Theory and Practice of Wet Spinning of Cellulose Solutions

Doctoral Course, Part 6

Aalto University
School of Chemical
Engineering

Herbert Sixta

March 10 – 11, 2022

Outline

1. Introduction, history
2. Pulps as raw materials
3. Cellulose solvents
4. Certain 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 -

6

Coagulation and regeneration of cellulose

- *Fundamentals of wet spinning*
  - *Viscose*
  - *Other aqueous alkaline cellulose solutions*

Annex

- *Air-gap spinning*

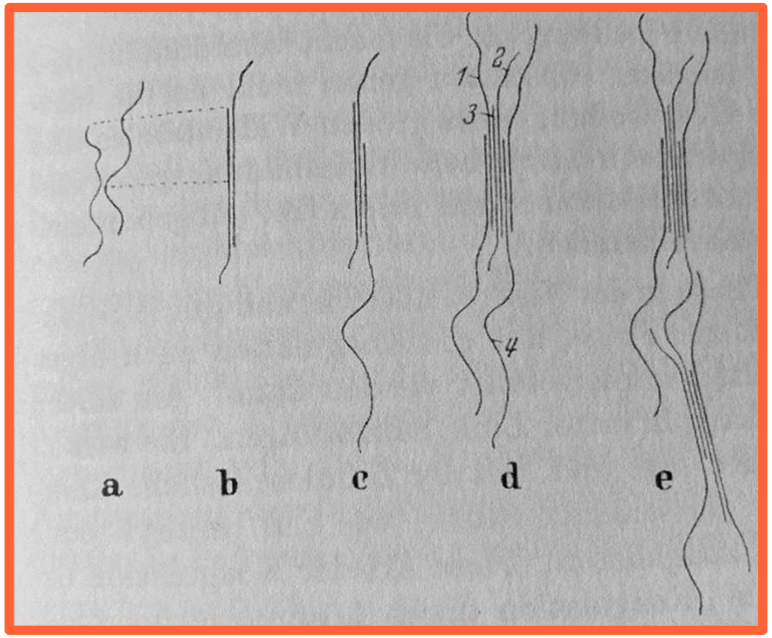
Introduction to the concepts of coagulation and other phenomena in aqueous alkaline systems as a precursor to cellulose regeneration

Coagulation (I)

VISCOSE AN ANIONIC COLLOID ELECTROLYTE with constitutively bound ionogenic groups (xanthogenate) and non-ionogenic water-affinity OH groups.

Coagulation is solidification of the colloidal disperse system into larger aggregates: Initially crystallized units are formed, which gradually increase in size

Coagulation is predominantly carried out by desolvating agents: Salt solution→
SALTING OUT EFFECT



a) Bundled single molecules
b) Mutual interaction
c) Capture of another molecules
d) Formed fringe micelle
e) Captured fringe micelle

Götze (1967)

Coagulation (II)

Water-binding forces of the added electrolyte ions overcome the water-binding forces of the disperse phase: Solvate water withdrawn, initiating solidification

IONOTROPIC GELATION: Exchange of Na(I) by Zn(II) forming $\mathbf{Zn(S(CS)OCell)_2}$ leads to a gradual solidification of the viscose sol.

Coagulation-promoting effect follows the Hofmeister's series:

$$OAc > Cl^- > NO_3^- > ClO_3^- > J^- > SCN^-$$

$$Li^+ > Na^+ > NH_4^+$$

Increasing ion radius, the coagulation effect weakens

Tendency to coagulation increases:

1. Higher gamma value
2. Higher temperature
3. Higher DP
4. Increasing PDI

Coagulation does not mean phase separation!
The coagulum remains largely solvated

Götze (1967)

The Gelation

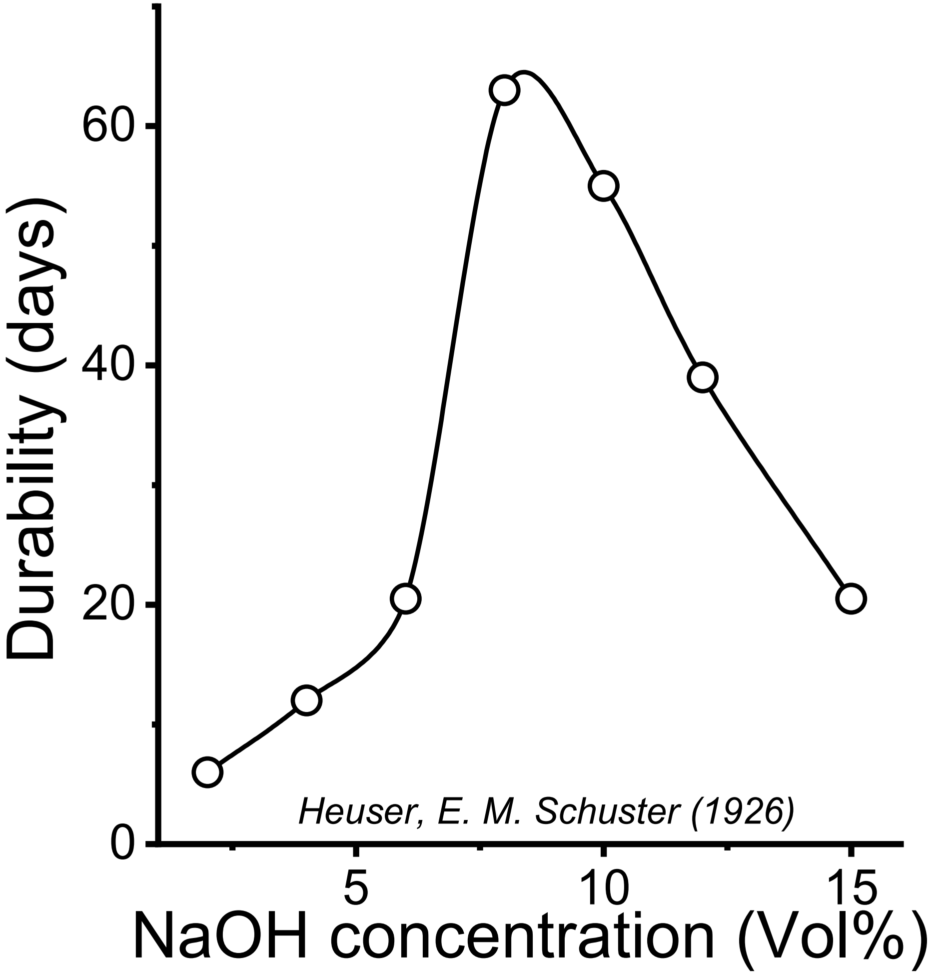
When viscose is stored, the sol gradually solidifies, it gels. Gelation is a precursor to coagulation

1. Formation of adhesion points between neighboring molecules due to Brownian motion.
2. Progressive dexanthogenation leading to increased formation of H-bonds between neighbouring molecules.

Gelation can be delayed:

- Higher gamma value
- NaOH conc between 8 and 10 vol%

Manegold (1941); Ostwald, (1928, 1937)



Heuser, E. M. Schuster (1926)

The Syneresis

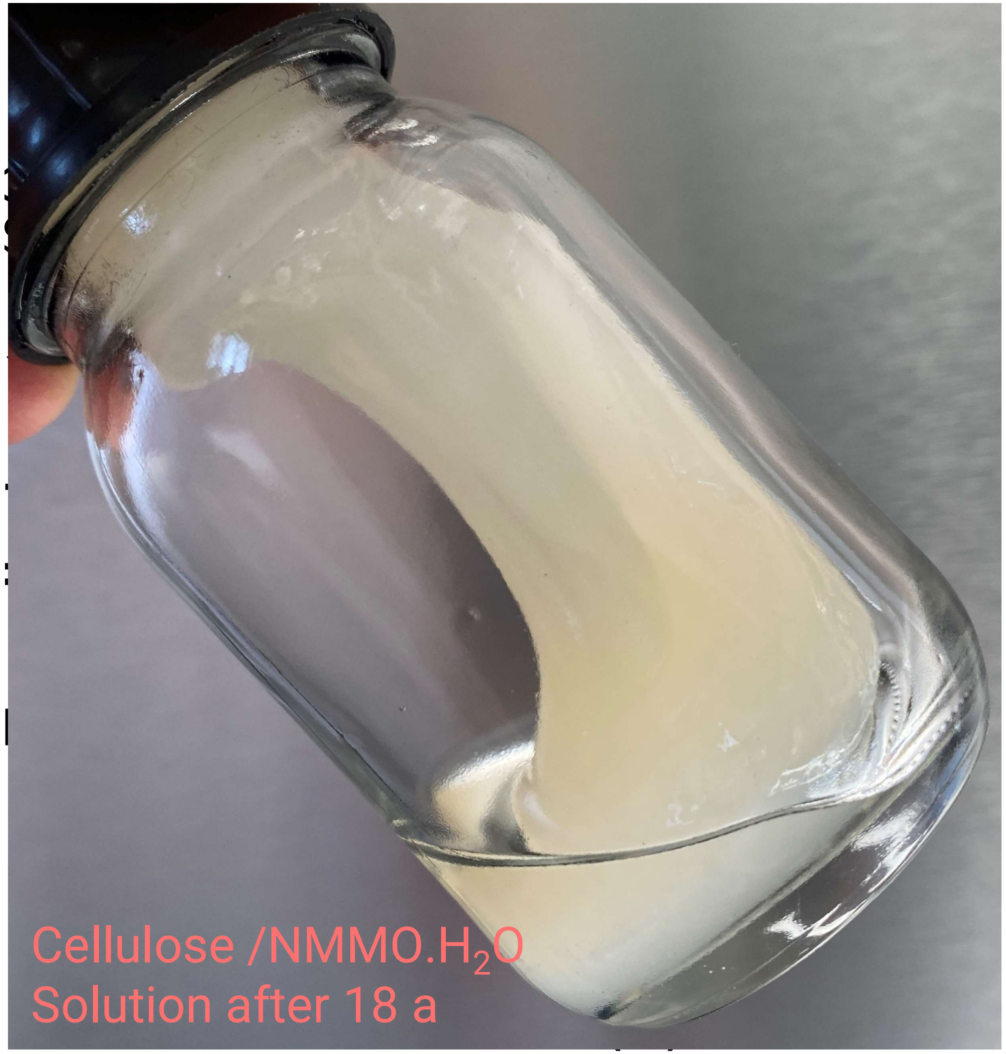
Viscose gel shows the phenomenon of syneresis after a longer period of time

Water is split off from the solvated cellulose xanthate.
The shrinkage increases the gel strength.
Emerging liquid contains considerable amounts of salts.

Examples from Food industry (cheese production):

Whey that escapes during the processing of the curd and is produced by the aggregation and contraction of the milk proteins

Götze (1967))



Cellulose /NMMO.H_2O
Solution after 18 a

Fundamentals of Viscose Spinning

Spinning baths: General

Task: Coagulation and saponification of $Na^{+}S^{-}(CS)\,OCell$

Saponification, regeneration to be delayed compared to coagulation to achieve good fibre properties.

