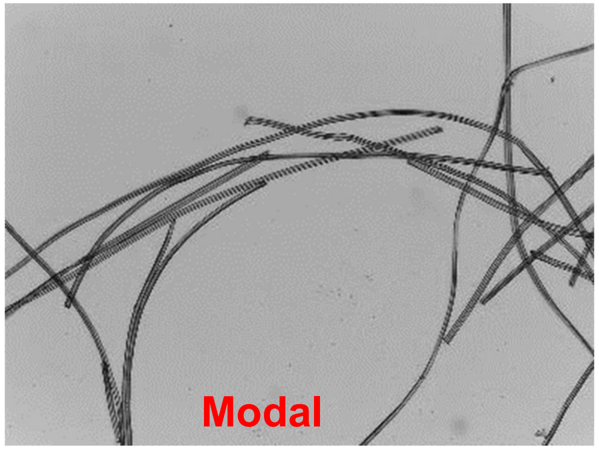
Yibo Ma, Sixta H. et al. Cellulose (2021) 28:31–44

Fibrillation of different fibres







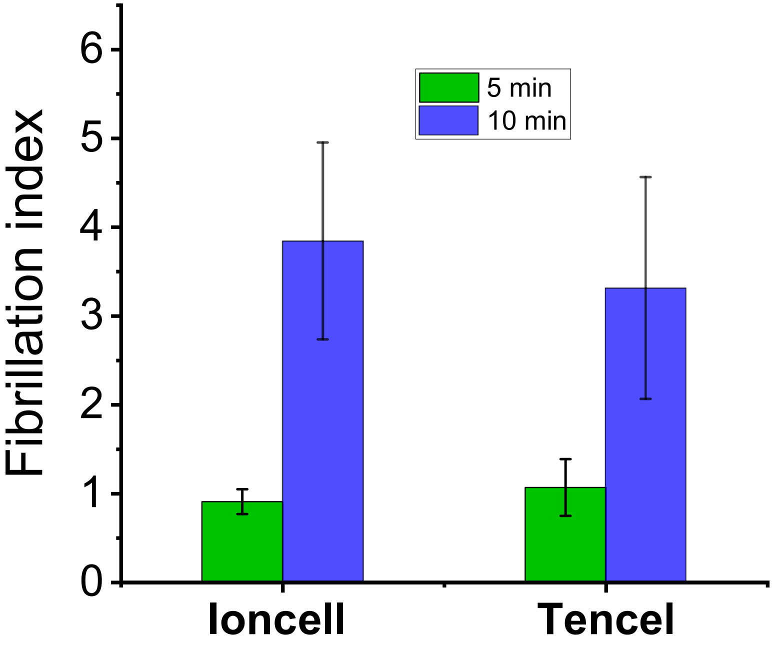


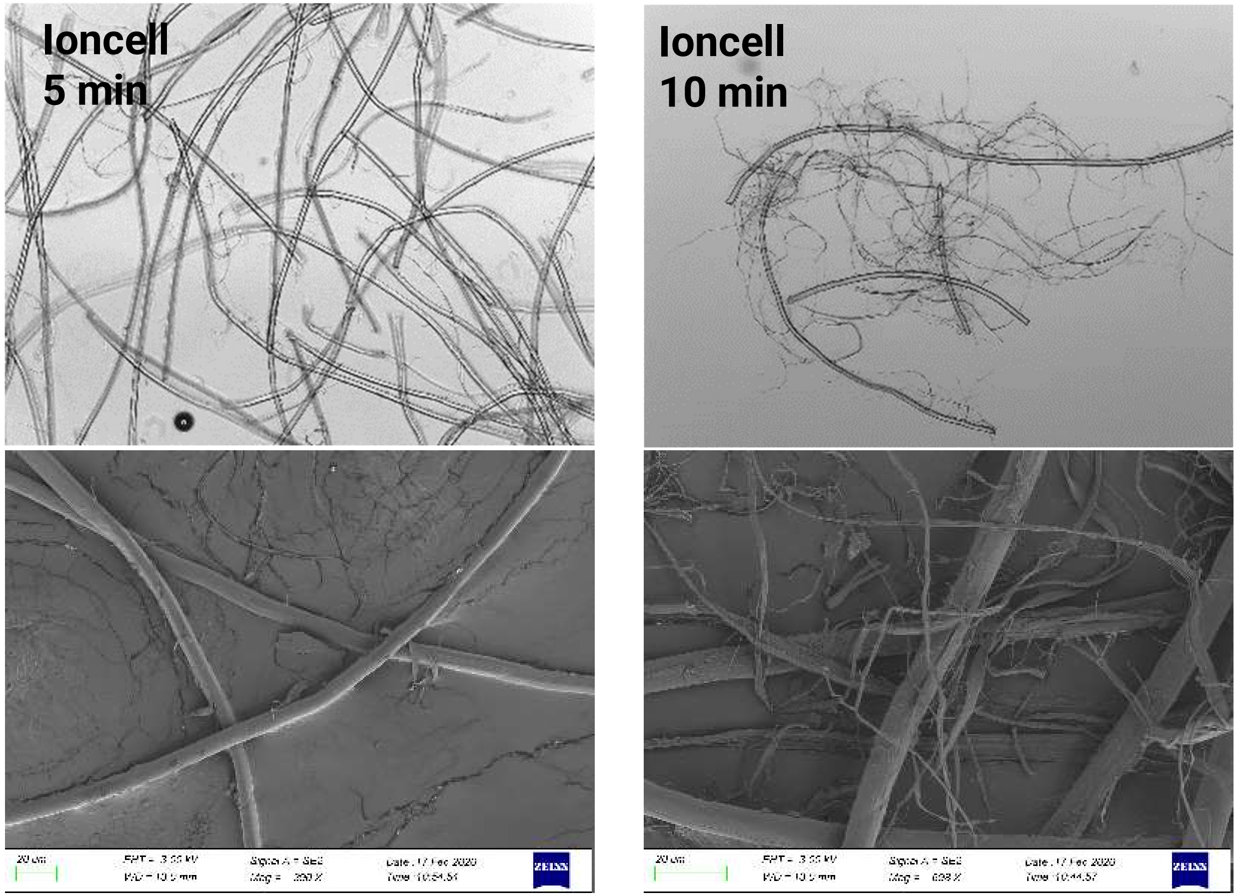
Fiber	$\mathbf{I_f}$	$\boldsymbol{\sigma_{cond}}$ cN/tex	$\boldsymbol{\varepsilon_{cond}}$ %
Ioncell	3,1	49,8	10,6
Tencel	2,6	36,8	15,6
