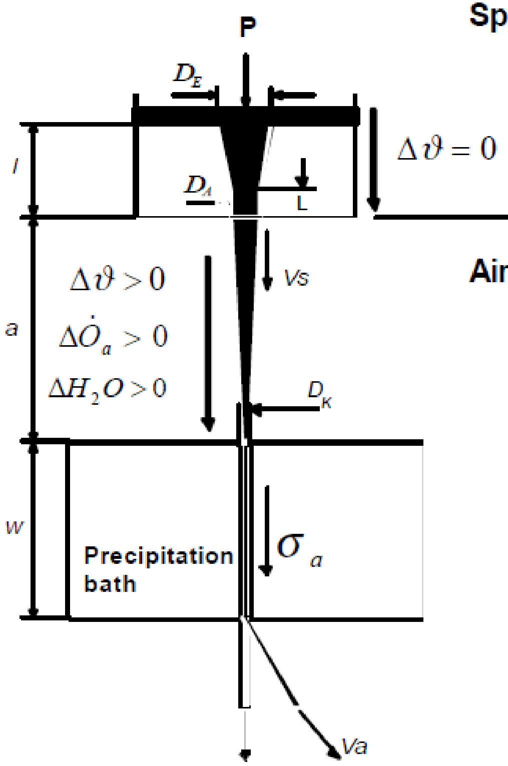
Aalto University
School of Chemical
Engineering

Filament breaches during spinning

Theory and Practice of Wet Spinning of Cellulose Solutions

Extrusion of cellulose (polymer) solutions



Spinneret – Shearing / Extensional shaping

$$\tau = \eta_{\dot{\gamma}} \cdot \dot{\gamma}$$

$$\sigma_D = \eta_{\dot{\varepsilon}} \cdot \dot{\varepsilon}_D \neq 0$$

Air gap – Extensional shaping

$$\sigma_a = \eta_{\dot{\varepsilon}_a} \cdot \dot{\varepsilon}_a \qquad \eta_{\dot{\varepsilon}_a} = f(\sigma_{Ob.})$$

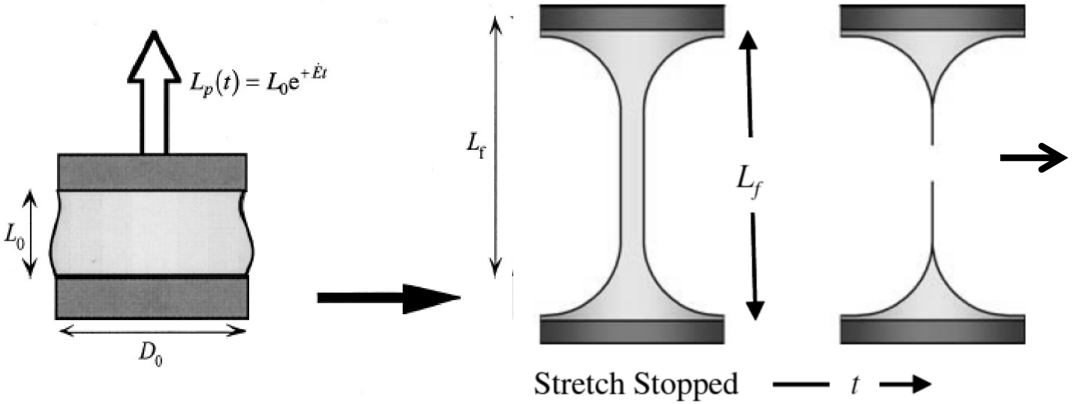
$$SV_a = \left(\frac{D_A}{D_K}\right)^2 = \frac{v_a}{v_s} \qquad \dot{E}_{Ob.} = \sigma_{Ob.} \cdot \Delta\dot{O}_a$$

$$\Delta\dot{O}_a = \pi \cdot D_A \cdot v_s\left(\sqrt{SV_a} - 1\right) \quad \left[cm^2 / \min K\right]$$

$$\bar{v}_{an} = 10 \cdot \frac{\Delta\dot{O}_a}{a} [mm / \min]$$

Michels and Kosan. Lenzinger Berichte, **2005**, 84. 62-70

Extensional rheology

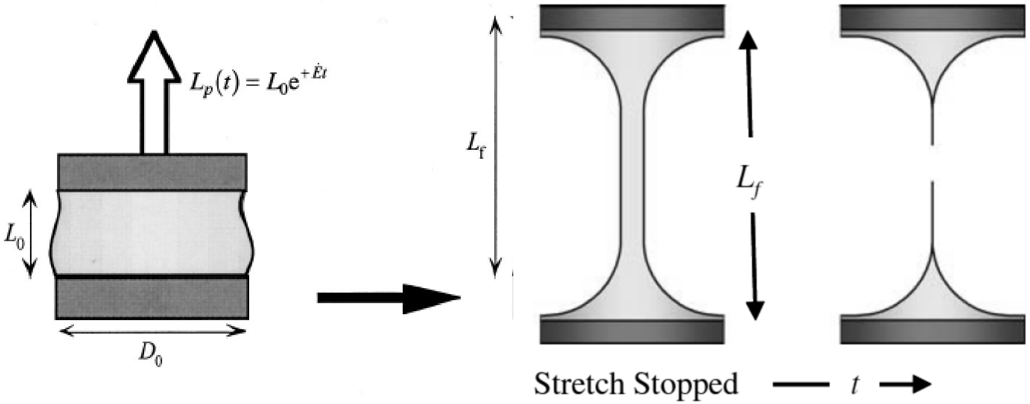


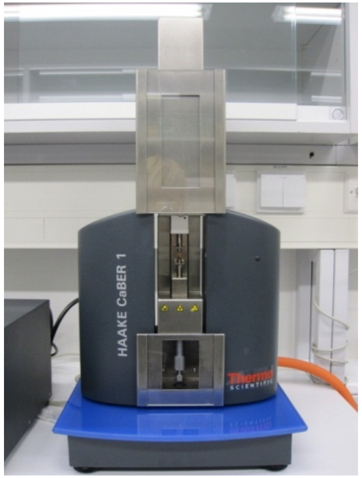
τ_e…extensional relaxation time
η_{app}…apparent extensional viscosity

- To investigate the sample's viscoelastic response under elongational stress
- Sample can be either stretched actively by the device or capillary forces can cause filament necking

Anna and McKinley *J. Rheol.* **2001,** 45, 115-138

Extensional rheology





$$\eta_{app} = \frac{-\sigma}{dD_{mid}/dt}$$

- L_0 = Sample initial height
- L_f = Sample final height
- Initial aspect ratio $\Lambda_0 = L_0/R$
- Final aspect ratio $\Lambda_f = L_f/R$

$$D_{mid}(t) = \left(\frac{\eta_p D_1^4}{2\tau\sigma}\right)^{1/3} exp\left(-\frac{t}{3\tau}\right)$$

τ	extensional relaxation time
η_{app}	apparent extensional viscosity
σ	surface tension

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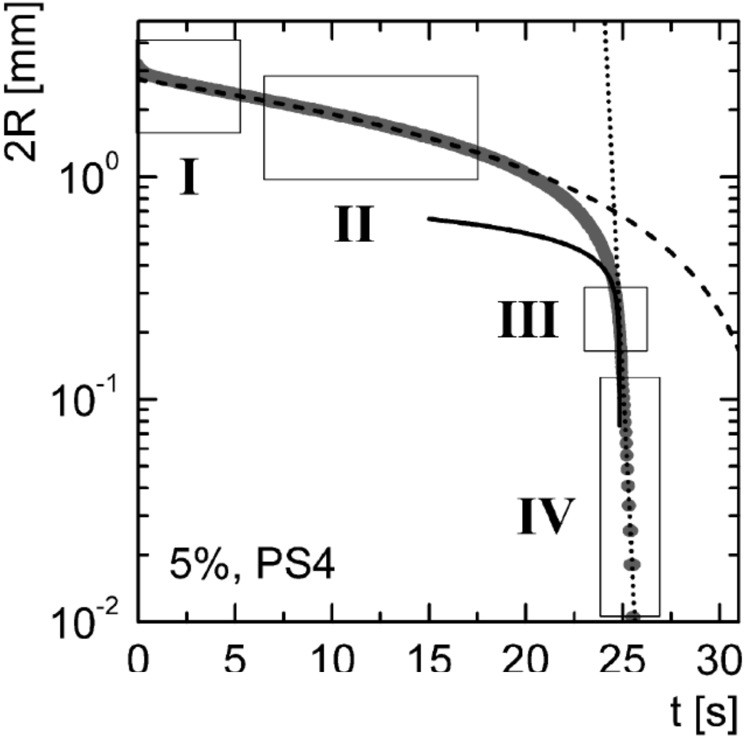
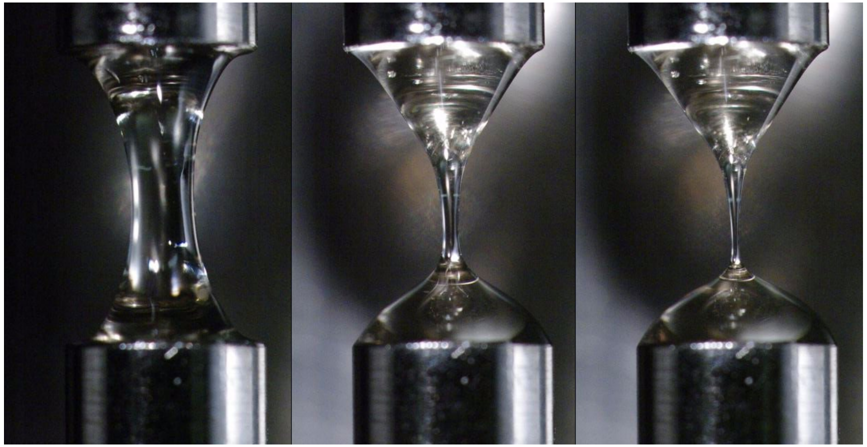
Anna and McKinley *J. Rheol.* **2001,** 45, 115-138

Extensional rheology





I ill-defined thinning profile that still contains strong contributions of gravitational sagging

II is controlled by a visco-capillary balance of the capillary

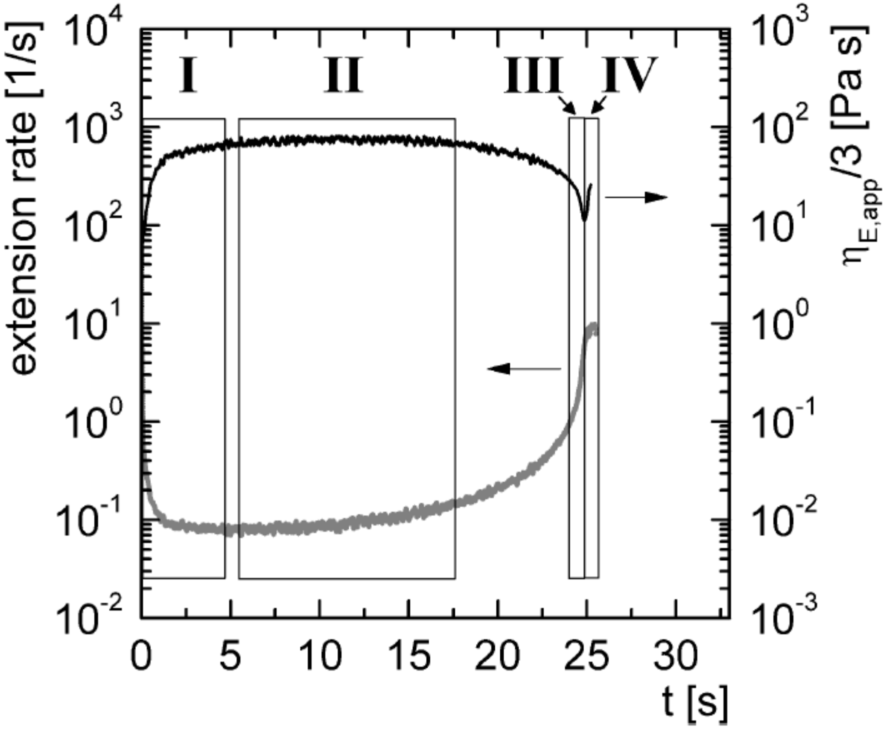
pressure and the viscous stresses in the filament