Coagulants: Salts (Na_2SO_4, $ZnSO_4$)

Xanthate dehydration causes particle ordering

In gel zones:

$$Na_2CS_3 + NaHSO_4 \rightarrow H_2CS_3 + 2Na_2SO_4$$

Saponifiers: Acids (H_2SO_4)

via cellulose xanthogenic acid $at\ pH \leq 2$ $Cell - O(CS)SH$

Secondary inorganic reactions occur faster than xanthate decomposition

Götze (1967)

Spinning baths: Müller baths

Müller Bath I

$[H_2SO_4] > [Na_2SO_4] \rightarrow$ Rapid saponification, brittle fibers

Müller Bath II

$[Na_2SO_4] > [H_2SO_4]$ **leads to delayed saponification**

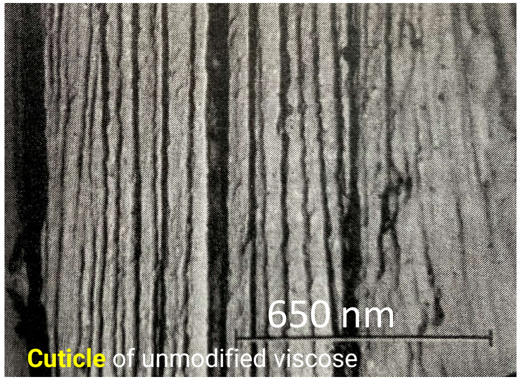
Moore (1935) and Poznanski (1938)
Klare and Gröbe (1960, 1961)
* Cumberbirch (1959, 1960, 1961)

Zinc containing baths since 1935

Conversion into $Zn(S(CS)OCell)_2$ only in a very thin skin, the **cuticle*** forming around the gel filament. **Cuticle** slows down the diffusion process

Gel skin around the emerging viscose, enclosing the liquid Sol and preventing Viscose to creep over the spinneret surface

Gröbe et al (1962)



Cuticle of unmodified viscose

Cuticle = Gel skin consists of coagulated, undecomposed xanthate

Viscose with **high DP**, high **γ value** **require less salt.**
At lower retention time, higher acid concentration in spin bath is needed

Multi-bath spinning baths

Bath A

Option 1: Xanthate largely saponified, subsequent Bath B for hot water stretching

Nowadays standard concept for regular viscose fiber production (CV)

Option 2: Viscose only coagulated, saponification and stretching in Bath B→ High tenacity

Modified viscose processes, especially for supercord fibres, carpet-type fibres, highly crimped fibres and HWM fibres, based on option 2

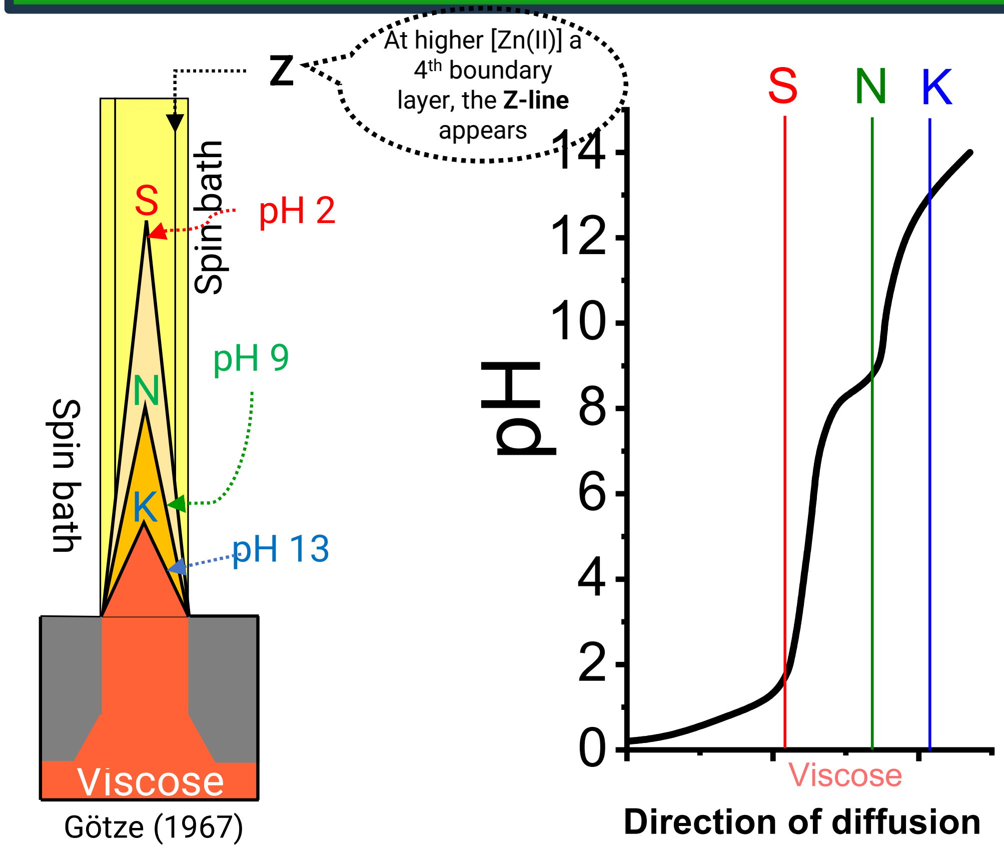
Bath A: little H_2SO_4, Na_2SO_4, very high $ZnSO_4$ of up to 100 g/l

Bath B: Diluted H_2SO_4 bath at >90°C for entire dexanthation, regeneration

Götze (1967)

General diffusion processes

Formation of a gel membrane, Cuticle, *via* coagulation in the boundary layer, viscose/spin bath, is a prerequisite for formation of a filament



Götze (1967)

Boundary line between **developing Gel and the Sol→ pH~13 (K)**

Neutralization boundary line at pH 9 when free [OH^-] is neutralized (N)

At the acid boundary line at pH 2 free xanthogenic acid is present (S)

With an increase in [Na_2SO_4], diffusion slows down due to the densification of the gel by dehydration

Diffusion in the presence of $ZnSO_4$?

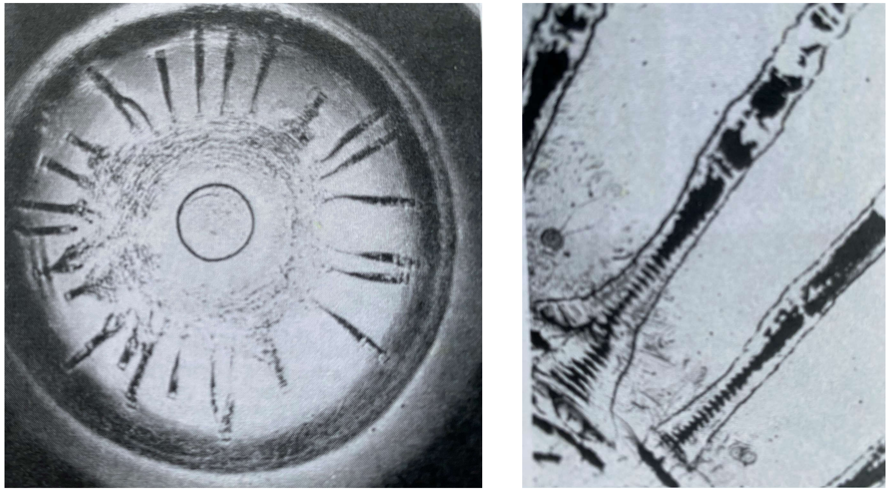
Zn^{2+} ions can penetrate viscose sol only to a certain depth, explaining a stationary zinc-cellulose-xanthate interface (4th BL)

Zn^{2+} ions react with the $Na^{+}S^{-}(CS)OCell$ to form a gel, denoted as ionotropic gelation resulting in a layer formation

The inorganic ions react with the Zn^{2+} flowing towards them, thus forming insoluble zinc salts which clog capillaries

Diffusing H^+ ions generate S-containing inorganic side products in the sol, which seeks to escape into the spin bath

The characteristic gel structure formed by Zn(II) ions strongly delays H^+ diffusion and thus explains the general delay in xanthate regeneration



Ionotropic gel formation by centrifugal diffusion of Zn(II) into a cellulose xanthate solution-> Radial tangential gel structures

Gröbe et al (1963)

Vermaas, D. (1962); Thiele, H.; et al. (1952)

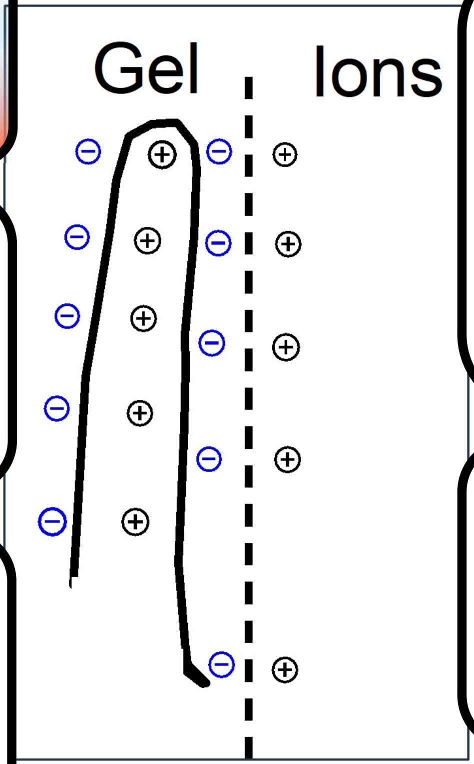
Skin core effect

Fibres with pronounced skin core differentiation are all fibres spun in salt-containing acid baths

Fibre periphery & interior cannot coagulate simultaneously: Stretching induces chain orientation only in coagulated zone, not in liquid core

Skin thickness increases:

- **with increasing DP, Cell-conc, DS, Salt-conc, esp., $ZnSO_4$**
- **with decreasing °H & Temperature**



Cellulose in skin higher oriented than in the core because of a pre-orientation: When a polyanion approaches the skin zone, counterions diffuse through and form a diffusion potential leading to an orientation of cellulose molecules parallel to the membrane

ALL-SKIN FIBERS:

Coagulate fibers spun in pure salt baths, High-DP Cellulose in very dilute acid (Polynosic) and very concentrated acid baths (Lilienfeld)

HIGHER STRENGTH SKIN:

Presence of small and uniform crystallites (10.4 nm) than in core (20.6 nm). Cellulose molecules pass through more crystallites than in case of long crystallites

Schramek & Zehmisch (1938)
Morehead und Sisson (1945)
Thiele, H.; et al. (1952)
P.H. Hermans (1951)

Gel swelling

Primary swelling is defined as the swelling of the not yet dried gel filament from the spin bath

It affects the spinning capacity and the fiber properties: the larger, the **lower the capacity and the fiber tenacity/toughness**

Primary swelling decreases:

1. **Increasing Cell conc**
2. **Increasing NaOH conc**
3. **Increasing γ value**
4. **Higher salt conc,** *esp.* **$ZnSO_4$**
5. **Decreasing acid**

Shrinkage

Shrinkage is a consequence of liquid discharge from the forming filament reducing its volume

1. Pre-shrinkage in the spin bath
2. Post-shrinkage during fiber drying

Outer skin acts as a membrane (osmotic effect): Dehydration and gradual solidification

Shrinkage increases with salt conc., esp. **with higher value cations**

Longitudinal and **transverse shrinkage.** The latter dominates since filament is under tension

Bath shrinkage (7-8%):

must be taken into account when calculating the **linear density**, for example by enhancing the take-off speed $\left(T = \frac{Q \cdot \rho \cdot c \cdot f \cdot \boldsymbol{h}}{v_{tup} \cdot n} = \frac{Q \cdot \rho \cdot c \cdot 1.08\ \mathbf{1.11}}{v_{tup} \cdot n}\right)$

Cross-sectional shape

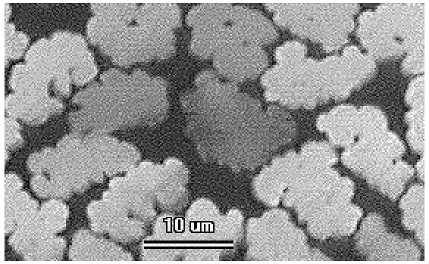
With increasing amounts of salt, fiber cross-sections deviate from circular shape, forming lobed shapes

All parameters accelerating the coagulation of the viscose lead to rounder cross-sections

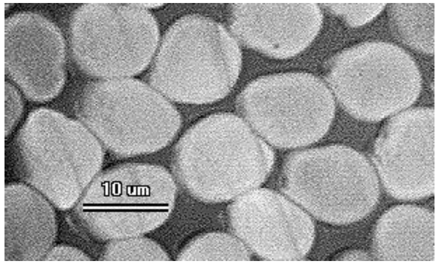
With the same viscose, increasing temperature and higher °H leads to round cross-sections

Slow coagulation leads to folded cross-sections

Centripetal shrinkage of the resulting gel due to osmotic processes



Regular Viscose



Polynosic

Fiber drawing vs Fiber stretching

$$\boldsymbol{Fiber\ drawing} = \frac{v_{take-up}\ 1^{st} godet\ (m/min)}{v_{extrusion}\ (m/min)}$$

$$\boldsymbol{Stretch\ ratio} = \frac{v_{take-up}\ 2^{nd} godet\ (m/min)}{v_{1^{st} godet}\ (m/min)}$$

Fiber draw largely **undefined** since stretching of liquid core does not lead to orientation (X-ray)

Stretching after a draw of ~ 0.6 optimum. Under these conditions, coagulation may be completed.