Modal	0	29,4	13,6
Viscose	0	26,8	21,3

20 g/L $NaHCO_3$, 5‘, 80°C

Yibo Ma, Sixta H. et al. Cellulose (2021) 28:31–44

Effect of mixing time





A significant enhancement in the fibrillation observed as treatment time increases (room temperature)

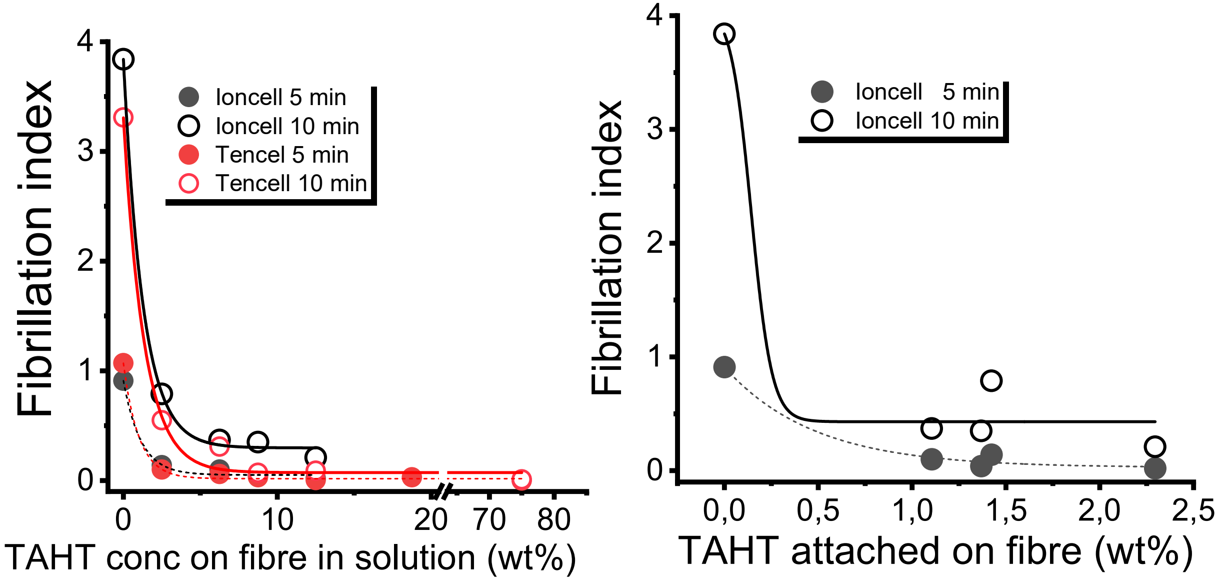
Yibo Ma, Sixta H. et al. Cellulose (2021) 28:31–44