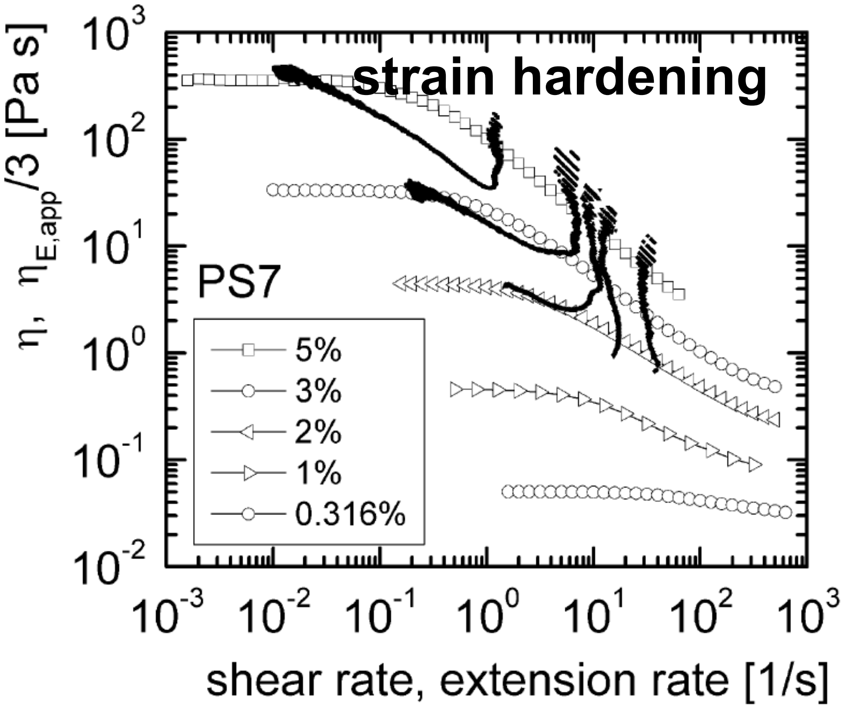
III is still showing a visco-capillary balance, however, the polymer solution is showing an extensional thinning, originating from the increased disentanglement and orientation of the polymer chains

IV is showing then the onset of an elasto-capillary balance where the surface pressure is balanced by the elastic stresses of the unraveling polymer chains

Clasen, C. *Korean*-Aust. *Rheol. J.* **2010,** 22, 331-338.

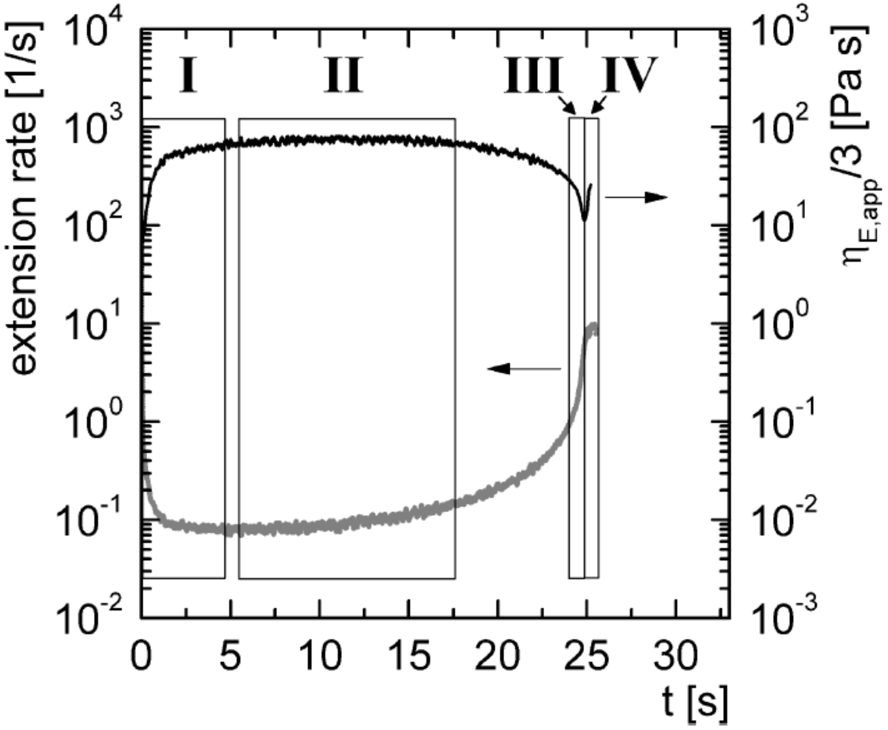
Extensional rheology

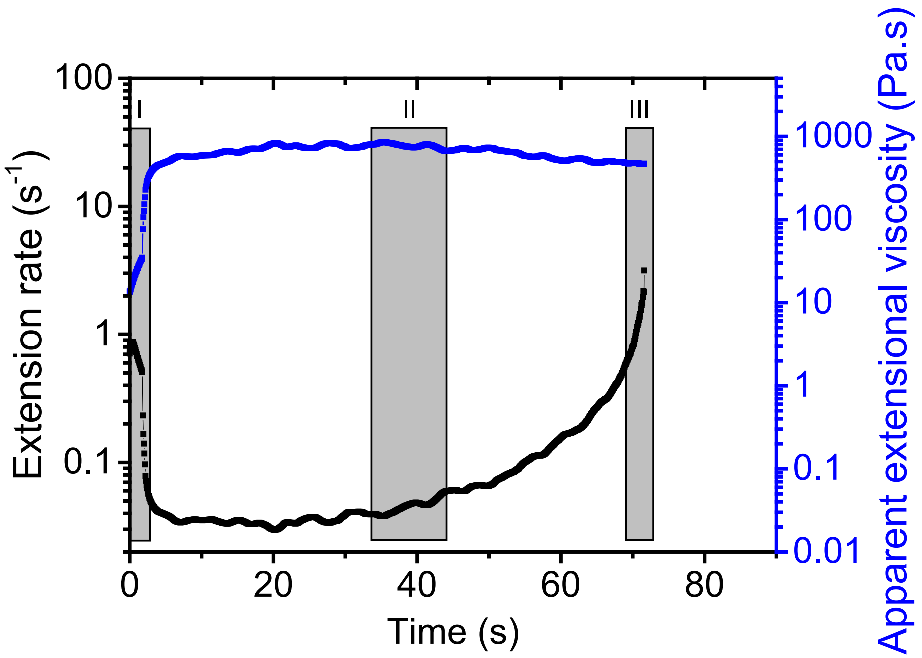




Clasen, C. *Korean*-Aust. *Rheol. J.* **2010,** 22, 331-338.

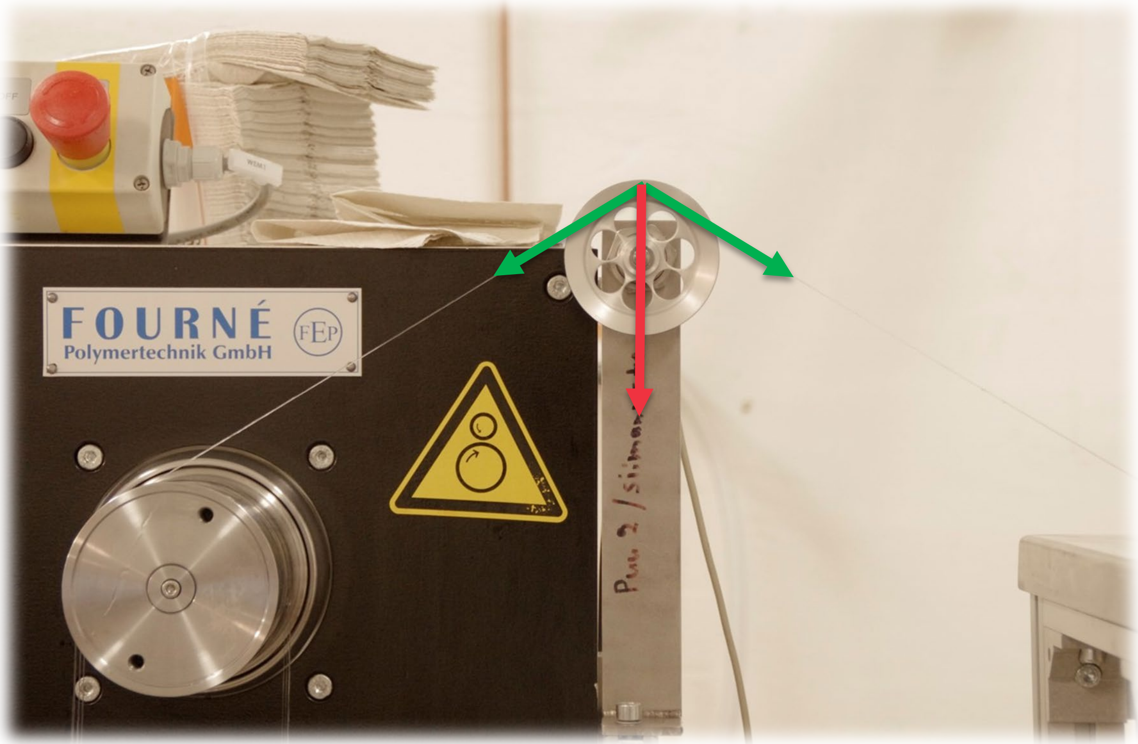
Extensional rheology



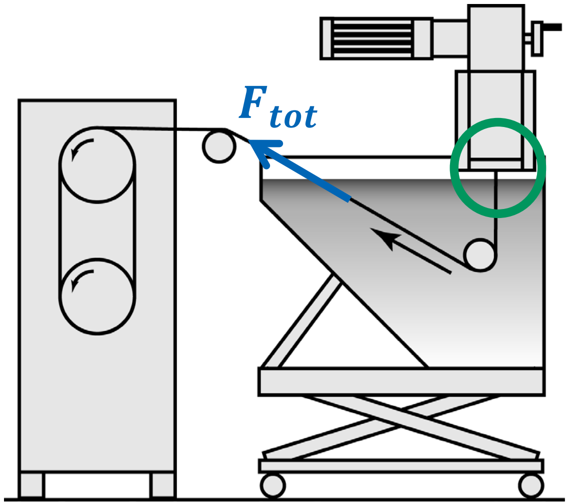


Clasen, C. *Korean*-Aust. *Rheol. J.* **2010,** 22, 331-338.