Upper limit for the draw for good spinning at ~ **2.2-2.5**.

In the presence of Zn(II), formation of large crystals avoided; limited diffusion allows higher draw(!)

Optimal if a **coherent network** of small ordered structures has formed in the filament **before stretching**, but the alignment of the crystallites has not yet been achieved by the stretching process.

Stretching of plasticised fibers

HOT WATER STRETCHING

Stretching of coagulated fibres up to 50% in water at T > 90°C

Coagulated and partially saponified cellulose xanthate **swells strongly** in hot water and becomes very plastic

Example:

Viscose

7% Cellulose , 7% NaOH, 38% CS_2 charge spun into a

BATH A: 100 g/l H_2SO_4, 230 g/l Na_2SO_4 and 8 g/l $ZnSO_4$

BATH B: plasticizing bath at 92-95°C with limited carry-over from bath A results in a strength increase from

σ 27 → 38 cN/tex

ε 20 → 17%

U_T 40 → 48 MJ/m^3

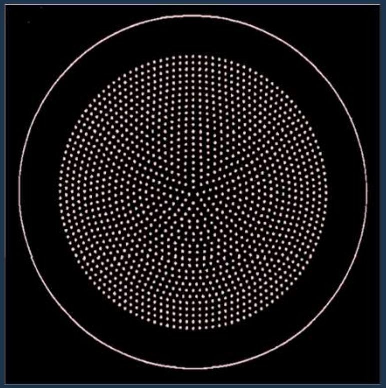
Coagulated and crystallites acquire a **greater mobility due to the swelling agent water** and the high temperature, so that they can slide past each other

Rose, Entwistle and Preston (1945)

Viscose spinning process

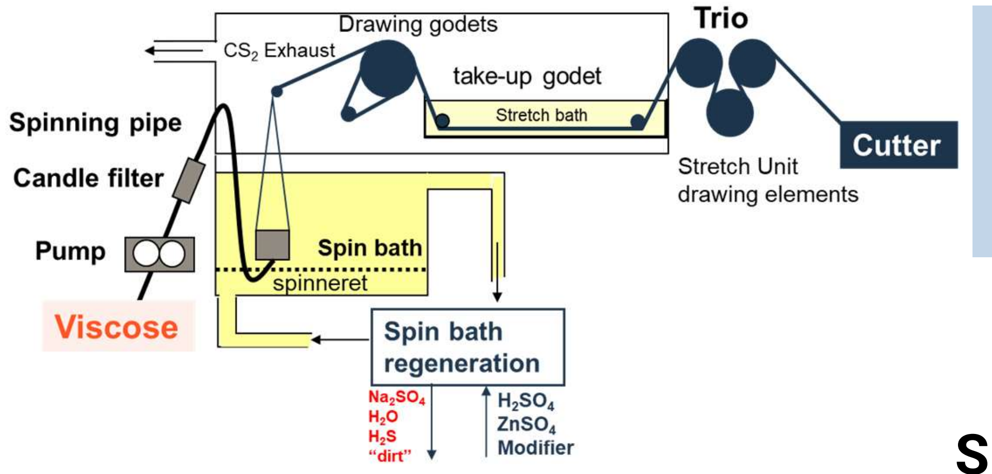
VISCOSE

- **Wet Spinning**



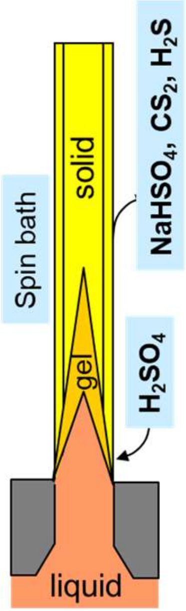
Spinneret:
Au, Pt, Rh, Ir
L:D = 1-3
Conical inlet
Holes, profiled spinnerets

Spinning scheme



H_2SO_4	~ 2,0-2,2 mol/L
Na_2SO_4	~ 2.5-2.7 mol/L
$ZnSO_4$	~ 0.1-0.2 mol/L
Temp	~ 50°C

Structure Formation



Coagulation

- Xanthate gel dispersed by Zn precipitates
- Cuticle formation controlling diffusion
- Syneresis, deswelling, crystallization starts

Regeneration

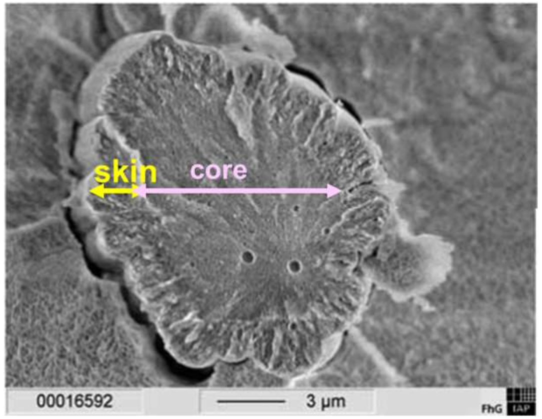
- Saponifcation, Orientation, Crystallization

Stretch ratio

- $\boldsymbol{Stretch,\%} = \left(\frac{\boldsymbol{take\!-\!up}}{\boldsymbol{take\!-\!off\ 1^{st} galette}}\right) \cdot \mathbf{100}$

Regular viscose	~ 60%
Modal	~ 100%

Skin core cross-s.



Skin: higher orientation, smaller crystals

Core: less orientated (diffusion retarded)

Viscose Spinning Process

Spinning

↓

Stretching

↓

Cutting

↓

Washing

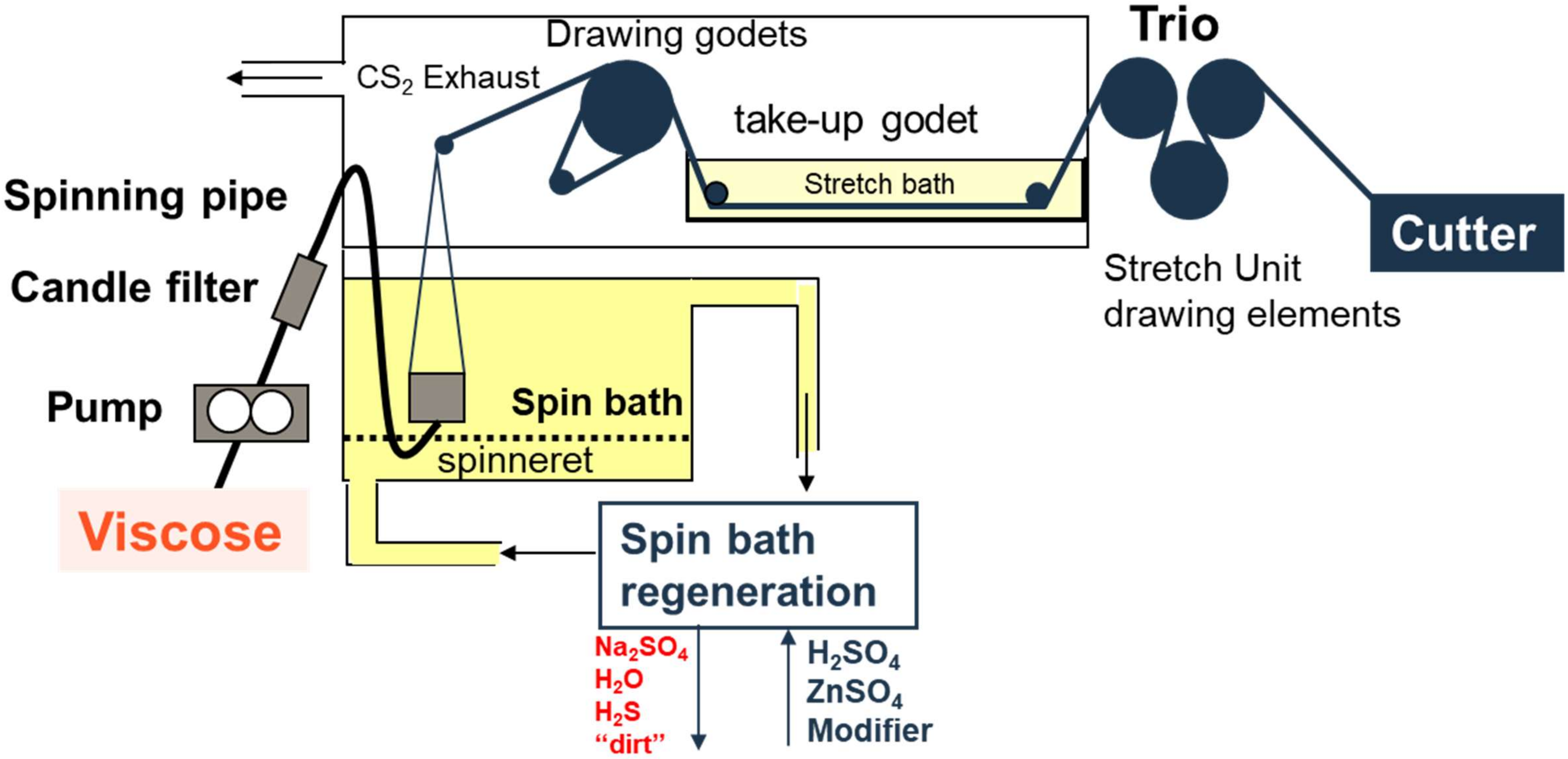
↓

Drying

Advantages of wet spinning route

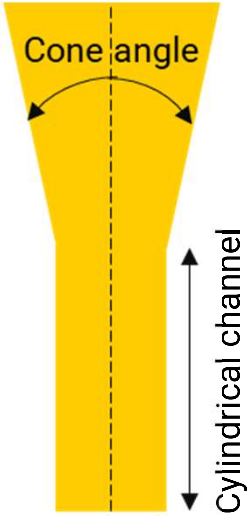
- Easy incorporation of additives
- Low viscosity-dope
- Production of profiles fibers
- Natural stretch

Viscose - Wet Spinning Process



Spinneret design

Only corrosive resistant metals (Au, Pt, Rh, Ir alloys)



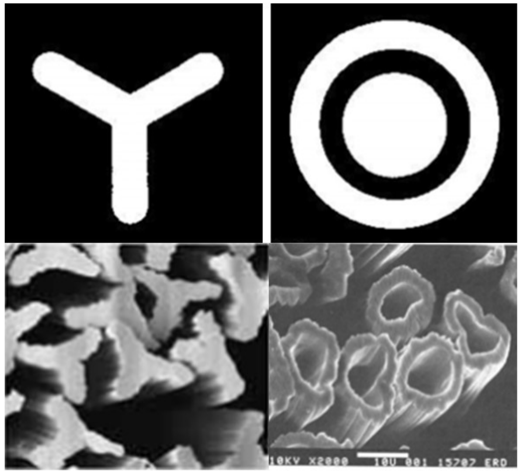
Staple fibers:

- Spinneret cluster plate

Filament yarns:

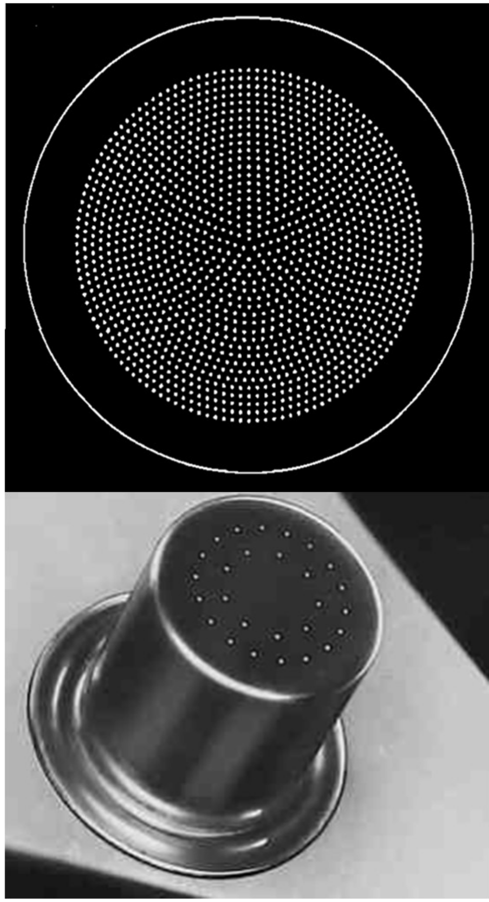
- Individual spinnerets
- Conical inlet: length/angle entry cone
- Hole length:diameter = 1-3

Profiled fibers



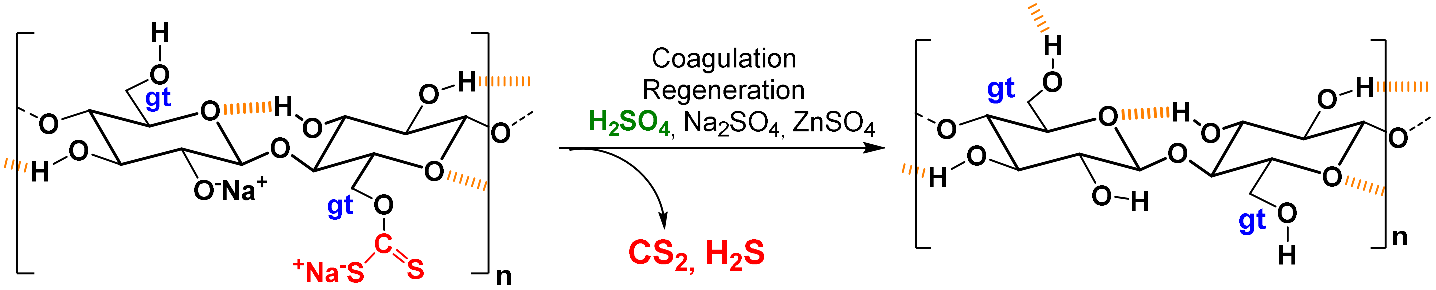
Spinning stability depends on:

- Undisturbed viscose flow free of inhomogeneity
- Undisturbed spinbath flow
- Distance to the next spinneret hole



H. Harms

Spinning chemistry



cellulose xanthate

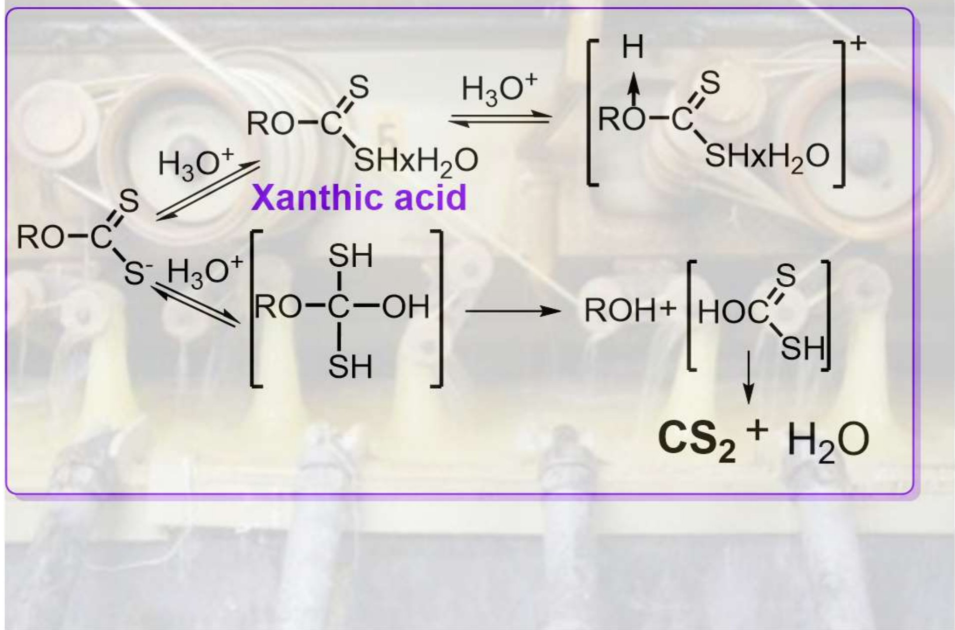
cellulose-II

Spin bath composition:

H_2SO_4	~ 2,0-2,2	mol/L
Na_2SO_4	~ 2.5-2.7	mol/L
$ZnSO_4$	~0.1-0.2	mol/L

Temperature ~50°C

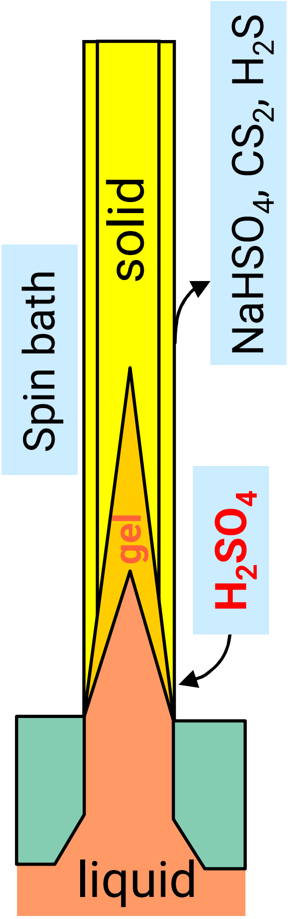
Xanthate decomposition



Fiber Formation

- Diffusion of protons and Zn^{2+} into the liquid
- Generation of a highly swollen gel by coagulation
- Deswelling and solidification of the fiber by diffusion (syneresis, osmotic effects)

Phenomena during viscose spinning



Primary Structure Formation

- Coagulation

Secondary Structure Formation

- Dehydratation, densification through the effect of Na_2SO_4

Regeneration

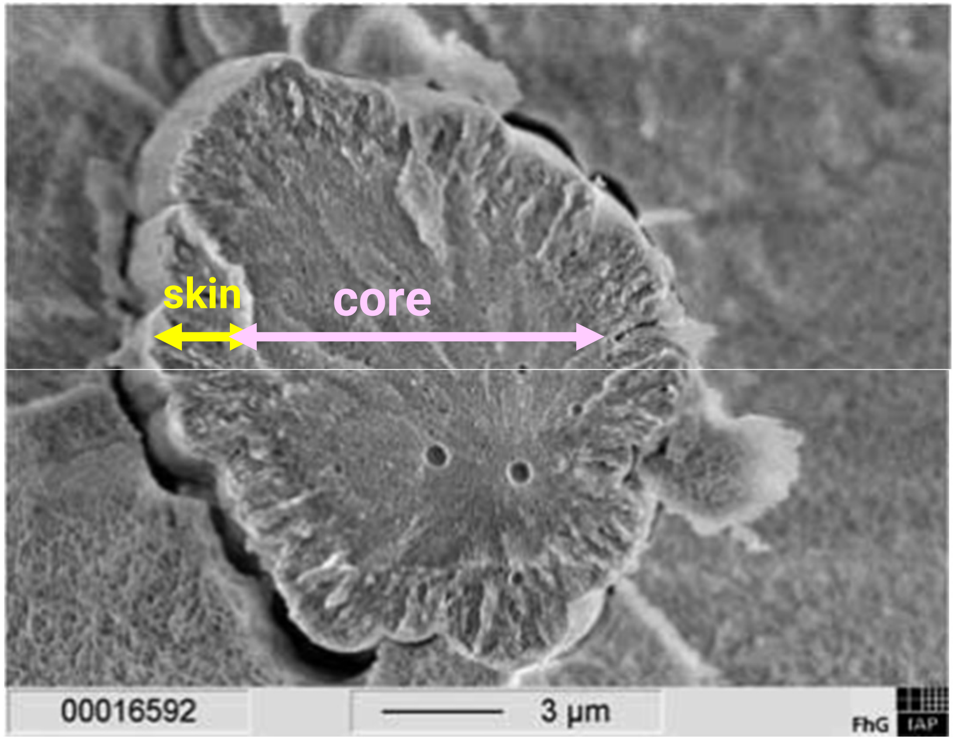
- Orientation, Crystallization

Stretch ratio

$$\boldsymbol{Stretch, \% = \left(\frac{take-up}{take-off\ \ 1^{st} galette} - 1\right) \cdot 100}$$

- Regular viscose ~ 60%
- Modal ~ 100%

Skin-Core Structure

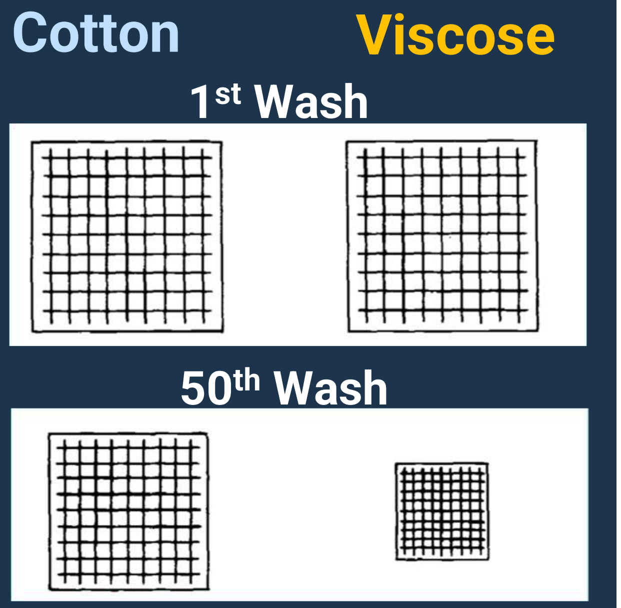


- Fast freezing of a solid outer layer
- Skin shows higher orientation; smaller sized crystallites
- Core less oriented (diffusion retarded)
- Skin thickness can be increased by additives which retard coagulation (Modal, Supercord)

Modified Viscose Fibers

Modified Viscose Fibers

- MODAL (CMD)



Regular Viscose is shrinking

Heuer Kurt (1966), Symposium Helsinki

Regular viscose

- low wet tenacity
- Poor dimension stability
- progressive shrinking

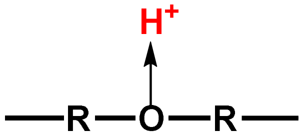
Götze (1967), 627 pp
Lund, G.V.; Waters, W.T. Text. Res. J., 1959, 29, 950

Chemical Modifiers (Cox)

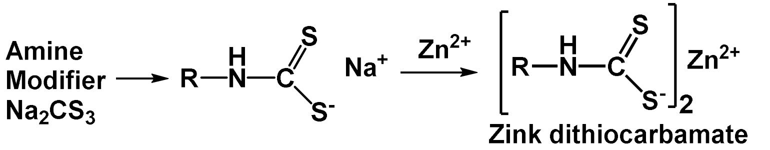
- Amines, PEGs
- Ethoxylated phenols
- Polyoxyalkylenes,..

