Postgraduate course on

Cellulose Chemistry

Lyocell Fibers

Herbert Sixta, 21.-22. June 2016
Overview MMCFs

![Graph showing production of Viscose and other Cellulosics from 1990 to 2020.](image)

- **Years**: 1990, 2000, 2010, 2020
- **kt/a**: 0, 200, 3000, 6000, 9000
- **Viscose and other Cellulosics**
- **Tencel**, **CV**, **CMD**, **CLY**

![Images of Tencel, CV, CMD, CLY fibers](images)
BISFA Definition of man-made cellulose fibers (MMCF)

1. Viscose: CV
2. Modal: CMD
3. Cupro: CUP
4. Lyocell: CLY
5. Cellulose acetate: CA
6. Cellulose triacetate: CTA
What is a Lyocell Process?
Since 1989, solvent-spun fibers are denoted as **LYOCELL** fibers derived from *lye*<em>in</em> (dissolve)

In a dry-jet wet fiber spinning process the fluid filament is drawn in the **air gap**

- **Take-up velocity**
- **Extrusion velocity**
CLY Process Scheme
Scheme of Lyocell Process

- Pulp/NMMO
- Slurry
- NMMO/water
- Dissolution (Filmtruder)
- Spinning
- Cutting
- Washing
- Drying
- Evaporation
- Ion exchange
- Filtration
- Flotation
- Waste water
- Air
- Baling Press
- Dispatch
NMMO Chemistry
Degradation paths of NMMO

N-O-cleavage requires activation by e.g. protonation.

Heterolytic Cleavage of N-O

Intramolecular redox reaction
(Polonowski-reaction)

Formation of Carbenium-Iminium-Ion, Morpholin and Formaldehyde

Autocatalytical cleavage of NMNO

Spinning Dope Preparation
Phase diagram NMMO / water

0 x $H_2O$ (A)  $T_m = 182^\circ C$
1 x $H_2O$ (MH)  $T_m = 76^\circ C$
2 x $H_2O$ (DH)  $T_m = 40^\circ C$
8 x $H_2O$ (OH)  $T_m = -45^\circ C$

O. Biganska, P. Navard. Polymer 44(2003) 1035-1039
Morphology of crystallizing NMMO-water mixtures at high water contents

The parallel arrangement could be due a spinodal demixing phase change

NMMO Dope Preparation

- Disintegrated pulp mixed with 77% aqueous NMMO solution.
- Stabilizer added.
- Mixing at 80°C.
- Resultant slurry fed to a filmtruder operated under vacuum to keep temperature at 90-110°C.
Lyocell Dope Preparation

Filmtruder cross-section: shearing the dope to create thin films and new surfaces to facilitate water evaporation

*Int. J. of Mat. Eng.* (2012), 2:10-16
**Filmtruder:**
Long vertical vessel with steam heating in jackets around the vessel.

A shaft down the centre of the vessel with blades attached to its circumference is rotated to smear the material around the heated surface to promote the evaporation process.
Solution Structure

Ch. Michels, B. Kosan. Lenzinger Ber 84, 62 – 70 (2005)
Modes of Solvent Cellulose Interaction

- **Good quality solvent** (e.g. NMMO- under 17% water)
  - Dissolution
  - Fragmentation
- **Moderate quality solvent** (e.g. NNMO- 18 to 24% water)
  - No complete Dissolution
  - Swelling by ballooning
- **Bad quality solvent** (e.g. water- 8% NaOH or NNMO- 25 to 35% water)
  - No Dissolution
  - Swelling by ballooning
- **Non solvent** (e.g. NMMO- 35% water and over)
  - Homogeneous swelling

Phase diagram

Cellulose-NMMO-water (m%)
Cellulose Aggregate Solution

0.2-0.3 wt% Pulp dissolved in NMMO.MH

Molecules laterally aligned, core surrounded by disordered regions; aggregate size not affected

Interpenetrated network solution

Static light scattering measurements (Guinier-Zimm)

T. Röder, B. Morgenstern, Polymer 40 (1999) 4143 - 4147
Solution filtration

Prior to spinning various impurities have to be filtered out of the solution.