Extensional rheology

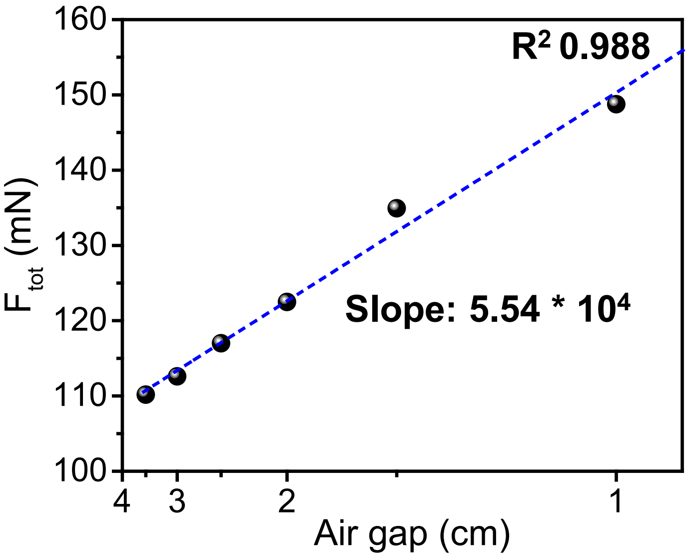


$$\boldsymbol{F_{tot}} = \frac{Q\eta_e}{l}\, ln\left(\frac{v_{tu}}{v_e}\right) + F_{hydr}$$

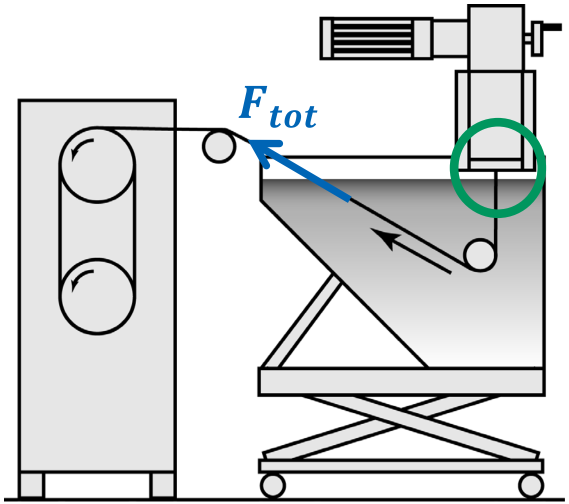


Boerstoel, H. Doctoral Thesis 1998

Extensional rheology



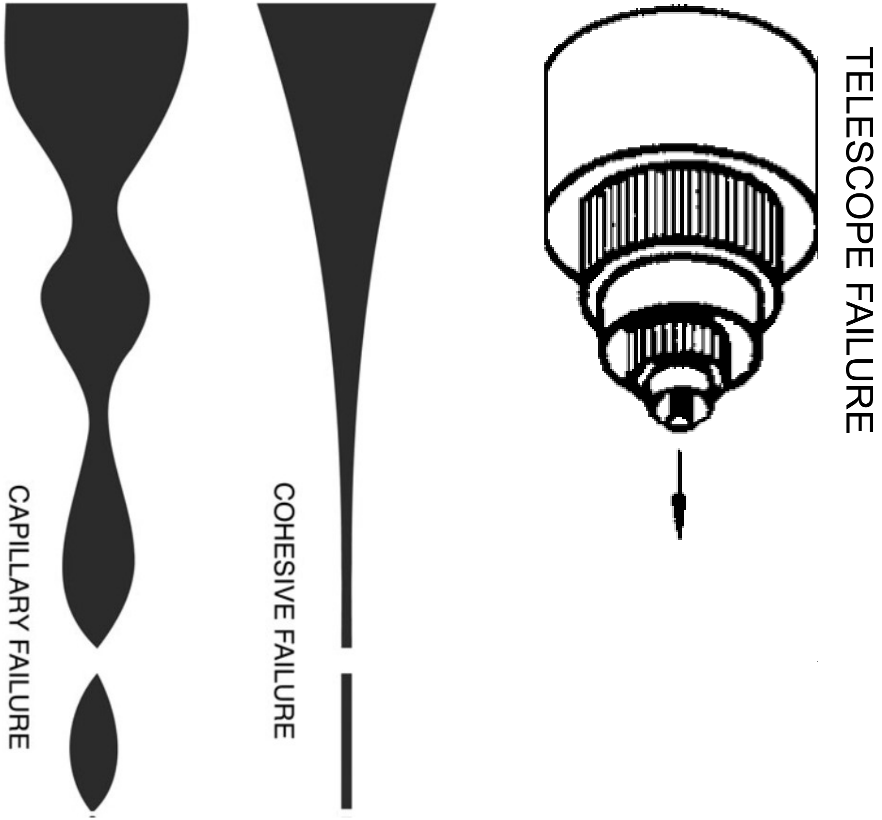
$$F_{tot} = \frac{Q\eta_e}{l} ln\left(\frac{v_{tu}}{v_e}\right) + F_{hydr}$$



Apparent extensional viscosity for IL: 8.22 * 10^4 Pa.s

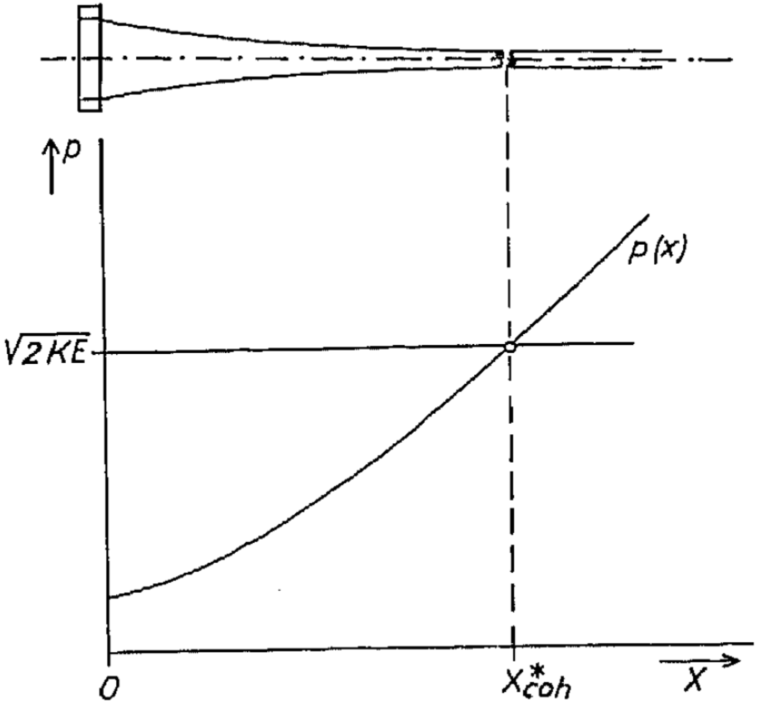
(cellulose-phosphoric acid solutions: 0.8 – 4.4 * 10^4 Pa.s)

Filament break



Bengtsson et al. Identifying breach mechanism during air-gap spinning of lignin–cellulose ionic-liquid solutions. *J. Appl. Polym. Sci.* 2019, 47800

Cohesive break



For linear visco-elastic (Maxwellian) fluid:

p(x)	tensile stress
K	resilience
E	modulus of elasticity

$$p(x^*) = (2KE)^{1/2}$$

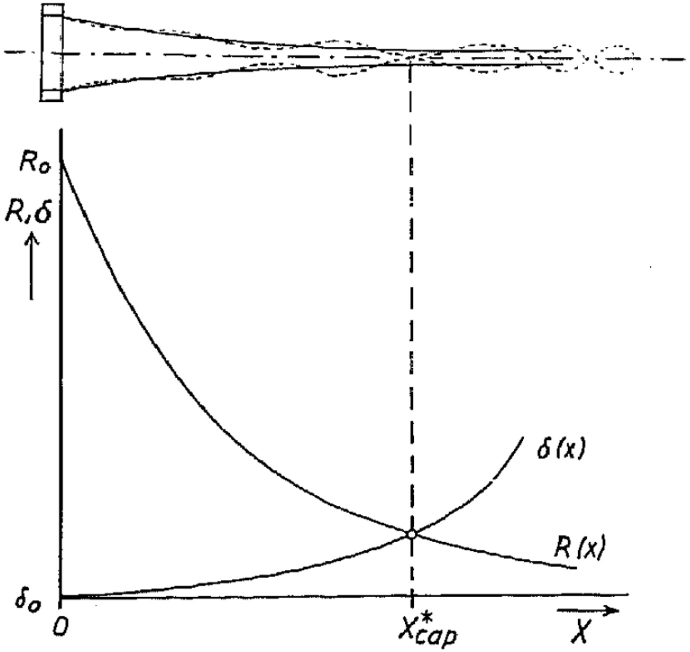
V	jet velocity
ξ	gradient of deformation
η	viscosity of fluid

$$V = V_0 \exp(\xi x)$$

$$x^* = \frac{1}{\xi} \ln\left[(2KE)^{1/2}/3 V_0 \xi \eta\right]$$

Ziabicki, Kolloid Zeitschrift und Zeitschrift für Polymere 1964, 198, 60-65

Capillary break



δ	deflection
R	radius of undistorted filament
μ	growth factor

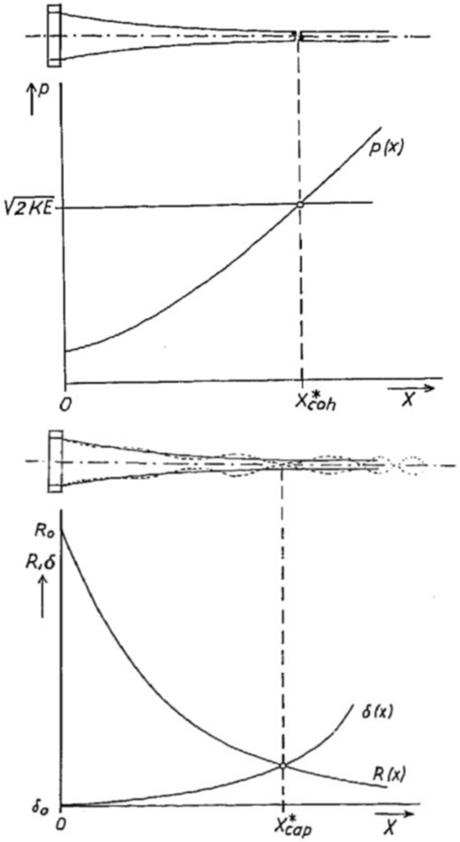
$$\delta = \delta_0 \exp(\mu t) \cos(2\pi x/\lambda)$$

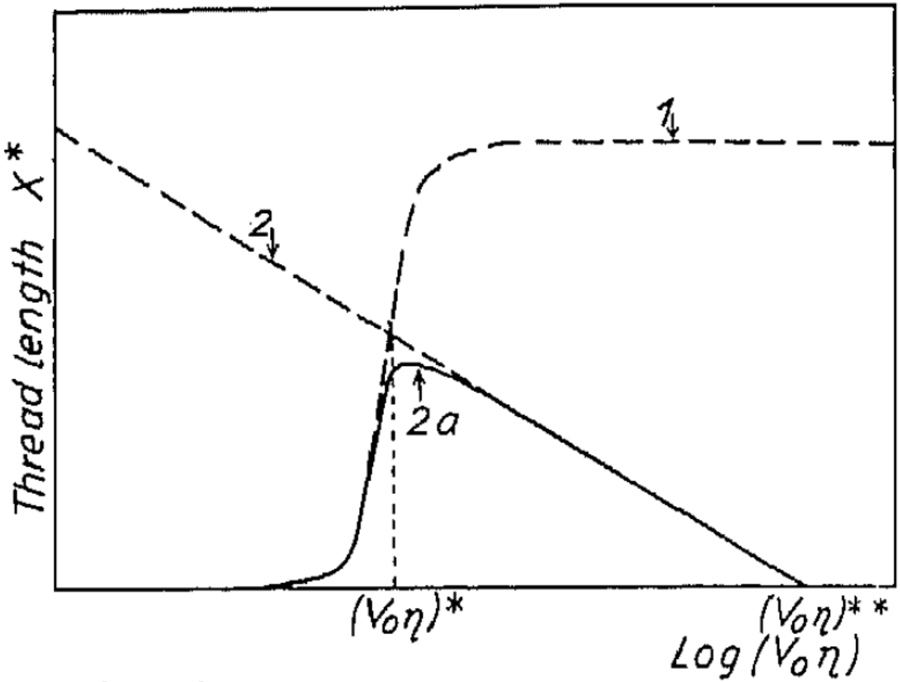
$$\lambda > 2\pi R$$

$$x^* \simeq \frac{1}{\xi}\left[2 \ln(R_0/\delta_0) - 2\alpha/3\,\eta\,\xi\,V_0\,R_0\right].$$

Ziabicki, Kolloid Zeitschrift und Zeitschrift für Polymere 1964, 198, 60-65
Wirth, Gries et al. Filament breaches during air-gap spinning. Man-made Fier Year Book 2011, 64-65.