Cox, N.L. US Patent 2,535,045 (1950)

Combined action of Zn salt & Modifier: controlling ion diffusion through a cuticle; disturbance of crystal growth



protonation of ether-O



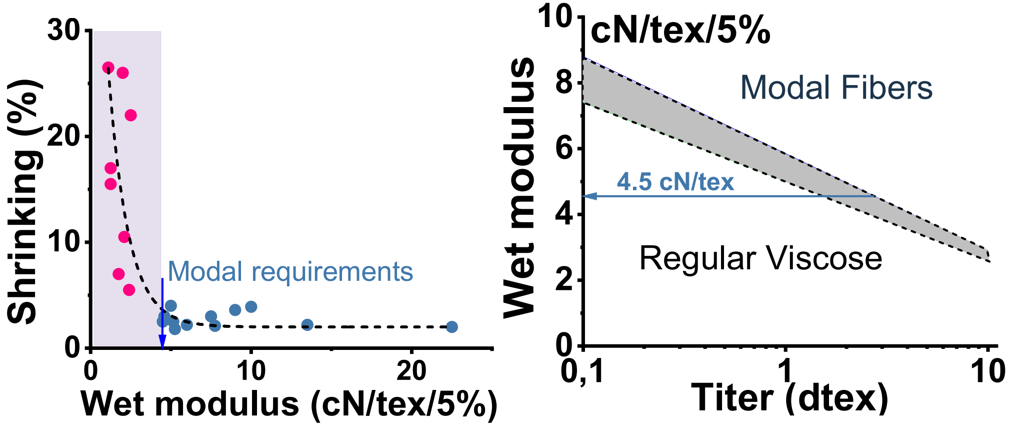
Proton diffusion barrier

Conditions

- **High purity, high DP pulp**
- **6% Cellulose** (viscose)
- **6% NaOH** (viscose)
- **36-40% CS_2** on cellulose
- **2-4% Modifier** on cellulose
- **50 g $ZnSO_4$/L** (spin bath)
- **Low acid & salt** (spin bath)
- **Hot acid stretch bath >90°C**
- **100 % stretch**

Lenz. Ber. (1982), 53, 24-34

Modal™ fiber definition



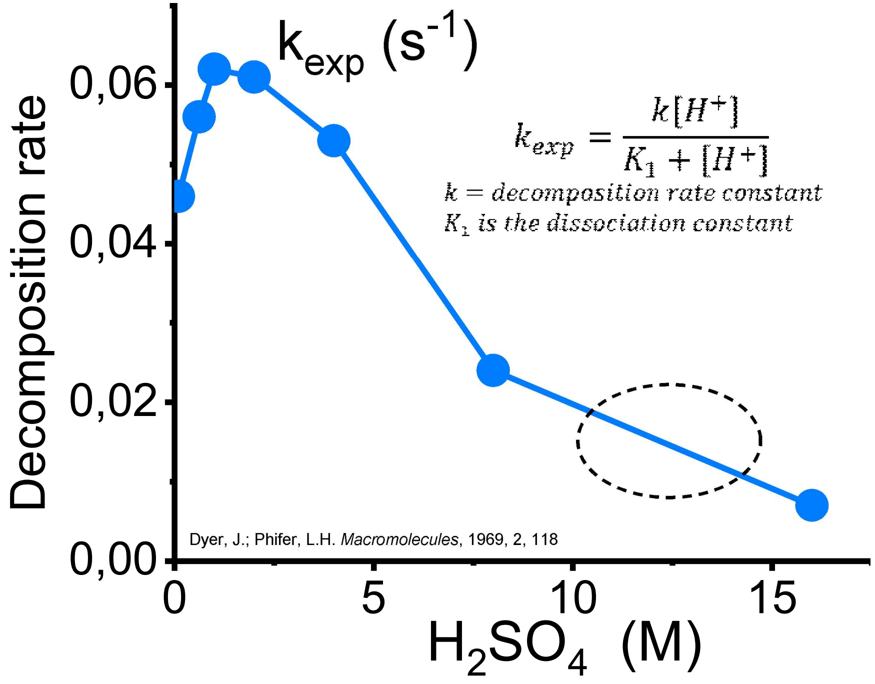
Daul, G.C.; Chem. Tech., 83 (1981)

Modified Viscose Fibers

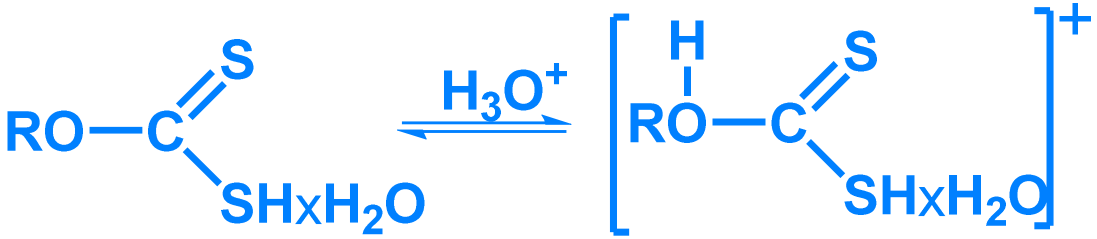
1. *Lilienfeld* Fiber
2. **Modal fibers (high-wet modulus)**
3. Polynosic fibers
4. **Supercord fibers**

Lilienfeld Fibers

- **High DP-pulp (850)**
- **Alkali ratio > 1**
- **CS_2 charge > 40% on cellulose**
- **H_2SO_4 conc in spin-bath > 55%**



Dyer, J.; Phifer, L.H. *Macromolecules*, 1969, 2, 118



$$k_{exp} = \frac{k[H^+]}{K_1 + [H^+]}$$

k = decomposition rate constant

K_1 is the dissociation constant

– **Ten$_{cond}$ ~ 60 cN/tex; Ten$_{wet}$ ~ 40 cN/tex**

– Shortly on market as **BX fiber**

– Fiber too brittle for textile applications

Lilienfeld, L. (1928), US 1683199.

High-tenacity viscose fibers

Modifiers in viscose to delay regeneration

- Zn salts
- Organic modifiers
- Mixed modifiers
- Formaldehyde

Plasticizing coagulation bath

- Hot water or steam
- Hot diluted sulfuric acid solution

Modified viscose fibers

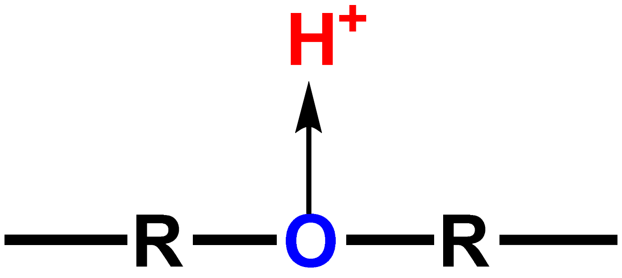
Regular viscose fibers had low wet tenacity,
No dimension stability & suffer **progressive shrinking**!

Cox (1950): introduced **Chemical modifiers**
(PEGs, amines, ethoxylated phenols, polyoxyalkylenes, mixtures)

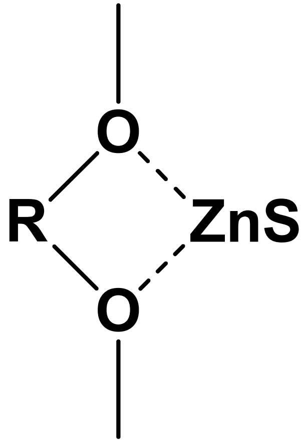
Combined action of Zn salt & Modifier: controlling ion diffusion through a cuticle; disturbance of crystal growth

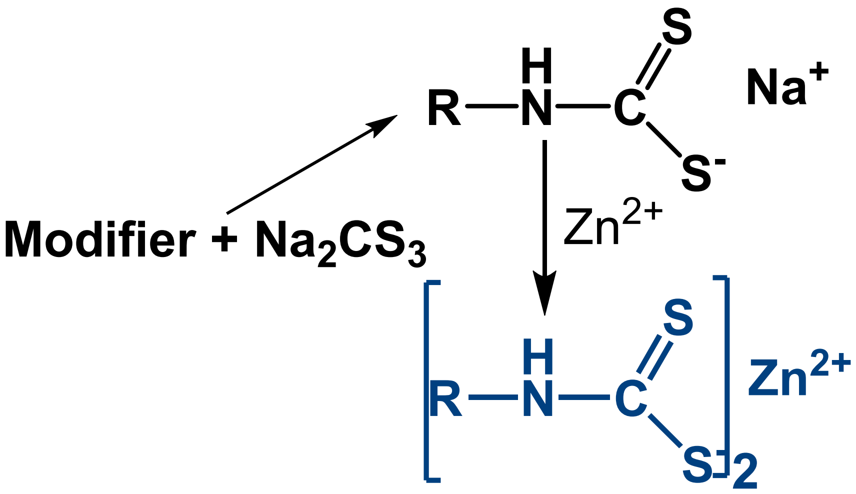
Cox, N.L. US Patent 2,535,045 (1950) *Götze (1967), 627 pp* *Lund, G.V.; Waters, W.T. Text. Res. J., 1959, 29, 950*

Effect of Modifiers



protonation of ether-O





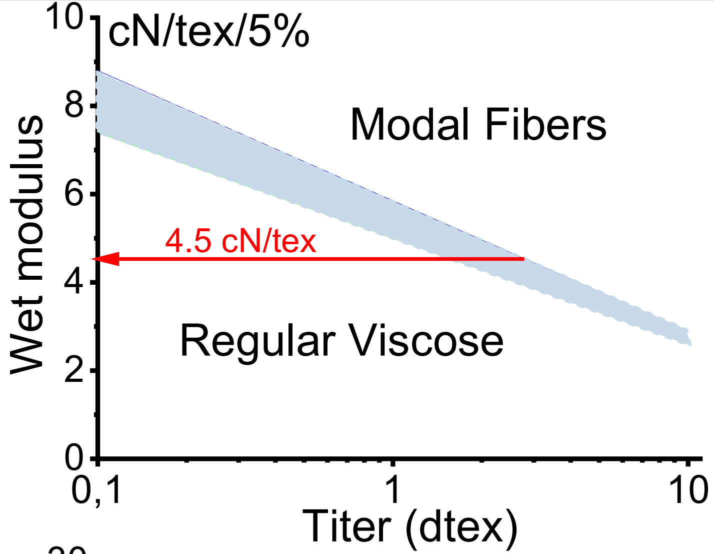
Zink sulfothiocarbaminate
=proton diffusion barrier

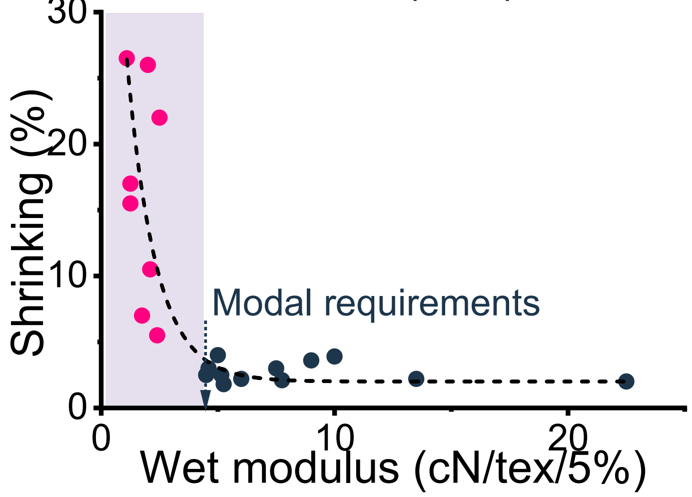
Cox, N.L. US Patent 2,535,045 (1950) *Götze (1967), 627 pp* *Lund, G.V.; Waters, W.T. Text. Res. J., 1959, 29, 950*

Modal® Fibers

- High tenacity and elongation
- High dimension stability
- Higher wet tenacity
- Good mercerizability

- Wet modulus ≥ 4.5 cN/tex/5%
- Reduced shrinking
- Low fibrillation
- Short crystallites





Treiber, E. Lenz Ber, 53, (1982), 24-34
Puchegger, Ernst. Lenz Ber. 52, (1982), 13-19