The solution is passed through two stages of filtration.

• **Primary filtration** consists of sets of sintered stainless steel media candle filter elements.

• **The secondary stage of filtration** is achieved by candle filter elements associated with each spinning machine position.

Filters are washed for re-use by an off-line process involving rinsing with hot amine oxide, chemically decomposing the residual compounds and then ultrasonic washing.

Spinning:
Dopes extruded into the air-gap
Dope Rheology

**Dynamic moduli, Pa**

- $G'$
- $G''$

**Complex viscosity, Pas**

**Angular frequency, 1/s**

- $[\eta]_0^*$

**Temperature, C**

- 70, 75, 80, 85, 90, 95, 100

**Complex viscosity, Pas**

- $[\eta]_0^*$

**AMOxH$_2$O**

**IONCELL**

**Ioncell-F Solvent**

- [DBNH][OAc]
- 1,5-diazabicyclo[4.3.9]nonenium acetate

**OAc$^-$**

'PCT/FI2014/050238, Application 04/04/2014
Spinning, Precipitation

**Spinneret, airgap:**
chain orientation

**Coagulation bath:**
desolvation, re-formation of hydrogen bonds -> highly swollen gel in fibrillar form -> fibrillar cellulose II crystal structure

**Structure Formation:**
Build-up of a fibrillar network.
Phase separation time < relaxation time

Air Gap Spinning

- Extrusion through orifices: **shear stress**
- Extrusion through air-gap: **extensional stress**
- Draw through spin bath: **spinodal decomposition**, solidification, structure formation
Dry-jet wet Spinning

**Force Balance**

\[ F_{ext} + F_{grav} = F_{rheo} + F_{inert} + F_{surf} + F_{aero} \]

For highly viscous samples, \( F_{grav} \), \( F_{inert} \) (inertial), \( F_{surf} \) (surficial) and \( F_{aero} \) (aerodynamical) forces are considered to be small.

\[ F_{ext} = F_{rheo} \]

Shear stress

\[ \dot{\gamma}_R = \left( \frac{4Q}{\pi \cdot R^3} \right) \]

Number of holes: \( n \) \[ \] \( 1000 \)
Diameter of holes: \( d \) [mm] \( 85 \)
Extrusion velocity: \( Q \) [mL/min] \( 25 \)

\[ \dot{\gamma}_R = \left( \frac{4 \cdot 25 \cdot 10^{-6}}{\pi \cdot 60 \cdot 1000 \cdot (42.5 \cdot 10^{-6})^3} \right) = 6911 \text{ s}^{-1} \]

Valid only for a Newtonian fluid.
Wall effects can be considered by the 
**Weissenberg-Rabinowitsch correction:**

\[ \dot{\gamma}_R = \left( \frac{4Q}{\pi \cdot R^3} \right) \left[ \frac{1}{4} \left( 3 + \frac{d\ln \dot{\gamma}_a}{d\ln \tau_R} \right) \right] \]

Typically \( \sim 1.5 \)
Elasto-capillary force balance predicts that the filament radius decays exponentially in time:

\[
\frac{D(t)}{D_0} \approx \left( \frac{G_1 D_0}{4\sigma} \right)^{1/3} \exp(-t/3\lambda_e)
\]

\[
\eta_E = -\frac{\sigma}{dD(t)/dt}
\]

\[
\dot{\varepsilon}(t) = -2 \frac{dD(t)}{D(t)dt}
\]

- \(\eta_E\) apparent extensional viscosity (Pas)
- \(D\) filament diameter (m)
- \(\dot{\varepsilon}\) extension rate (s\(^{-1}\))
- \(G_1\) elastic modulus (Pa)
- \(\sigma\) surface tension, 35 mN/m [emim][OAc]/Cell
- \(\lambda_e\) longest fluid relaxation time (s)
Elongational viscosity