Filament break

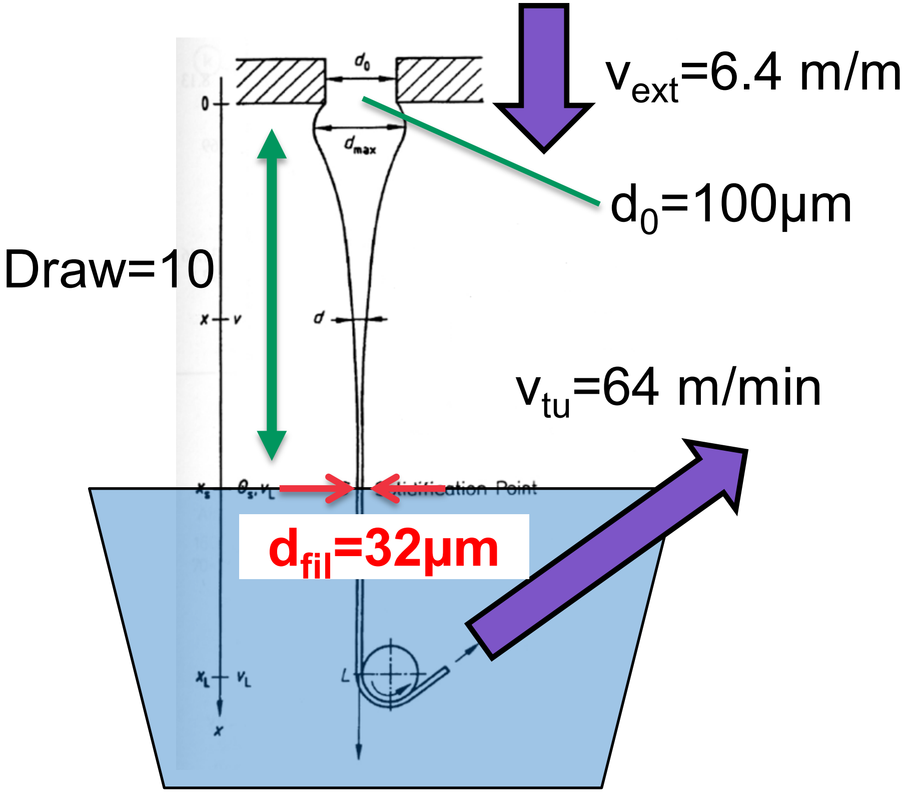




1 capillary break-up curve
2 cohesive break-up curve
2a cohesive break-up in the presence of capillary waves

Ziabicki, Kolloid Zeitschrift und Zeitschrift für Polymere 1964, 198, 60-65

Telescope break



v_{ext}=6.4 m/min

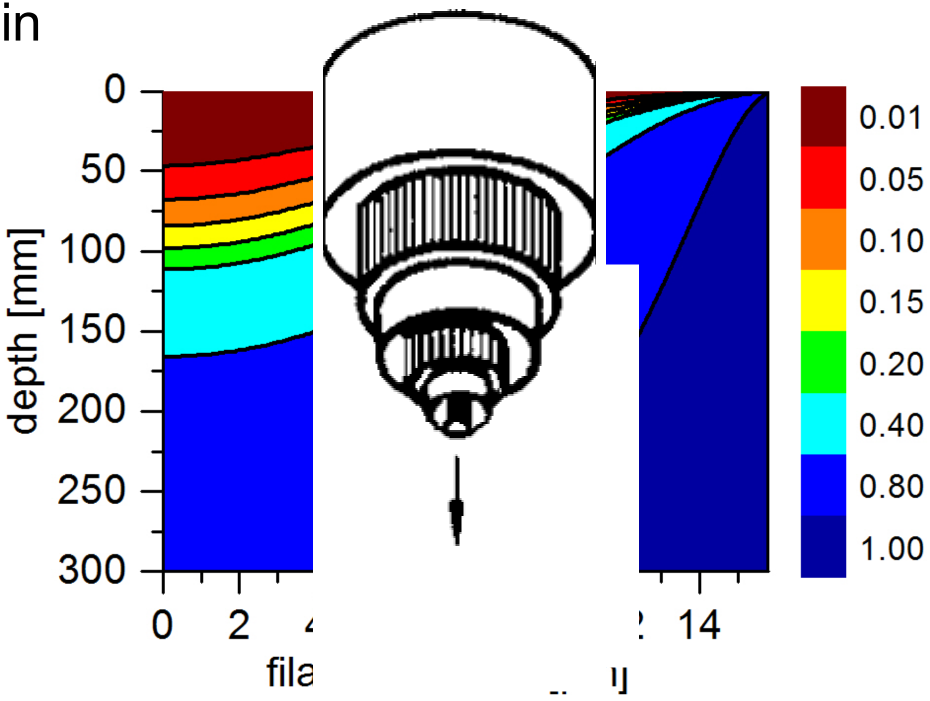
d_0=100µm

Draw=10

v_{tu}=64 m/min

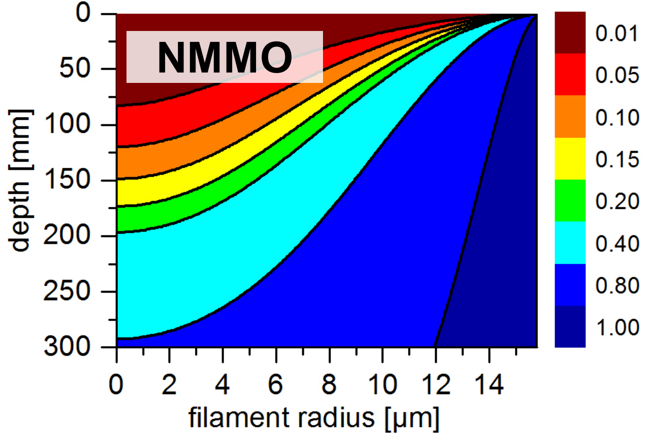
d_{fil}=32µm

Water content

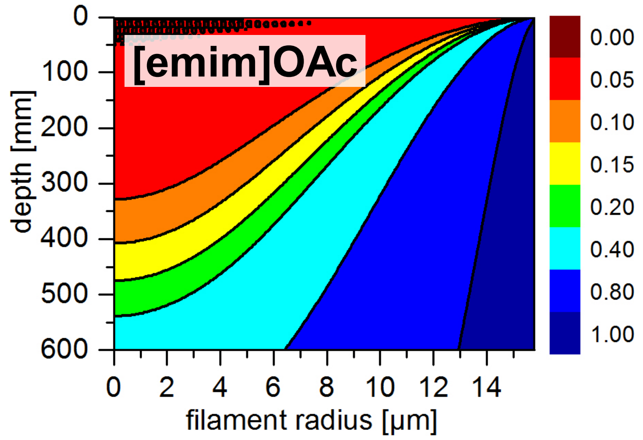


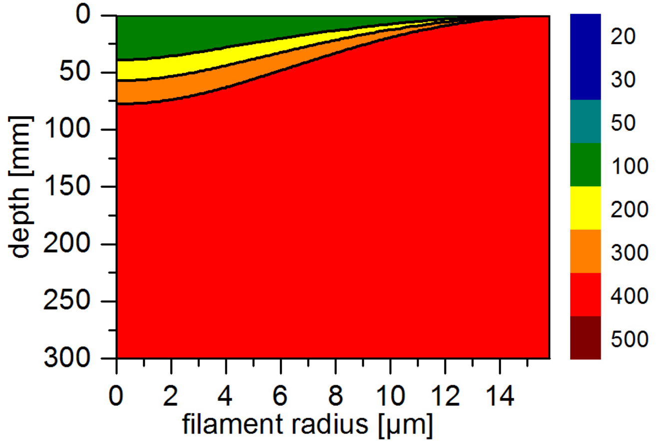
Hauru, Sixta et al. Cellulose regeneration and spinnability from ionic liquids. Soft Matt. 2016, 12, 1487-1495.

Telescope breach

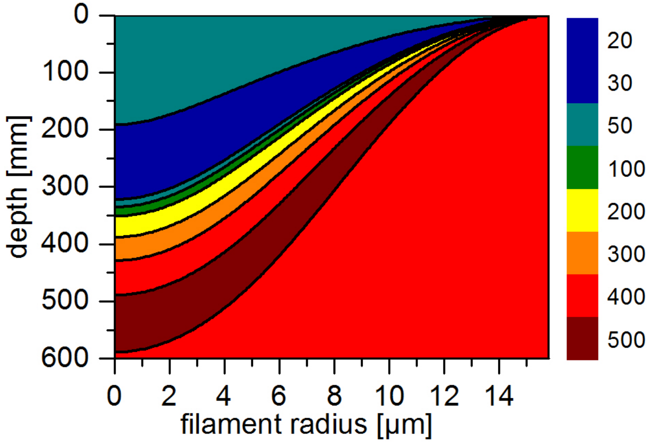


IL/water profile





Filament tensile strength [kPa]



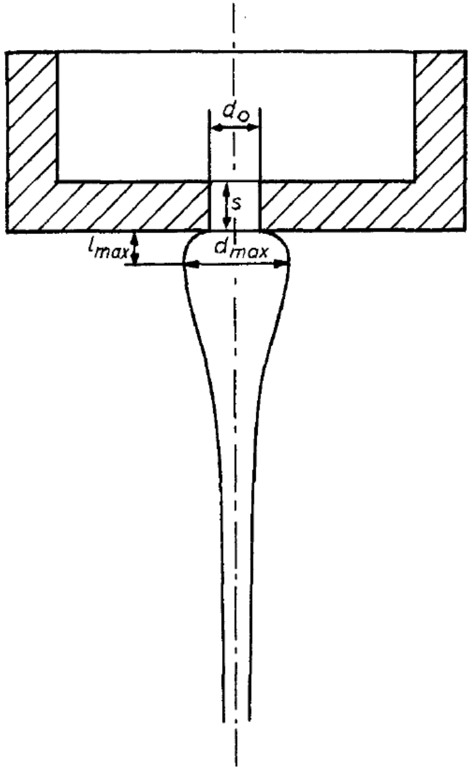
Hauru, Sixta et al. Cellulose regeneration and spinnability from ionic liquids.
Soft Matt. 2016, 12, 1487-1495.