Crosslinking with TAHT

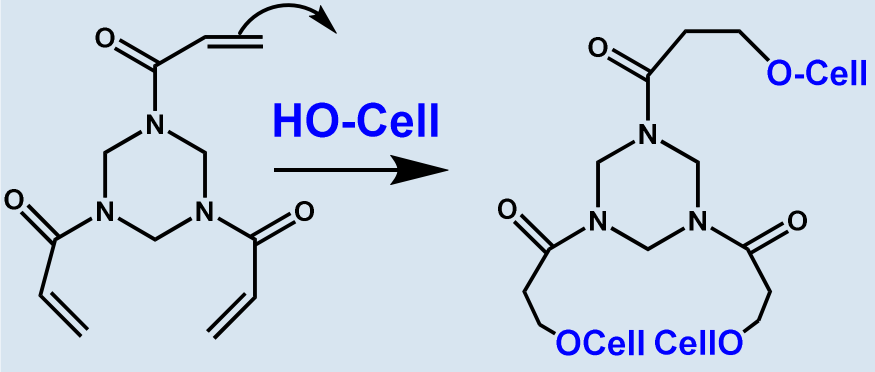
Dissolve TAHT in alkaline solution (pH 10-13)

Fibres mixed with TAHT in alkaline solution (consist. 12.5%) at 80 °C for 15 min.