Assumption: \( F_{ext} = F_{rheo} \) external force balances the rheological force

\[
\begin{align*}
\tau &= \dot{\varepsilon} \cdot \eta_E = \eta_E \frac{dv}{dx} \\
F_{rheo} &= \tau \cdot A \\
F_{rheo} &= \eta_E \frac{dv}{dx} \cdot A \\
\int_0^x \frac{F_{rheo}}{Q\eta_E} \, dx &= \int_{v_0}^{v_x} \frac{1}{v_x} \, dv_x \\
\text{integration} &\rightarrow \quad v_x = v_0 \exp \left( \frac{F_{rheo}x}{Q\eta_E} \right)
\end{align*}
\]

A fluid with a constant elongational viscosity shows an exponential profile

\[
\begin{align*}
v_L &= v_0 \exp \left( \frac{F_{rheo}L}{Q\eta_E} \right) \\
F_{rheo} &= \frac{Q\eta_E}{L} \ln \left( \frac{v_L}{v_0} \right)
\end{align*}
\]

\( v_L \) velocity at bath surface
\( L \) air gap length

\( \tau \) extensional stress
\( \dot{\varepsilon} \) extension rate
\( \eta_E \) extensional viscosity
\( F \) extensional force
\( A \) cross-sectional area

Boerstel, H. *PhD thesis*, University of Groningen (1998)
Elongational viscosity

\[ F_{tot} = F_{rheo} + F_{hydro} \]
\[ F_{tot} = \frac{Q \eta_E}{l} \ln \left( \frac{v_{tu}}{v_e} \right) + F_{hydro} \]

- \( F_R = F_{EM} - F_G \)
- \( \cos \left( \frac{\alpha}{2} \right) = \frac{|F_R|}{2|F_{tot}|} \)
- \( F_{tot} = \frac{F_R}{2 \cos \frac{\alpha}{2}} \)

- \( |\vec{F}_{tot}| \) tension force
- \( |\vec{F}_{EM}| \) force measured by the sensor
- \( |\vec{F}_R| \) force resulting from tension force and wrap angle
- \( |\vec{F}_G| \) roller weight

\( \eta_E \)
- 82.000 Pa.s
- 42.000 Pa.s
- 96.000 Pa.s

Anne Michud, Michael Hummel, Herbert Sixta-J. APPL. POLYM. SCI. 2016
Temperature profile in air-gap

\[ T(x) - T_\infty \]
\[ \frac{T_0 - T_\infty}{T_0 - T_\infty} = \text{Exp}( -0.0354 \cdot x ) \]

Parallel to the exponential decay of temperature, the dope viscosity rises exponentially away from the spinneret.

Filament velocities

\[ v_x = \frac{4Q}{\pi d_x^2} \quad \Rightarrow \quad v_0 = \frac{4Q}{\pi d_0^2} \quad \Rightarrow \quad \frac{v_x}{v_0} = \frac{d_0^2}{d_x^2} \]

- Rapid rise of velocity followed by a roll-off.
- Good fit with the model

\( v_x \) - extrusion velocity
\( v_0 \) - velocity after distance \( x \)

200 \( \mu \)m orifice

\[ \frac{v_x}{v_0} = D_R \cdot \text{Exp}[-\ln D_R \cdot \text{Exp}(-ax)] \]

\( D_R = 10.0 \)
\( a = 0.0313 \)

Filament velocities

Spinning can be treated as uniaxial extensional flow (if air drag and relaxation of the shear flow is ignored)

\[ \tau = \dot{\varepsilon} \cdot \eta_E \]

\[ \frac{F}{A} = \eta_E \frac{dv}{dx} \]

\[ Q = v \cdot A \]

\[ \frac{Fv}{Q} \frac{dv}{dx} = \eta_E \frac{dv}{dx} \]

Substituting for \( 1/V \)

\[ \frac{d\ln v}{dx} = \frac{1}{\eta_E Q} F \]

\[ \frac{v_x}{v_0} = D_R \cdot \text{Exp}[-\ln D_R \text{Exp}(-ax)] \]