Die swelling

Barrus effect; Merrington effect

Extrudate Swell, Soft Materials Laboratory, Department of Materials, ETH Zürich
YouTube: https://www.youtube.com/watch?v=LWNhr2PM5_s

Die swelling



$$v \cdot A \cdot \rho = const. = \mathrm{U}$$

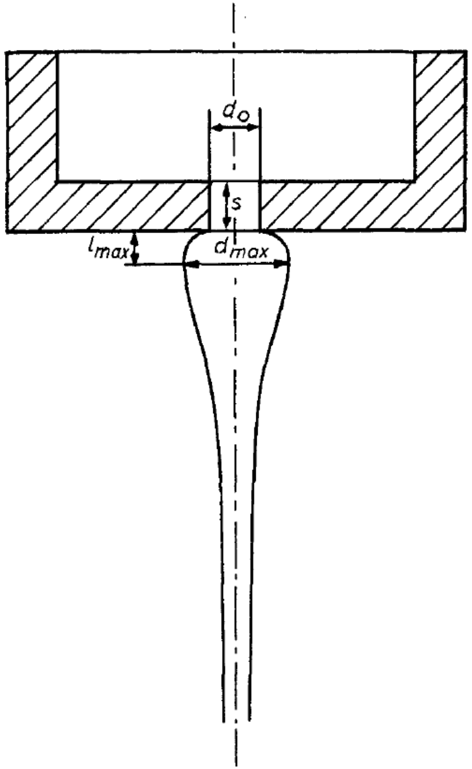
$$v_o = \frac{4U}{\pi d_o^2 \rho}$$

$$Q = \frac{d_{max}^2 - d_0^2}{d_o^2} = \frac{d_{max}^2}{d_o^2} - 1.$$

v	linear velocity
A	cross section area
ρ	density
U	volume flow
Q	maximum broadening

Ziabicki and Kedzierska. Mechanical aspects of fibre spinning process in molten polymers. Kolloid Zeitschrift 1960, 171, 111-118

Die swelling



$$p_o = E \cdot \frac{v_o - v_i}{v_i}.$$

$$p_o \propto const. \cdot E \cdot v_o$$

$$p = p_o \cdot \mathrm{f}(\mathrm{t}, \tau)$$

E	elastic modulus
η	viscosity
τ	relaxation time
p_0	initial stress for elastic deformation
v_i	velocity at capillary inlet
V	capillary volume
s	capillary length

Maxwellian relaxation

$$p = p_o \exp(-\mathrm{t}/\tau) \qquad t = \mathrm{V}\rho/U = s/v_o$$

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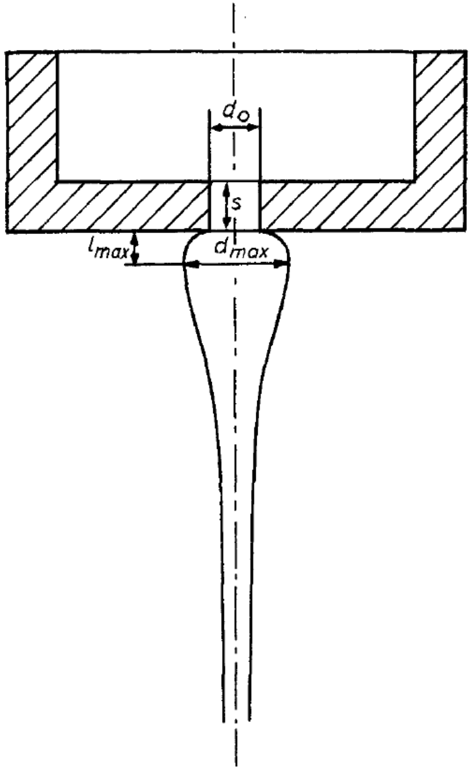
Ziabicki and Kedzierska. Mechanical aspects of fibre spinning process in molten polymers. Kolloid Zeitschrift 1960, 171, 111-118

Die swelling



$$Q = f(E, v_0, t = \frac{s}{v_0}, \tau = \frac{\eta}{E})$$

$$Q \propto v_0 \cdot E \cdot \exp(\frac{-s}{v_0 \tau})$$

$$v_0$$

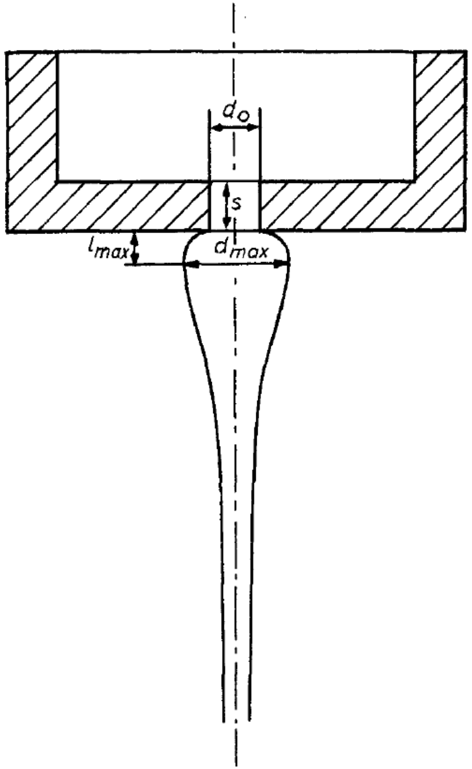
$$E$$

$$s$$

$$\tau$$

Ziabicki and Kedzierska. Mechanical aspects of fibre spinning process in molten polymers. Kolloid Zeitschrift 1960, 171, 111-118

Die swelling



$$Q = f(E, v_0, t = \frac{s}{v_0}, \tau = \frac{\eta}{E})$$

$$\theta_t \propto \theta_\infty \cdot [1 - \exp\left(\frac{-t}{\tau^*}\right)]$$

$$\theta_t \propto f(D, \tau^*) \cdot [1 - \exp\left(\frac{-t}{\tau^*}\right)]$$

θ degree of orientation
D transverse velocity gradient (shear rate)
K disorientation rate constant
τ^* disorientation (relaxation) time

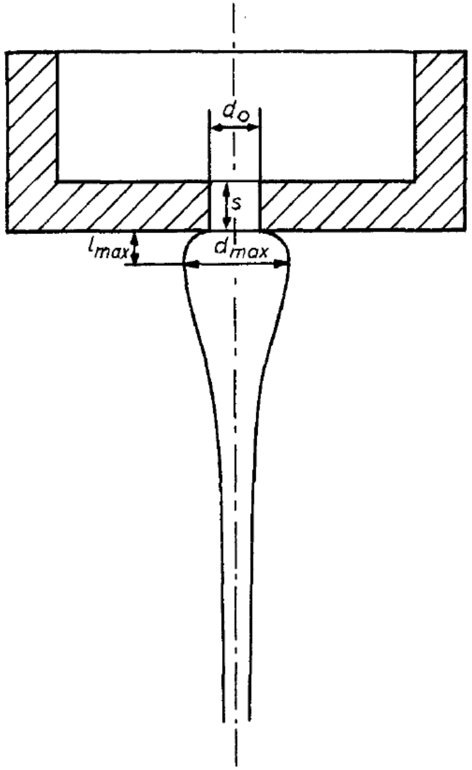
Ziabicki and Kedzierska. Mechanical aspects of fibre spinning process in molten polymers. Kolloid Zeitschrift 1960, 171, 111-118

Die swelling

$$Q = const.\cdot D \cdot \tau^*[1 - \exp\left(\frac{-t}{\tau^*}\right)]$$

$$\partial Q/\partial t = const.\cdot D \cdot \exp\left(\frac{-t}{\tau^*}\right)]$$

$$\partial Q/\partial \tau^* = const.\cdot D \cdot \tau^*[1 - \exp\left(\frac{-t}{\tau^*}\right) \cdot \left(1 + \frac{t}{\tau^*}\right)]$$



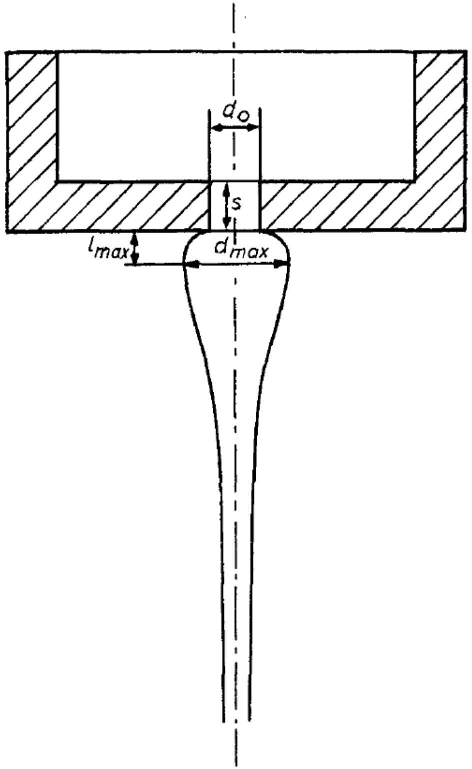
$$v_0$$
$$d_0$$
$$s$$
$$\tau^*$$

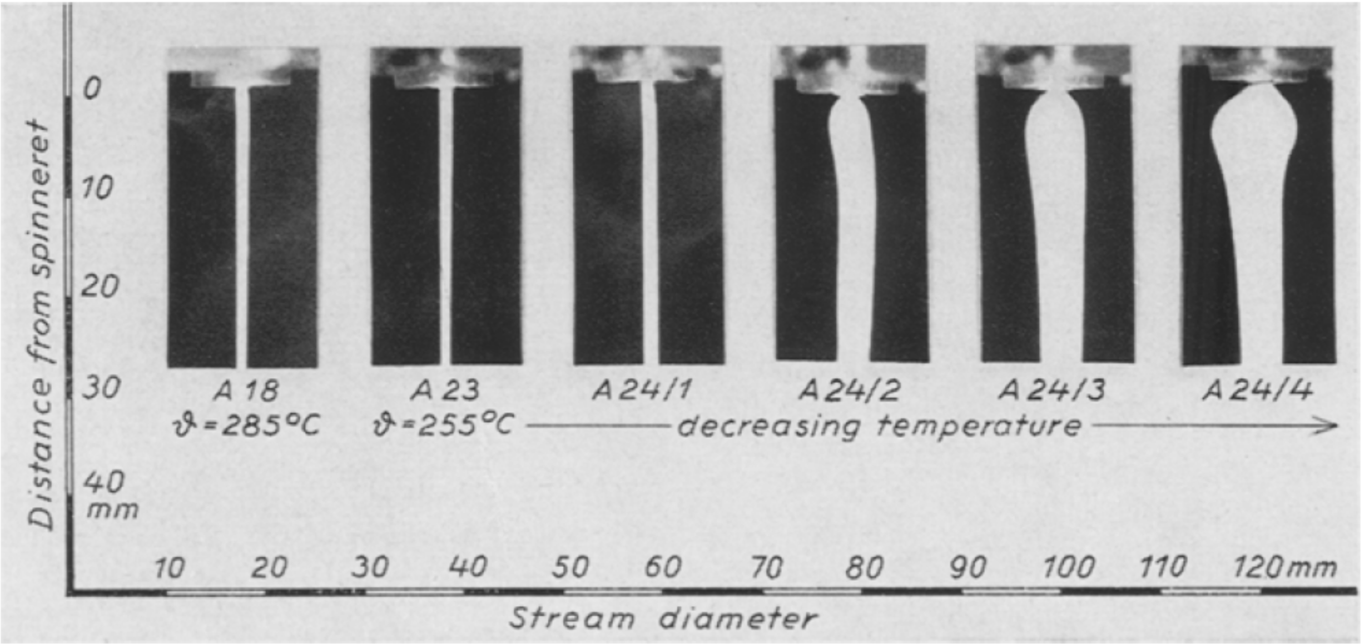
Ziabicki and Kedzierska. Mechanical aspects of fibre spinning process in molten polymers. Kolloid Zeitschrift 1960, 171, 111-118