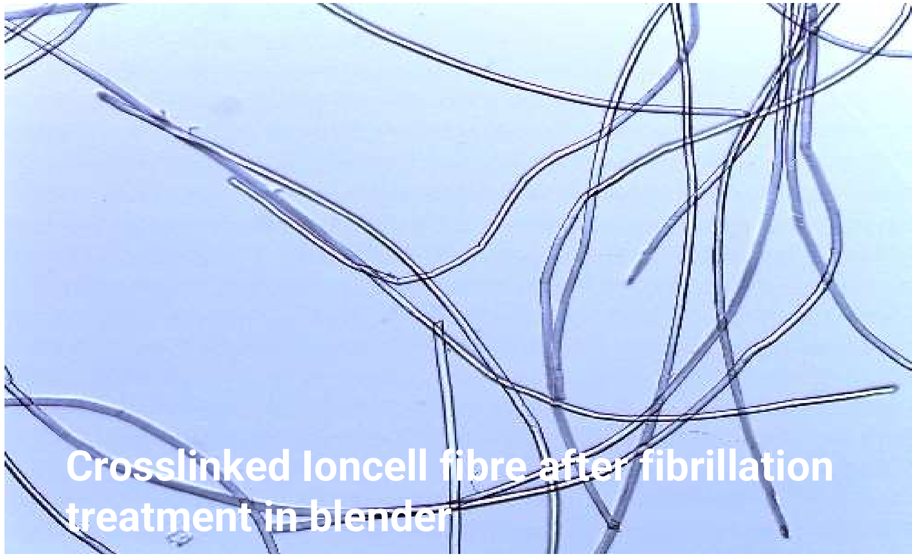
Fibre drying at 120°C



Yibo Ma, Sixta H. et al. Cellulose (2021) 28:31–44

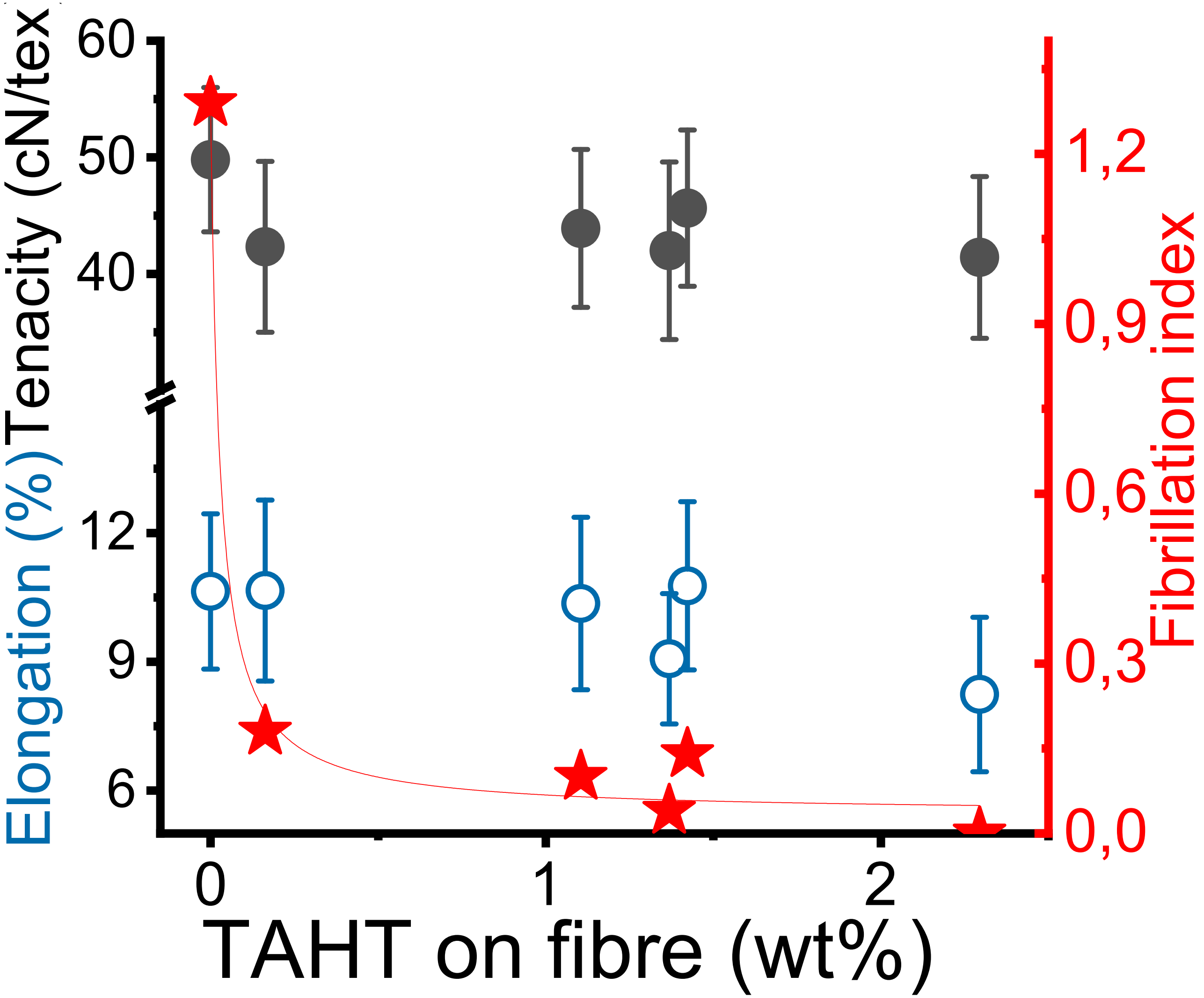


1,3,5-triacryloyl-hexahydro-1,3,5-triazine (TAHT)



Crosslinked Ioncell fibre after fibrillation treatment in blender

Effect of crosslinking on fibre properties



Crosslinking with THAT has a minor effect on the mechanical Ioncell fiber properties

Less than 0.5 wt% THAT on the fiber sufficent to avoid fibrillation

Yibo Ma, Sixta H. et al. Cellulose (2021) 28:31–44