Assuming \( \eta_E = ke^{ax} \)

\[ \frac{d\ln v}{dx} = \frac{e^{-ax} F}{kQ} \cdot d\ln v = \frac{F e^{-ax}}{Qk} dx \]

\[ \int d\ln v = \int \frac{F e^{-ax}}{Qk} dx \rightarrow \ln v = -\int \frac{F e^{-ax}}{Qk} dx \rightarrow \ln v_0 = -\frac{F}{Qk} e^{-ax} + \frac{F a}{Qk} \]

\[ \ln \frac{v}{v_0} = -\frac{F a}{Qk} e^{-ax} + \frac{F a}{Qk} \rightarrow \frac{v}{v_0} = \text{Exp} \left( \frac{F a}{Qk} \right) \text{Exp} \left( -\frac{F a}{Qk} e^{-ax} \right) \]

boundary conditions: \( \frac{v}{v_0} = 1 \) at the spinneret;

\[ \frac{v}{v_0} = D_R \] for \( x -> 0 \)

Birefringence = Orientation growth

- Total orientation (birefringence) shows the same development than the dimensionless velocity.
- Stress on the filament is proportional to the inverse of the cross-sectional area.
- Thus, orientation is proportional to stress

Strain hardening and shear thinning

The **Deborah number** is defined as the ratio of the relaxation time (time it takes for a material to adjust to applied stresses or deformations) and the characteristic time scale of an experiment probing the response of the material:

\[ D_e = \frac{t_c}{t_p} = \frac{\lambda}{t_R} \frac{\text{relaxation time}}{\text{time of observation}} \]
Spinning: Coagulation, Regeneration
Dissolution vs Regeneration

- $\beta$ decreases upon water addition.
- [emim][OAc] water-tolerant $\sim 16$ w/w%
- [TMGH]-ILs water-intolerant 1-4 w/w%
- [TMGH]$^+$ hydrotrope, bulky, hydrophobic

Order of water tolerance:

$[\text{TMGH}][\text{OAc}] < [\text{TMGH}][\text{EtCO}_2] << [\text{emim}]\text{OAc}$

Coagulation – Phase Changes

1. At interface quick exchange of water and NMNO
2. Inside gel, NMNO diffusion impeded
3. Later, rapid desolvation, phase separation inside the biphasic region, where spinodal decomposition occurs:

formation of mutually interconnected polymer chains and pores.

Diffusion of water into the filament

Diffusion front of water monitored via microscope

- Water diffusion
  - fastest for NMMO
  - slowest for [emim]OAc

Regeneration time and depth

The incipient diameter of a filament, \( d = 2\sqrt{\frac{r_0^2}{DR}} \)

Diffusion equation for water, \( \frac{M_t}{M_{\infty}} = \frac{4}{\sqrt{\pi}} \sqrt{\frac{D_w t}{L_x}} \) is solved for time where the diffusion front has reached the filament radius, or \( d = 1 = r \), and \( L_x^2 = L_0^2 / DR \), to yield the regeneration time, \( t_{reg} \):

\[
1 = \frac{4}{\sqrt{\pi}} \sqrt{\frac{D_w t}{r_x^2}} \quad \Rightarrow \quad t_{reg} = \frac{r_0^2 \pi}{16D_w} \frac{1}{DR}
\]

Regeneration depth, \( \Delta X_{reg} = v_x t_{reg} \) with \( DR = v_x / v_0 \)

\[
\Delta X_{reg} = \frac{v_0 \cdot \pi \cdot r_0^2}{16 \cdot D_w}
\]

- \( v_0 \) = extrusion velocity
- \( v_x \) = take-up velocity
- \( r_0 \) = spinneret diameter, 100 \( \mu \)m
- \( D_w = 1.55 \cdot 10^{-10} \text{ m}^2 / \text{s} \)

Regeneration time and depth

\[ D_w = 2.70 \times 10^{-10} \text{ m}^2/\text{s} \]

\[ t_{\text{reg}} = \frac{r_0^2 \pi}{16D_w} \frac{1}{DR} \]

\[ \Delta X_{\text{reg}} = \frac{v_0 \cdot \pi \cdot r_0^2}{16 \cdot D_w} \]

Filament simulation

\[ d_0 = 100\mu m \]

\[ v_{\text{ext}} = 6.4 \text{ m/min} \]

\[ v_{\text{tu}} = 64 \text{ m/min} \]

\[ d_{\text{fil}} = 32\mu m \]