Die swelling

Extrudate Swell, Soft Materials Laboratory, Department of Materials, ETH Zürich
YouTube: https://www.youtube.com/watch?v=LWNhr2PM5_s

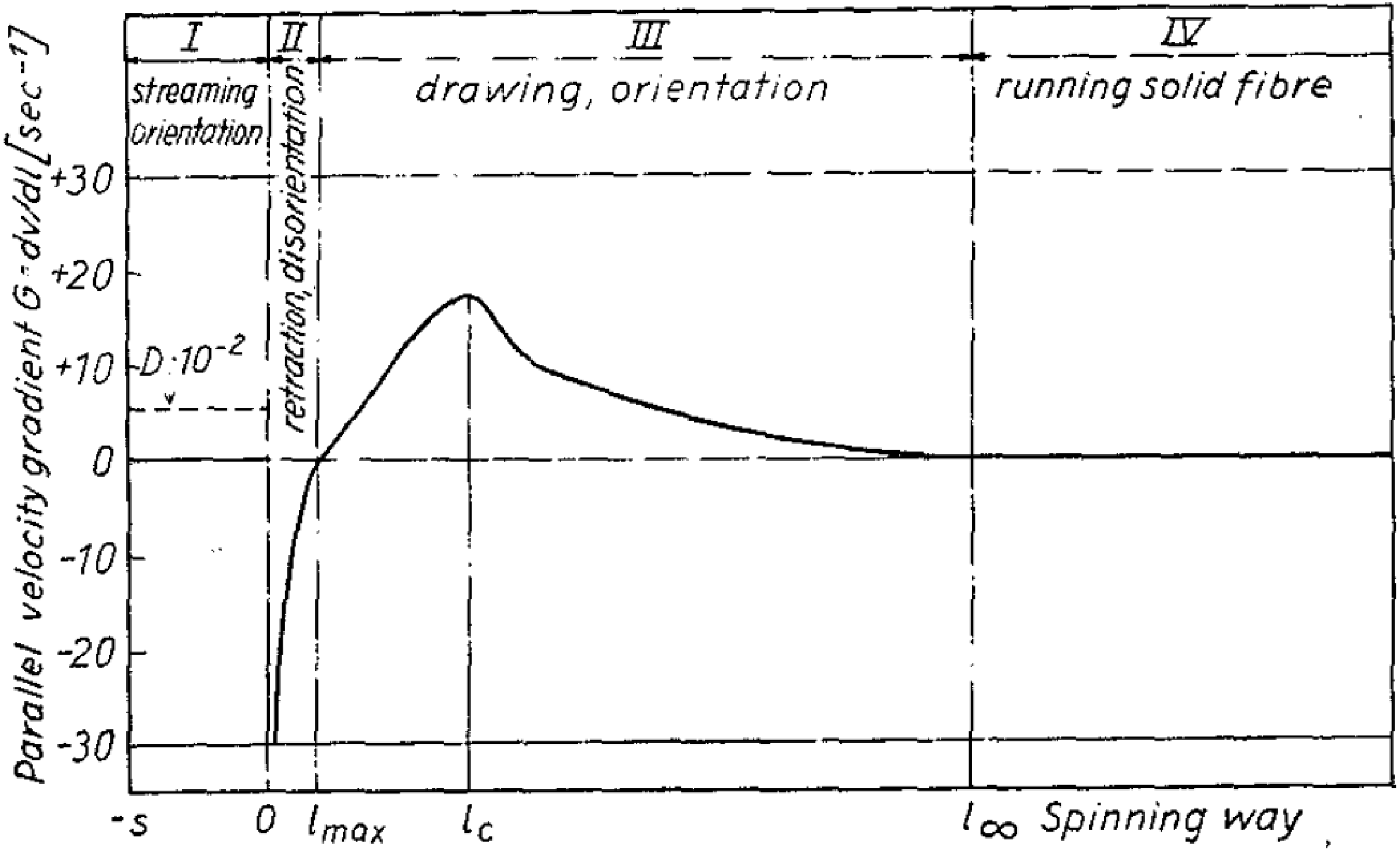
Die swelling

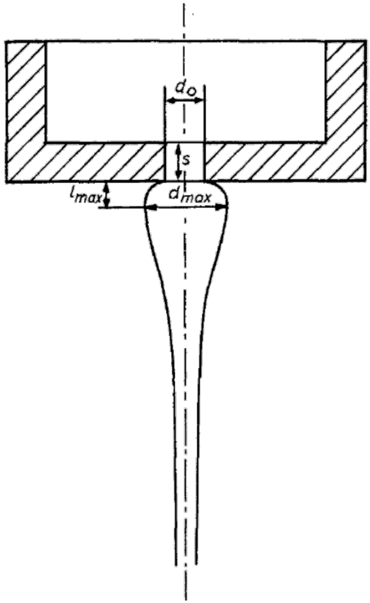




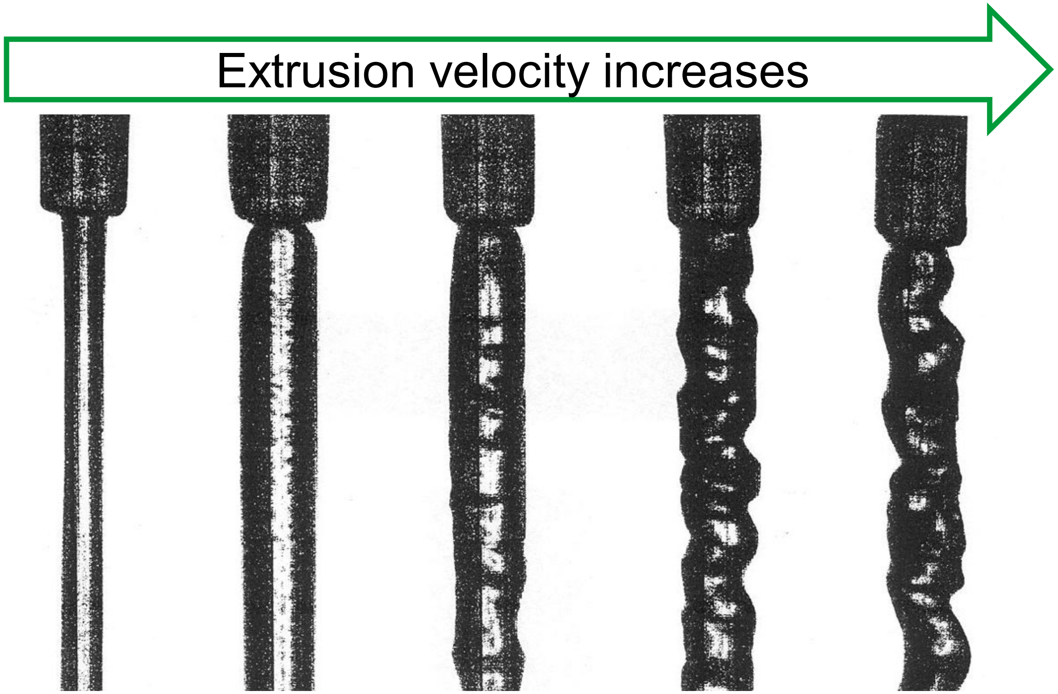
Ziabicki and Kedzierska. Mechanical aspects of fibre spinning process in molten polymers. Kolloid Zeitschrift 1960, 171, 111-118