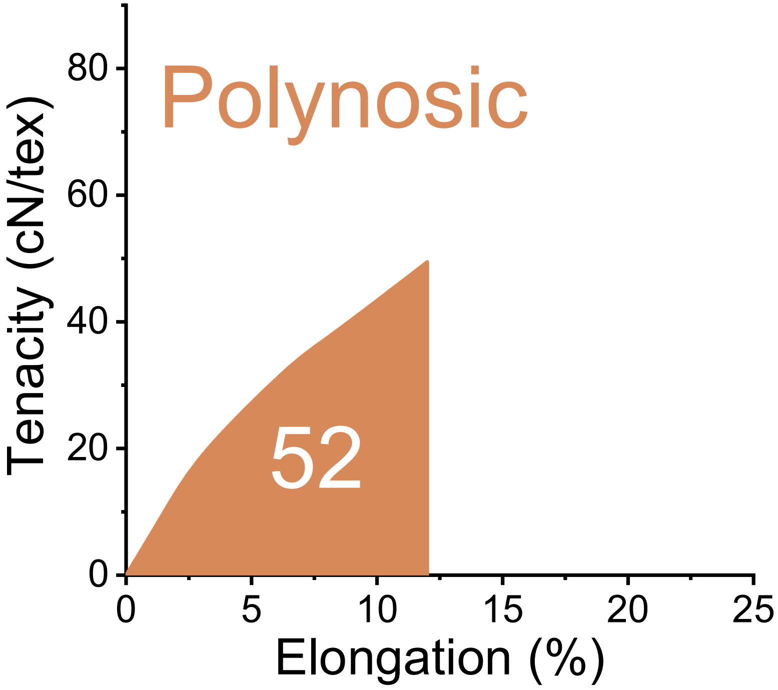
Polynosic Fibers

Tachikawa Patent (1952):

- Nonmodified viscose with a high DP-pulp
- High degree of xanthation
- Spin-bath of low acidity (10 g/L) and salt, low T (< 35°C)
- High stretches up to 300%

- **σ_{cond}: 35-55 cN/tex; ε_{cond}: 6-10%**
- **σ_{wet}: 27-40 cN/tex; ε_{wet}: 7-12%**
- Wide recognition, esp. in France
- **However, too brittle! Fibrillating**
- Meanwhile, completely replaced by Modal®

Tachikawa, S. US Patent 2,592,355 (1952)

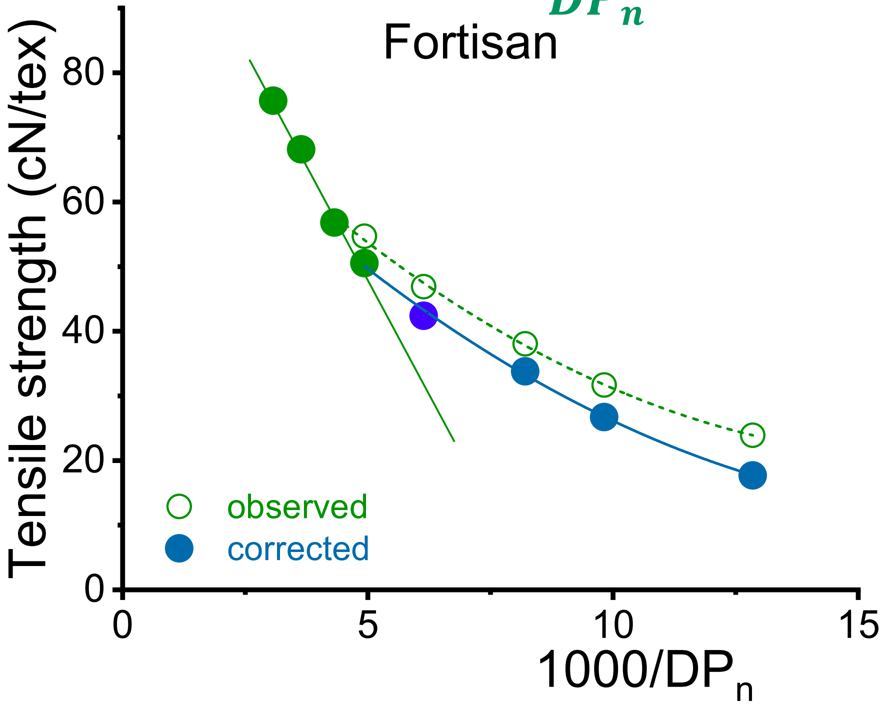


Requirements for strong fibers

1. Green processes: closed-loop, no toxic chemicals, product recyclability
2. Dyeability, recycling of dyes
3. **High strength, high toughness, high fatigue**
4. Low fibrillation
5. Production of low titers (microfibers)
6. Controlled interaction with water
7. Tuning hydrophilicity, hydrophobicity
8. Others

Structure vs Mechanical Properties

$$\textit{Tensile Strength} \propto \frac{1}{DP_n}$$



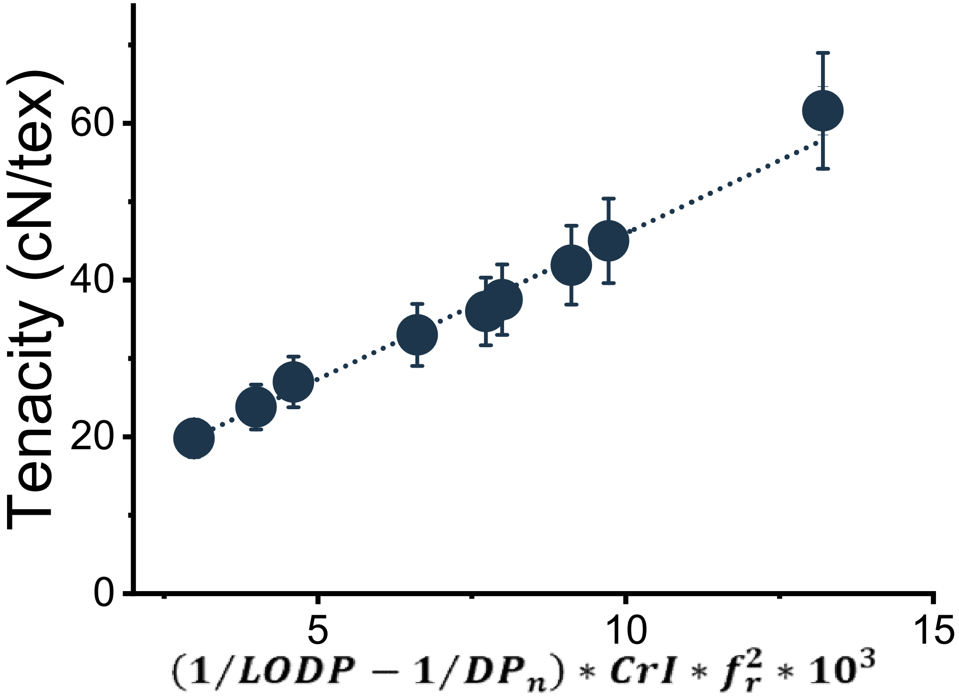
$$\textit{Tensile Strength} \propto \left(\frac{1}{LODP} - \frac{1}{DP_n}\right)$$

Molecular interlinks between the crystallites

Flory, JACS (1945) *Kitchen, Krässig; J. Polymer Sci. 51, 123 (1961)*

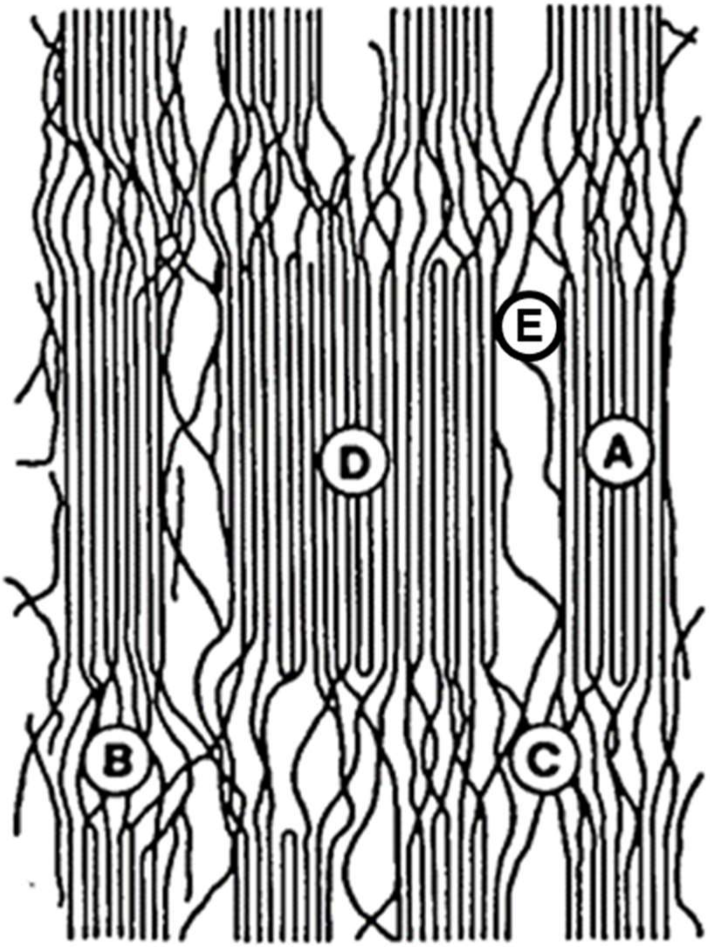
$$\textit{Tensile Strength} \propto CrI_{(f_r, DP_n = const)}$$

$$\textit{Tensile Strength} \propto f_r^2{}_{(CrI, DP_n = const)}$$



Hans Krässig: Cellulose (1993), p161

Fringed Fibrillar Structure



Schurz, J.; Lenz, J. *Macromol. Symp.* 83, 273-289 (1994)
Schurz, J. *Lenz. Ber.* 9, 94, 37-40 (1994)

A	Crystallites: size, orientation
B	Amorphous zone: connect successive crystallites; size, density, orientation, degree of coiling
C	Lateral connections of adjacent amorphous regions
D	Lateral connections between crystallites (Kratky "Clusters") Small-to-medium size leads to non-fibrillating fibers of high (lateral) strength and sufficient extensibility
E	Elongated voids preferred

Ratio between long period and crystallite length

Supercord Rayon Fibers

Today, the strongest commercial MMCFs.

Mainly used for the reinforcement of high-speed tires.

- **Super 3 cord:** 50 cN/tex (cond); 39 cN/tex (wet) [>1963]

Concept of High-Tenacity Fibers

Shrunken gel

Structure determined **before** stretching; low primary gel swelling!

Crystallization precedes orientation.

Medium stretch ⇒ small crystals, intermediate orientation, low modulus, high extensibility and high fatigue

⇒**Supercord**, **Modal®**, HWM **(Modulus < 20 GPa)**

Highly swollen gel

Structure determined **at stretching**

Orientation occurs **before** crystallization.