Spinnability of Filaments
Solvent Effect on Spinnability

Pulp: Eucalyptus Prehydrolysis Kraft: Mw = 269 kg mol\(^{-1}\), Mn = 79 kg mol\(^{-1}\)  
Polymer concentration 13 wt%  
NMMO.H\(_2\)O stabilized by propyl gallate and spun with a 18 x 100 mm spinneret; 1 cm air-gap, 100 \(\mu\)m spinneret, 15\(^\circ\)C air bath temperature, 0.04 mL min\(^{-1}\) extrusion velocity.

Spinning result

<table>
<thead>
<tr>
<th>Spinning solvent</th>
<th>$d_0$</th>
<th>$T_{extr}$</th>
<th>$T_{bath}$</th>
<th>DR$_{max}$</th>
<th>Titer</th>
<th>Tenacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>[DBNH][OAc]</td>
<td>100</td>
<td>70</td>
<td>15</td>
<td>7.5</td>
<td>3.0±0.9</td>
<td>38.5±8.4</td>
</tr>
<tr>
<td>NMMO.H$_2$O</td>
<td>100</td>
<td>95</td>
<td>15</td>
<td>6.2</td>
<td>3.7±0.7</td>
<td>31.2±6.6</td>
</tr>
<tr>
<td>[TMGH][OAc]</td>
<td>100</td>
<td>80</td>
<td>15</td>
<td>2.0</td>
<td>15.5±0.9</td>
<td>10.9±1.1</td>
</tr>
<tr>
<td>[emim][OAc]</td>
<td>250</td>
<td>90</td>
<td>45</td>
<td>2.9</td>
<td>44.4±1.7</td>
<td>13.9±1.6</td>
</tr>
</tbody>
</table>

**NMMO.H$_2$O** and **[DBNH][OAc]** give spinnable dopes, while the dopes made from **[TMGH][OAc]** and **[emim][OAc]** were not spinnable.
Poorly orientable network indicative for poorly spinnable dopes as prepared from [TMGH][OAc] and [emim][OAc].

Gelatinous regenerated polymer network forms → main resistance to further diffusion

Incipient [emim][OAc] filament

Telescopic-type breach because of very low resilience in the core during the onset of regeneration.

Both, yield strain and stress decrease at $0.5 \frac{n_{H_2O}}{n_{IL}}$ obviously due to a low water diffusion.

Final fiber orientation vs. DR

[emim][OAc] fibers: orientation develops poorly due to low resilience in the core.

[TMGH][OAc] fibers: solidified gel->solution behaves as a permanent network.

Spinnability Problems
Filament breaches during Spinning

Spinnability defined as the
**Maximum length of a filament (thread),** $L_{\text{max}}$

- Cohesive fracture
- Capillary fracture
- Melt fracture
- Telescopic fracture
Cohesive fracture - Limits DR

When the tensile stress, $\sigma^*$, exceeds a critical value, $\sigma_b(x^*)$:

**Cohesive break conditions:**

$$\sigma_b(x^*) = \sqrt{2K \cdot E} = \text{failure stress}$$

Decrease of the filament diameter leads to an increase of the tensile stress, which may induce a filament failure, as described by $L_{max}$:

Maximum fiber length

$$L_{max} = x^* = \ln \frac{\sqrt{2K \cdot E}}{3\eta v_0 \xi}$$

To avoid cohesive breaches, the product $v_0 \cdot \eta$ should be reduced; godet should run on a constant force.

---

$K = \text{resilience} = \text{elastic energy capacity (area underneath the stress - strain curve until elastic limit)}$

$E = \text{Young's modulus, } v_0 \text{ is the extrusion velocity}$

$\xi = \text{gradient of deformation} = \frac{F}{3\eta \pi R_0^2 v_0}$

Capillary fracture (typical in dry spinning)

Capillary waves associated with **too high surface tension:** Thread breaks into drops when the amplitude of the capillary waves reaches the radius of the undistorted fluid.