Die swelling



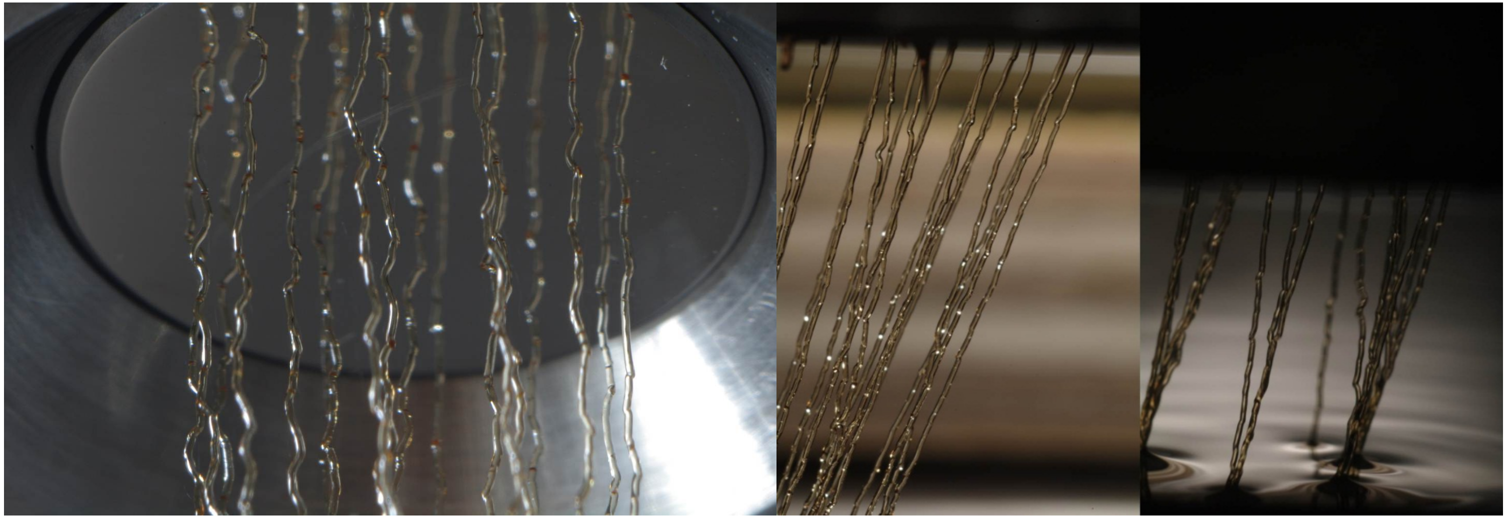


Melt fracture



http://wwwhome.lorentz.leidenuniv.nl/~saarloos/Patternf/meltfracture.html

Melt fracture



Melt fracture

- Flow speed lowest at wall
- Shear stress highest at wall

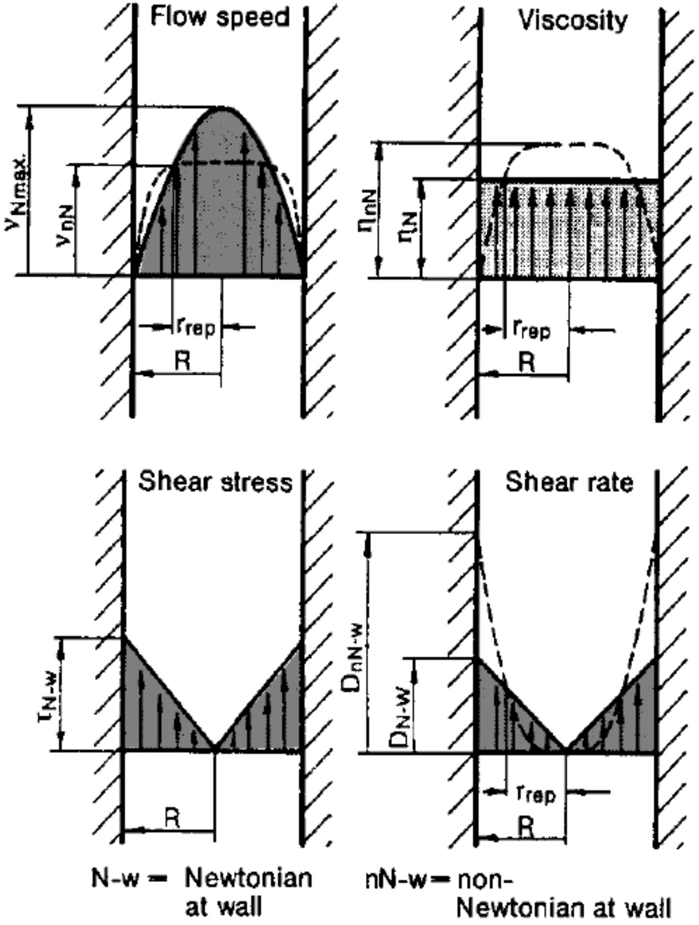


Fig.38 Functions of flow speed, viscosity, shear stress and shear rate in capillary viscometers.

Gebhard Schramm, A practical approach to rheology and rheometry, Gebrueder Haake GmbH, Karlsruhe (ASIN: B000BWY1WA)

Extrusion of cellulose solutions

shear stress at wall: $\tau_R = \left(\frac{R}{2 * \Delta L}\right) * \Delta P$

shear rate at wall: $\dot{\gamma}_R = \left(\frac{4Q}{\pi * R^3}\right)$

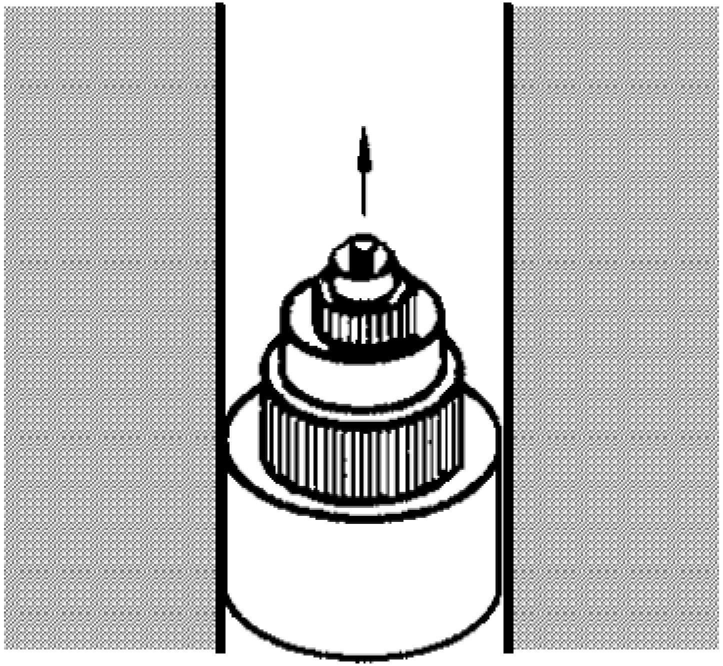
Weissenberg-Rabinowitch correction:

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

With power law assumption (Ostwald-de-Waele):

$$\dot{\gamma}_R = \left(\frac{4Q}{\pi * R^3}\right) * \left(\frac{1 + 3n}{4n}\right)$$

Melt fracture



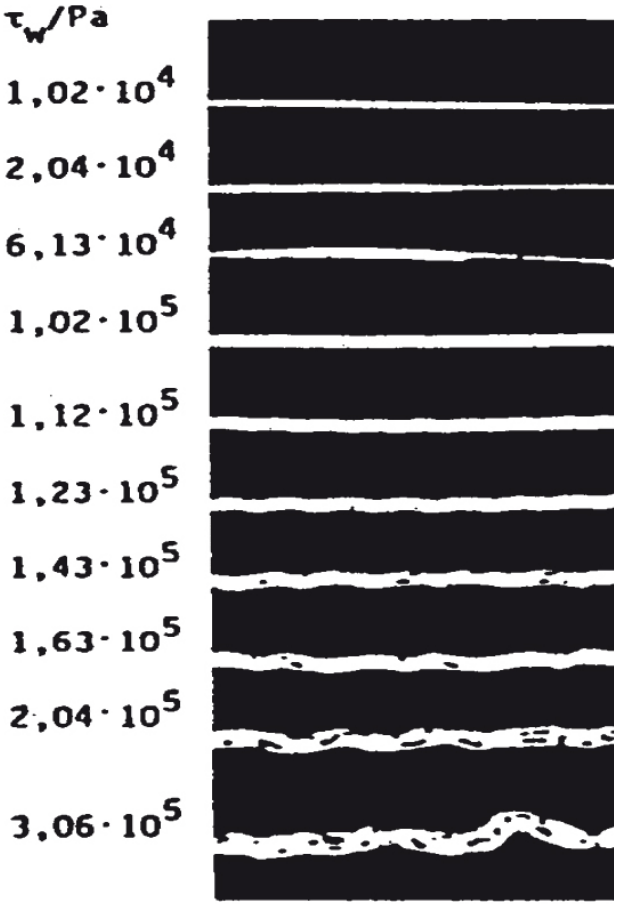
polymers in external layers are subjected to higher shear stress → radial orientation gradient

when solution exits dye, the polymers in the skin area relax and cause a skin contraction

→ system becomes unstable

Gebhard Schramm, A practical approach to rheology and rheometry, Gebrueder Haake GmbH, Karlsruhe (ASIN: B000BWY1WA)

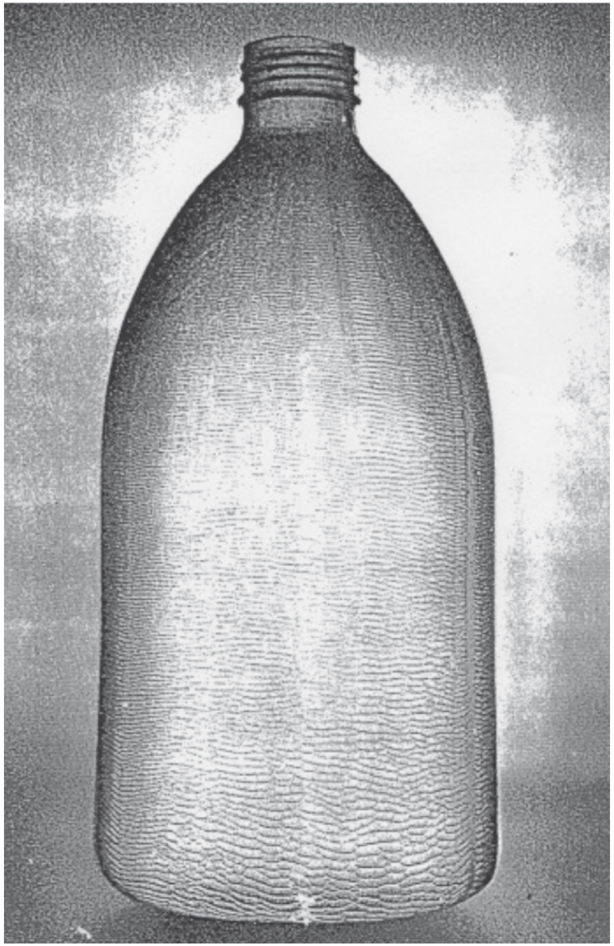
Melt fracture



Polymer melts

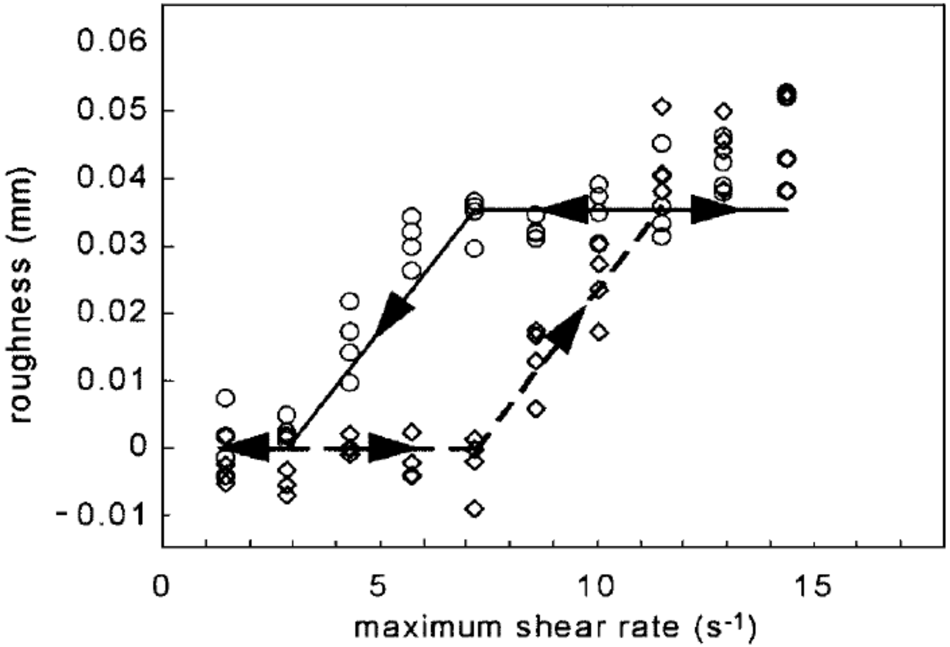
←**Extrusion**
(e.g. polystyrene, PS):
extrudate swelling
and
melt fracture

Blow moulding→
(e.g. polyethylene, PE):
orange peel
or
shark skin



Melt fracture

Transition from smooth to corrugated surface is found to exhibit a dynamical hysteresis



Bertola, V. et al. *Phys. Rev. Lett*. **2003**, 90, 114502.