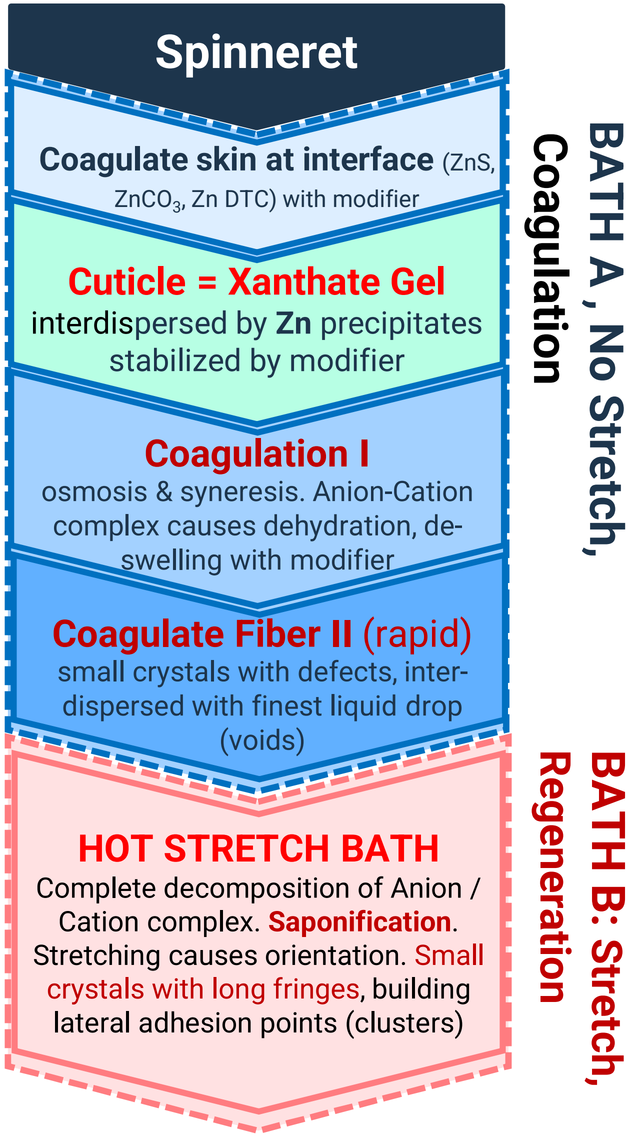
Maximum stretch→Fiber of high orientation, high modulus & tenacity, **low loop tenacity** and **low extensibility, high brittleness**

⇒**Polynosic**, Fortisan, Fiber “B” and others **(Modulus > 20 GPa)**

SUPERCORD FIBER PROCESS

Low-acid, high salt, high modifier BATH A producing a *pure* coagulate fiber with small crystallites

→ **Shrunken Gel**



Spinneret

Coagulate skin at interface (ZnS, $ZnCO_3$, Zn DTC) with modifier

Cuticle = Xanthate Gel
interdispersed by **Zn** precipitates stabilized by modifier

Coagulation I
osmosis & syneresis. Anion-Cation complex causes dehydration, de-swelling with modifier

Coagulate Fiber II (rapid)
small crystals with defects, inter-dispersed with finest liquid drop (voids)

BATH A , No Stretch, Coagulation

HOT STRETCH BATH
Complete decomposition of Anion / Cation complex. **Saponification.** Stretching causes orientation. Small crystals with long fringes, building lateral adhesion points (clusters)

BATH B: Stretch, Regeneration

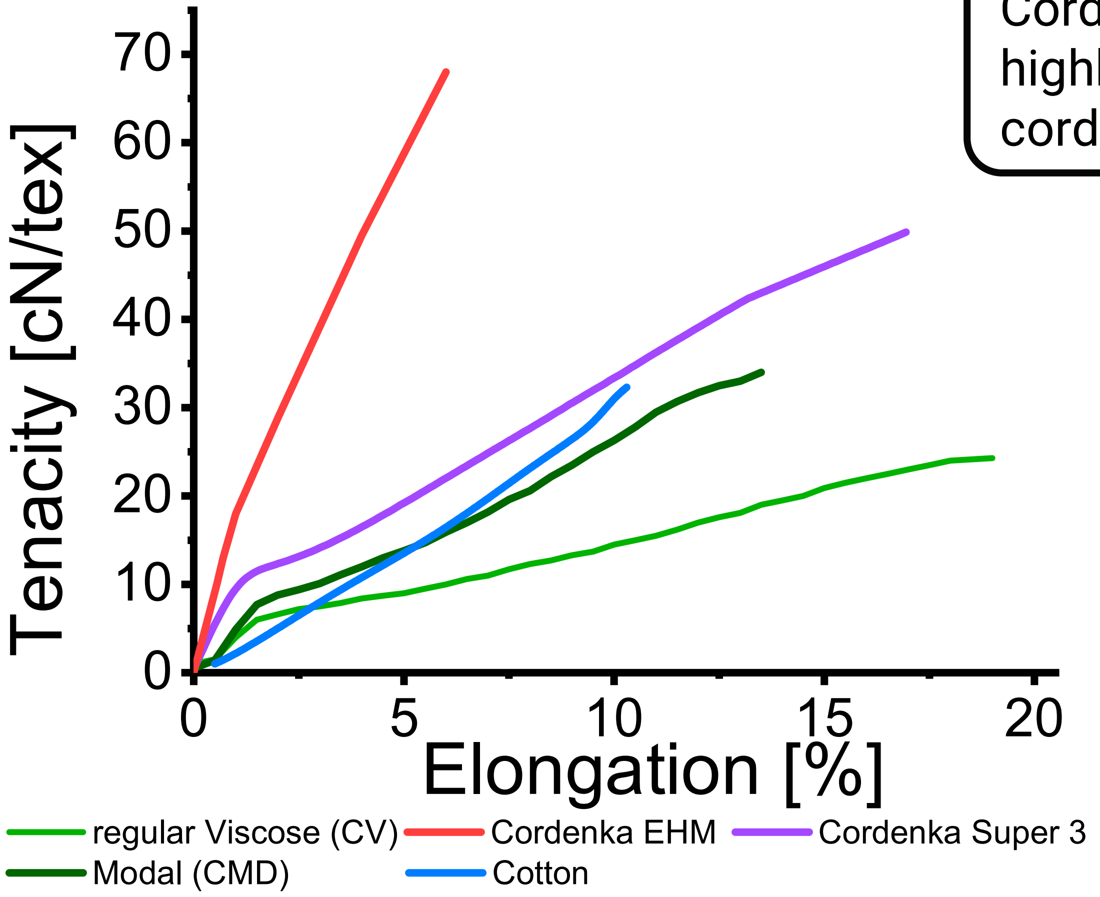
Super 2 and Super 3:

- higher DP pulps of better purity
- improved modifiers: coagulation separated from regeneration
- jets of smaller hole size
- lower spin bath acid concentration
- improved stretching techniques

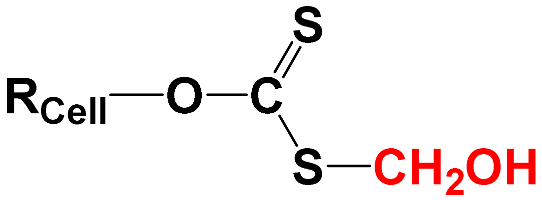
Characteristics

- Small crystallites through fast coagulation
- All-skin structure with a thin outer layer (cuticle)
- Structure can accommodate small-segments slippage (high extensibilities)
- Individual molecules pass through several crystallites giving a cooperative effect (high tenacity)
- **High toughness and fatigue**

Cordenka EHM® fiber



Cordenka EHM®, highly stretched tire cord



HCHO in spin-bath: S-methylol formation with the xanthate

Very slow decomposition→ formation of strong membrane, forms cross-links

Drawback: reacts with

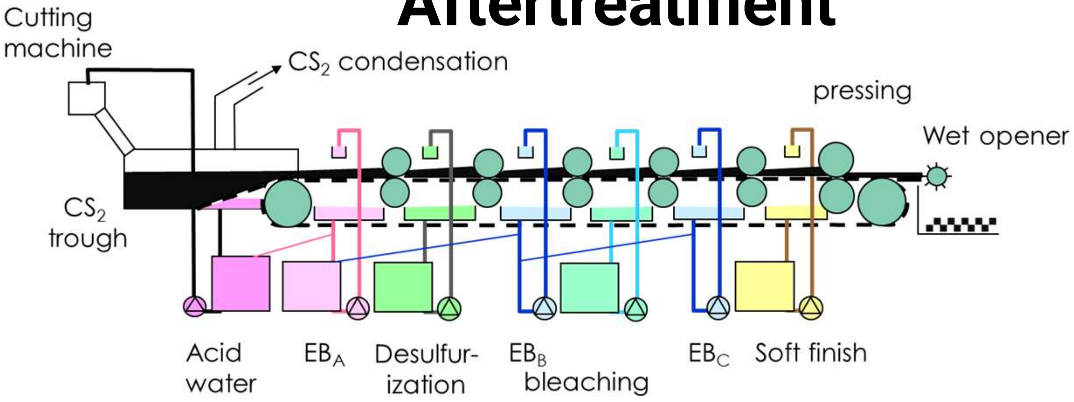
$$CS_3^{2-} + 2HCHO \overset{H^+}{\leftrightarrow} S = C(SCH_2OH)_2$$

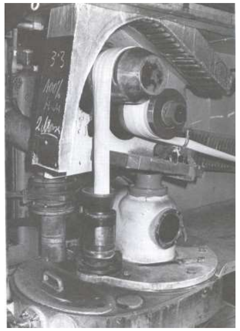
practical problems with spin bath regneration

VISCOSE

- Aftertreatment
- Drying
- Baling

Aftertreatment

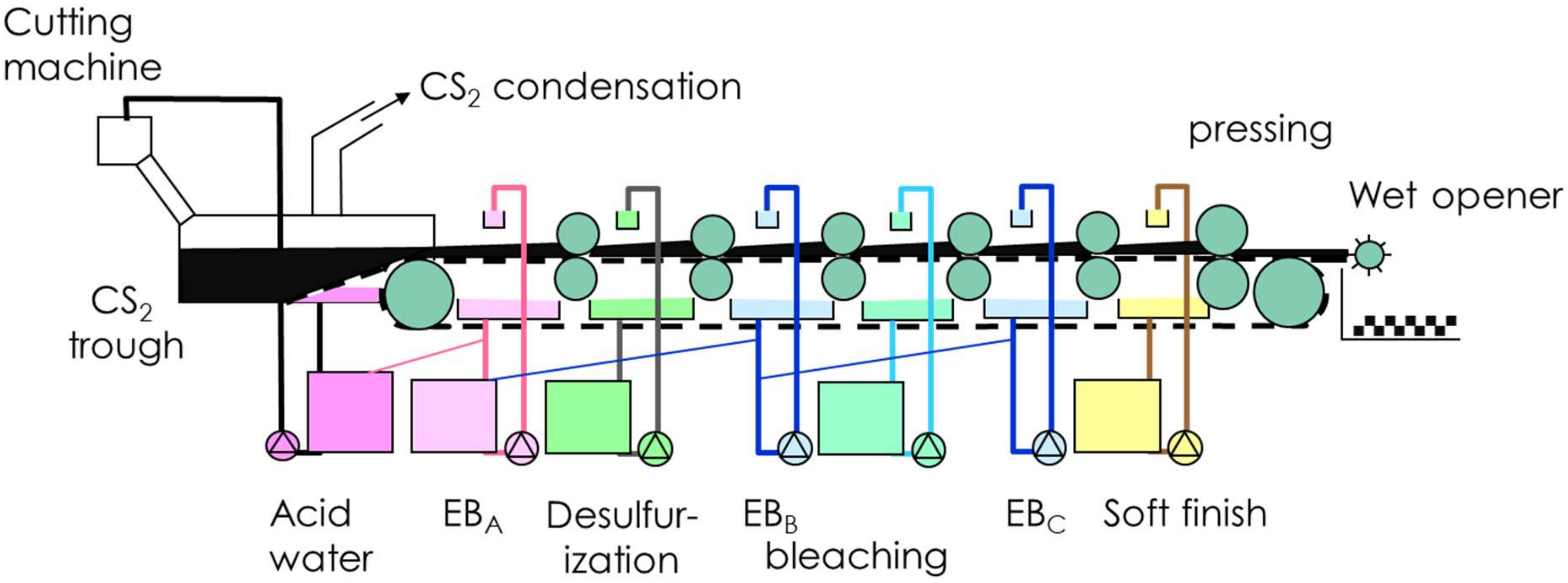




Dryer

Baling

Aftertreatment of Fibers



Cutter

Crimp

Prerequisite for yarn spinning
Staple CV fibres receive a spontaneous crimp through skin-core structure

Dryer

Staple fiber:

- Filter band dryer, vacuum dryer

Filaments

- Cylinder dryer

Baling press

Dried staple fibers are opened and pneumatically conveyed to the bailing press

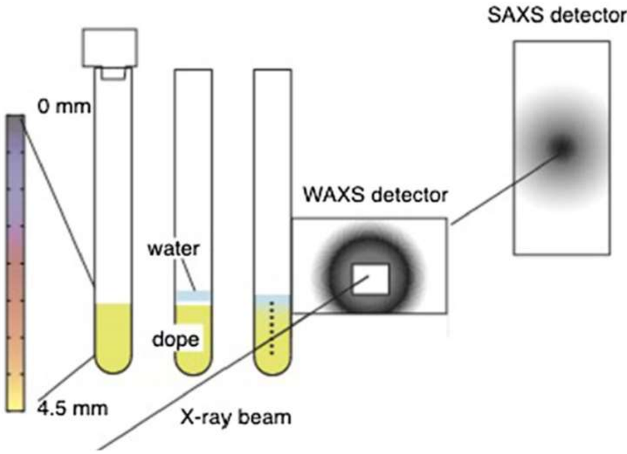
Wet spinning of *aqueous* alkaline cellulose solutions

Coagulation from alkaline (thio)urea solution

Inclusion complex consisting of Cellulose, NaOH and (thio)urea disrupted by nonsolvent addition

Synchrotron (Isobe): Initially, stacking of hydrophobic AHGs to form monomolecular sheets

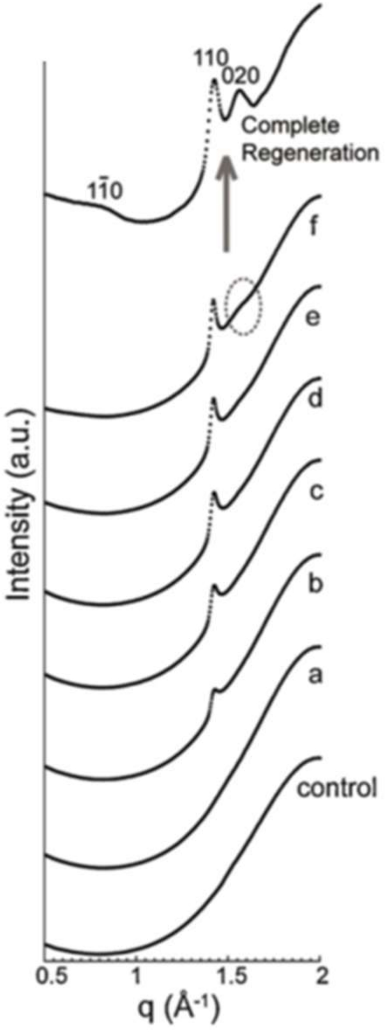
Synchrotron (Isobe): Subsequently, the sheets line up by H-bonding to form Na-cellulose IV crystallites

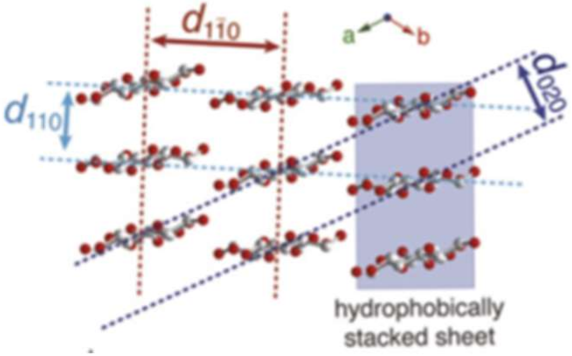


Medronho, B. Lindman / Advances in Colloid and Interface Science 222 (2015) 502–508

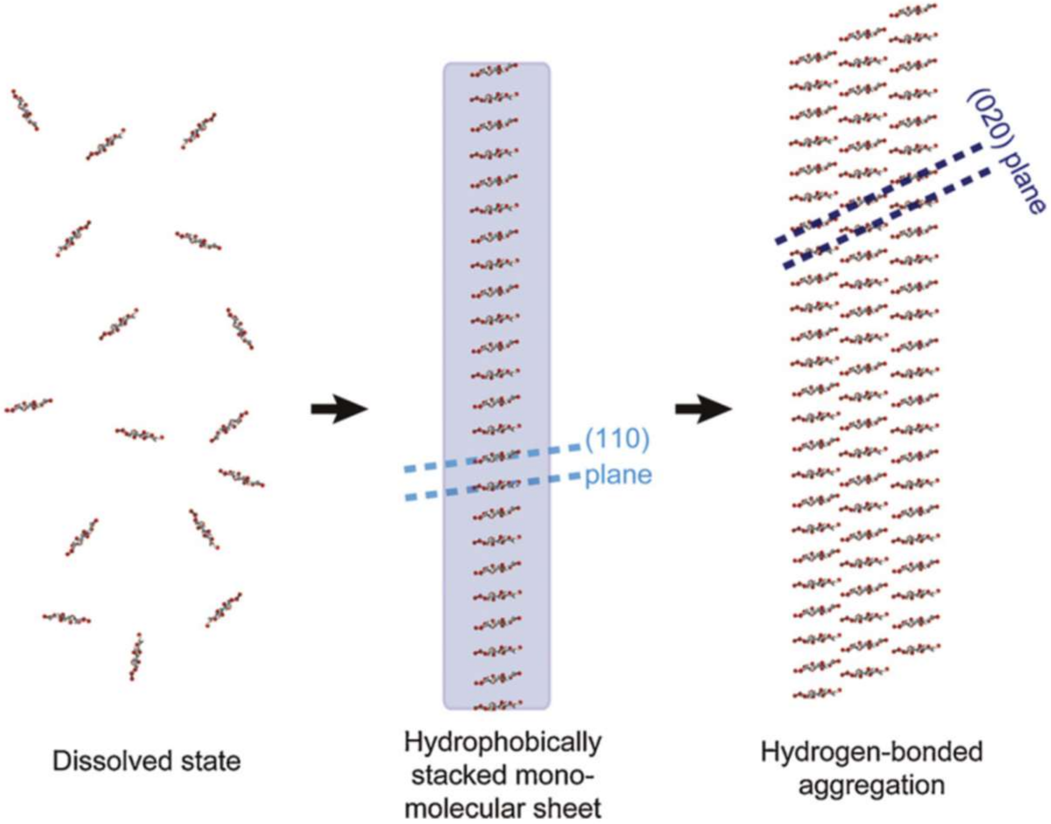
Miyamoto H. Carbohydr Res 2009, 344:1085 *Isobe N. et al. Carbohydrate Polymers (2012), 89, 1298-1300.*

Coagulation from alkaline urea solution





10 wt% Cellulose dissolved in 4.6% LiOH and 15 wt% urea, cooled to -15°C, dissolved and stored at 4°C.
Glass capillary filled with cellulose solution, 5 wt% Na_2SO_4 added as coagulant



Isobe N. et al. Carbohydrate Polymers (2012), 89, 1298-1300.

Cellulose crystallization from alkali solution

Three-step process:

1. Formation of glucan chain sheets by van der Waals forces
2. Association of these sheets into mini-crystals by H-bonding
3. Convergence of the mini-crystals (= subelementary fibrils) into the native crystalline microfibril

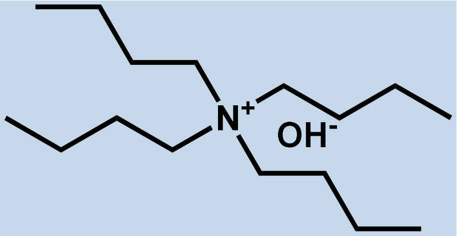
Fringed micellar model has been proposed to reflect the semi-crystalline structure of the native cellulose fibers

J. Phys. Chem. Lett. 2016, 7, 5044–5048

Cellulose coagulation from NaOHaq vs TBAHaq

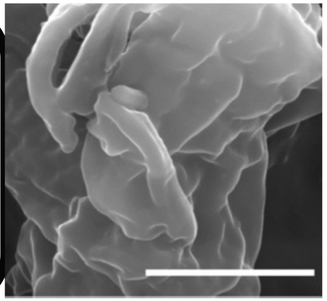
MCC solution in 8 wt% NaOH vs. 40 wt% TBAH.
Regeneration in diluted H_2SO_4

Why this difference?



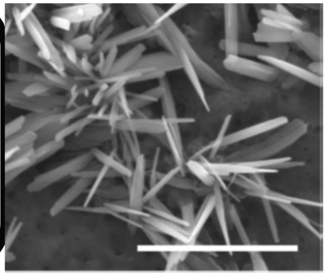
Cellulose in **TBAH/H_2O**, cellulose loses its crystallinity. Dissolution progresses down to the molecular level: **10-20 nm particle size** (DLS)

TBAH amphiphilic & large cation:



Cellulose in **NaOH/H_2O**→keeps its crystallinity:
200 nm large particle size.
Aggregate formation

NaOH high charge density & small cation



Provides support that cellulose contains polar and nonpolar regions

Colloids and Surfaces A: Physicochem. Eng. Aspects 483 (2015) 257–263

High strength fibers spun from NaOH/LiOH/urea

5.8 wt% CL pulp, DP 460, dissolved in
$NaOH$:$LiOH$:Urea:H_2O = 7:0.5:12:80.5
-12°C precooling and mixed at RT

→

1st BATH
15 wt% Phythic acid
5 wt% Na_2SO_4, 5°C

→

2nd BATH
60°C water
DR up to 2.0

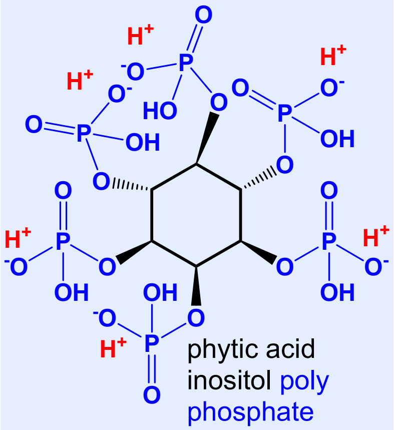
→

FIBER

Phytic acid /Na_2SO_4 are coagulants with low self-diffusion coefficients

More complete coagulation prior to regneration

Cellulose regeneration retarded due to slower diffusion rate of the protons



phytic acid inositol poly phosphate

Cellulose solvation with NaOH/urea maintained for a longer time.

GEL strengths of coagulates:

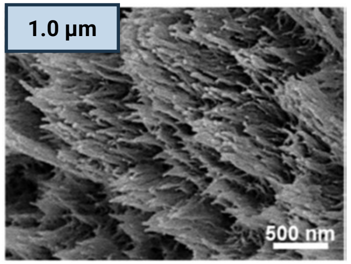
Phytic acid 9.5 MPa >> H_2SO_4 4.7 MPa

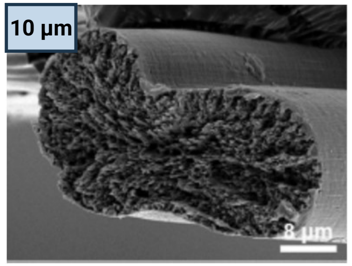
Kunkun Zhu, Lina Zhang et al., ACS Sustainable Chem. Eng. (2018), 6, 5314-5321

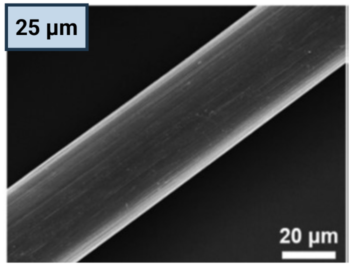
High strength fibers spun from NaOH/LiOH/urea

alkali–urea complex as shell on the cellulose chain destroyed

liberated **cellulose molecules aggregate sufficiently in parallel to form nanofibers**







SAXS

Fibrillar structure aligned parallel to the fiber direction

Needle-shaped voids

Periodic lamellar arrangement of crystalline and amorphous domains.

v_{ext} =7.46 m/min, DR2		
χ_C	%	65
f_{cryst}		0,90
$\sigma_{b,dry}$	cN/tex	**35**
$\sigma_{b,wet}$	cN/tex	**25**
$\varepsilon_{b,dry}$	%	7,7
$\varepsilon_{b,wet}$	%	8,7

Kunkun Zhu, Lina Zhang et al., ACS Sustainable Chem. Eng. (2018), 6, 5314-5321