Maximum possible fibre length, $L_{max}$:

$$L_{max} = x^* = \frac{2}{\xi} \left[ \ln \frac{R_0}{\delta_0} - \frac{\sigma_s}{3\eta \xi \nu_0 R_0} \right]$$

$L_{max}$ increased by a reduction of the relative strength $\frac{\sigma_s}{3\eta}$ of the fluid or by increase in $R_0$

---

$\sigma_s = \text{surface tension}$  
$\nu_0 = \text{spinneret velocity}$  
$\delta_0 = \text{original amplitude disturbance}$  
$R_0 = \text{original fiber radius}$  
$\xi = \frac{d(ln \nu)}{dx} = \text{axial deformation gradient}$

Melt fracture

Extrusion velocity increases

smooth flow

die swell

shark skin

Melt fracture

Large die swell ratios can be considered in industrial practice as a warning against the danger of coming melt fracture!
Melt fracture

Capillary waves initiated by elastic turbulences

- Nozzle geometry: (a) roughness inside the nozzle channel (b) length of the capillary and (c) the shape of the inlet

- Amplitude grows with increasing surface tension and decreasing viscosity and at constant shear when temperature is gradually decreased or with increasing shear rate.

- Appears as curl or rotation of the thread at the exit of the nozzle.

Onset of melt fracture at Weissenberg number, \( Wi = 5-8 \)

\[
Wi = \dot{\gamma} \cdot \lambda
\]

\( \lambda = \text{relaxation time} \)

\( \dot{\gamma} = \text{shear rate} \)
Telescopic fracture (typical in wet spinning)

Breach occurs at the entry of the coagulation bath:
**Liquid core and coagulated external (skin) layers.**

Skin absorbs traction forces until it breaks and a telescopic-like displacement of the solid fiber skin occurs.
Overall spinnability and productivity

Spinnability depends on the product of viscosity $\eta$ and spinning velocity $v$:

At low rates and low viscosity capillary fracture dominates triggered by surface tension, viscosity and extrusion velocity.

At high $\eta \cdot v$ when stored energy is exceeded (relaxation time too high), threads break by cohesive fracture.

Dopes must have high Deborah numbers, $De = \frac{t_c}{t_p}$

$t_c$ stress relaxation time
$t_p$ time scale of observation
Fiber thickness (titer) and orientation development
Effect of Draw ratio on Fibre Diameter

Fibre diameter is strongly related with draw ratio

The relationship of fibre diameter and draw ratio indicating that lyocell process is mass conversation: \( d_{\text{fibre}} = d_{\text{spinneret}} \cdot DR^{-0.5} \)


S. J. Eichhorn, K. Kong. 229th ACS National meeting March 13 – 17, 2005
Adjustment of Linear Density (Titer)

Number of holes: $n \quad [\text{ ]} \quad 1000$
Diameter of holes: $D \quad [\text{mm}] \quad 85$
Dope density: $ho \quad [\text{kg/mL}] \quad 1.2$
Cellulose content: $C \quad [\text{wt\%}] \quad 12$
Draw ratio: $DR \quad [\text{ ]} \quad 8$
Extrusion velocity: $v_0 \quad [\text{mL/min}] \quad 25$
$v_{\text{ex}} \quad [\text{m/min}] \quad 4.4$
Takeup velocity: $v_{\text{tu}} \quad [\text{m/min}] \quad 35.2$
Titer $T \quad [\text{dtex}] \quad 1.0$

$$v_{\text{ex}} = \frac{v_0}{(n \cdot (D/2 \cdot 10^{-4})^2 \pi) \cdot 10^{-2}}$$

$$T = \left( (D/2) \cdot DR^{-0.5} \cdot 10^{-6} \right)^2 \cdot \pi \cdot \rho \cdot C \cdot 10^8$$

The measured titer is higher than the calculated one:

Fibre shrinkage and equilibrium humidity (11% moisture) have to be taken into account by a correction factor (about 1.2)
Morphology, Orientation of Fiber

15% cellulose, DPv 600; Draw ratio = 10.4

Fiber aftertreatment
Fibre Aftertreatment

- Cutting machine
- CS₂ condensation
- CS₂ Expel tray
- Acid water
- EBₐ Desulfurization
- EBₐ bleaching
- EBₐ Soft finish
- Wet opener
- Pressing
Injector draws the cable into a chute where rotating knifes cut the filaments to staple:

**Staple Length: 38 - 40 mm**
Dryer

**Staple fibre**
- Filter band dryer, vacuum drum dryer

**Filaments**
- Cylinder dryer, vacuum dryer

Vacuum dryer
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 Stapel fibres receive a spontaneous crimp due to the skin-core structure
Deformation crimping

- **Stuffer box crimping** (thermoplastic deformation):
- **Take-up over hot edges** (Agilon Verf.)
- **Gear crimping**
- **Texturing process**

![Diagram showing the crimping process with labels for pressure roller, stuffer box flap, dampening cushion, conveyor rollers, and cooling channel.]

*Lyocell (Cocell) Gear crimping*
Fiber characterization
Terms and Definitions

**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

**Diameter of a 1.3 dtex fibre?**

\[
D \ [\mu m] = 11.3 \sqrt[0.5]{\frac{c_{dtex}}{\rho}}
\]

\[
A = \frac{\pi D^2}{4}
\]

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

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

\[
\left( \frac{0.13 \cdot 1 \cdot 10^{-6}}{1000 \cdot \pi \cdot 1.53 \ g} \right)^{0.5} \cdot 2 = 10.5 \cdot 10^{-6} m = 10.5 \ \mu m
\]
Fiber Cross-Sections, Cryo Fractures

CV

CMD

CLY

Magn. *1070  *6000  *20000
Tensile properties

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

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

\[
\approx 1.5 \cdot 10^7 N = 15 MPa = 0.015 GPa
\]
**Structure and Mechanical Properties**

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Mechanical properties</th>
<th>Structural properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\sigma_C$</td>
<td>$\varepsilon_C$</td>
</tr>
<tr>
<td>CV</td>
<td>0.38</td>
<td>20</td>
</tr>
<tr>
<td>CMD</td>
<td>0.51</td>
<td>13</td>
</tr>
<tr>
<td>CLY-NMNO</td>
<td>0.60</td>
<td>15</td>
</tr>
<tr>
<td>CLY-IL</td>
<td>0.85</td>
<td>10</td>
</tr>
<tr>
<td>Bocell</td>
<td>1.30</td>
<td>7</td>
</tr>
</tbody>
</table>

$F_w$ = 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)
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

https://mediadb.lenzing.com/pindownload/pindownload.do?jsessionid=B7E0B3E7C2021492BA5EDB8AA91143EE
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 OsO₄ staining in aqueous solution:
Fibrillation of Lyocell Fibres
Cross-linking reduces Fibrillation

**Lyocell**

**Cross-linking**

**Lyocell LF**

**Triacrylamido-trihydrotriazin** (Lenzing, A100).

**2,4-Dichloro-6-hydroxy-1,3,5-triazin** (Lenzing, Lyocell LF).
Structure-Property-Relationship
Structure vs. E-Modulus
Lyocell Fiber – NanoMultifilament

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

Fibre, diameter
8 - 30 µm

Macro-fibril (0.5 - 1µm), made up of micro-fibrils (10 - 100 nm)

Skin, app. 100 nm dry, can swell widely in H₂O

Microfibrils (D & A), non swelling

H. Firgo et al., Dornbirn 2003
Mechanical vs. structural properties

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

- $E_{\text{max}}$: ~ 60 GPa (IC-F: 35)
- $\sigma_{\text{max}}$: ~ 2.1 GPa (IC-F: 0.9)

Sixta, H. et al. NPPRJ, 30(1), 2015, 43-57
Ultimate strength of cellulose fibers

Dynamic modulus depends only on the extension: $E$ as a function ($\varepsilon$) for well-oriented regenerated cellulose fibers: second loading cycle.

$E_{\text{max}}$: ~ 60 GPa (IC-F: 35)
$\sigma_{\text{max}}$: ~ 1.8 GPa (IC-F: 0.9)

Single-Phase Structure

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

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

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