Melt fracture

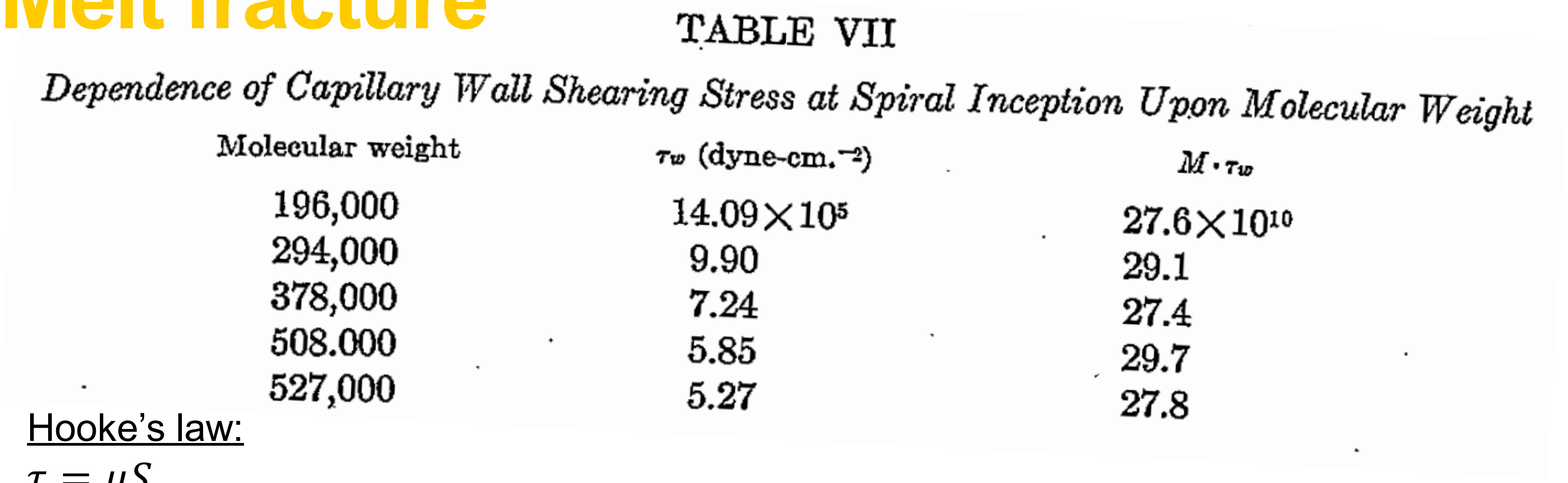


TABLE VII

Dependence of Capillary Wall Shearing Stress at Spiral Inception Upon Molecular Weight

Molecular weight	τ_w (dyne-cm.$^{-2}$)	$M \cdot \tau_w$
196,000	14.09×10^5	27.6×10^{10}
294,000	9.90	29.1
378,000	7.24	27.4
508.000	5.85	29.7
527,000	5.27	27.8

Hooke's law:

$$\tau = \mu S_r$$

$$\tau_w M = (RT\rho) S_{rw}$$

τ… shear stress

S_r… recoverable shear strain

solution:

$$\tau_w M = K * c$$

$$\tau_w M = (RT\rho) S_{rw}$$

$$\tau_w = \frac{5}{2} \frac{cRT}{M_w} S_{rw} \left(\frac{{M_w}^2}{M_z M_{z+1}} \right) \left(a + 2b \frac{cM_w}{\rho M_c} \right)$$

Rouse theory for poly-disperse samples

Aalto University
School of Chemical Engineering

Spencer, R.S. and Dillon R.E. *J. Colloid Sci.* **1949**, 4, 241-255.
Bagley, E.B. *J. Appl. Phys.* **1960,** 31, 1126-1127.
Southern, J.H. and Paul, D.R. *Polym. Enginer. Sci.* **1974,** 14, 560-566.

Melt fracture

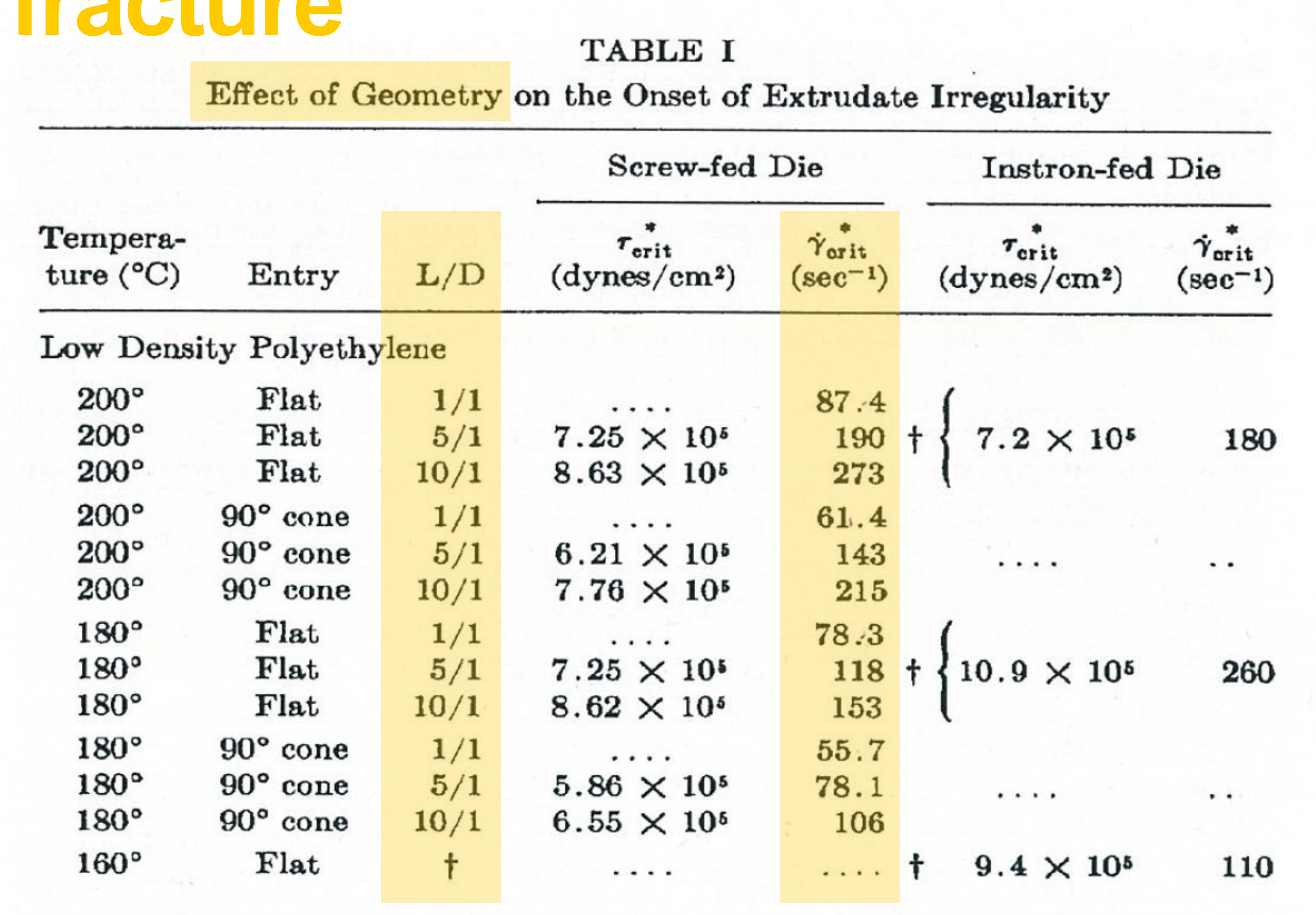


TABLE I

Effect of Geometry on the Onset of Extrudate Irregularity

			Screw-fed Die		Instron-fed Die	
Temperature (°C)	Entry	L/D	τ^*_{crit} (dynes/cm²)	$\dot{\gamma}^*_{\mathrm{crit}}$ (sec⁻¹)	τ^*_{crit} (dynes/cm²)	$\dot{\gamma}^*_{\mathrm{crit}}$ (sec⁻¹)
Low Density Polyethylene						
200°	Flat	1/1	....	87.4	† 7.2 × 10⁵	180
200°	Flat	5/1	7.25 × 10⁵	190		
200°	Flat	10/1	8.63 × 10⁵	273		
200°	90° cone	1/1	....	61.4	....	..
200°	90° cone	5/1	6.21 × 10⁵	143		
200°	90° cone	10/1	7.76 × 10⁵	215		
180°	Flat	1/1	....	78.3	† 10.9 × 10⁵	260
180°	Flat	5/1	7.25 × 10⁵	118		
180°	Flat	10/1	8.62 × 10⁵	153		
180°	90° cone	1/1	....	55.7	....	..
180°	90° cone	5/1	5.86 × 10⁵	78.1		
180°	90° cone	10/1	6.55 × 10⁵	106		
160°	Flat	†	....	....	† 9.4 × 10⁵	110

Ballenger, T.F. et al. *Trans. Soc. Rheol*. **1971**, 15, 195-215.

Melt fracture

transit time: $t^* = \frac{\pi {R_0}^2 \, l_o}{Q}$

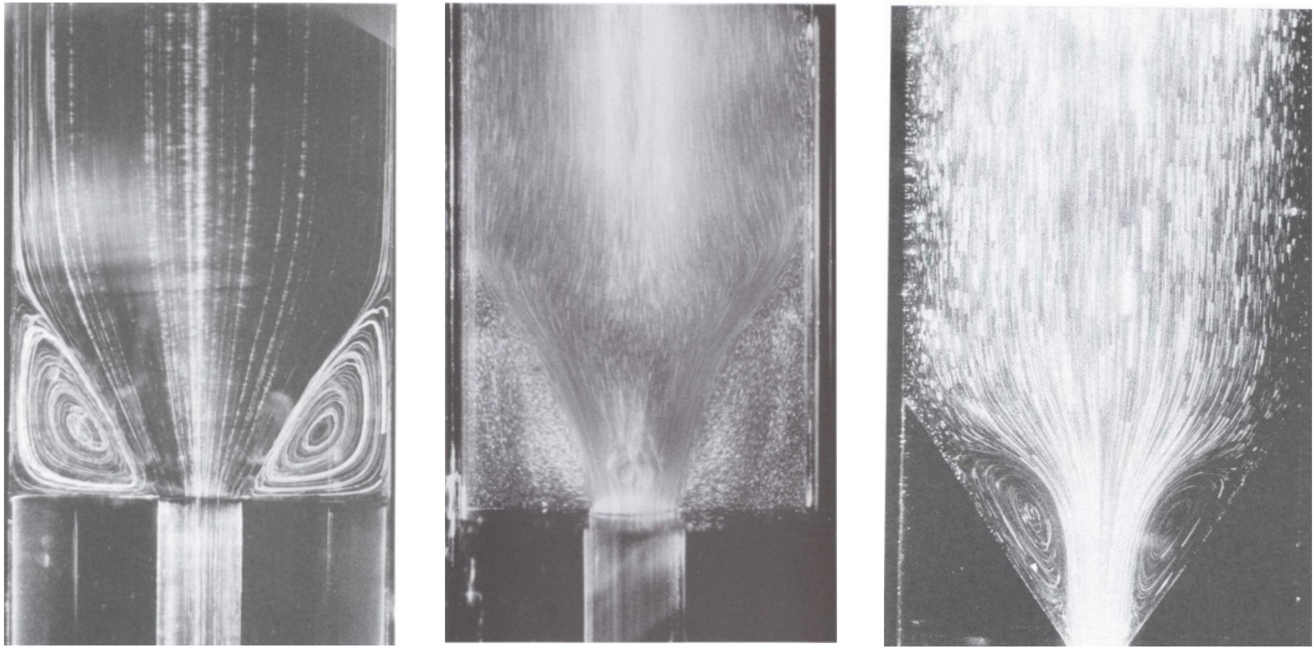
Newtonian fluids:
critical length: $l_{cr} = 0.006 * R_0 \, Re$
critical transit time: $t^*{}_{cr} = 0.12 * \rho R_0/\eta_0$

non-Newtonian fluids:
critical length: $l_{cr} = \frac{C\tau Q}{\pi {R_0}^2}$
critical transit time: $t^*{}_{cr} = C\tau$

C... constant characterizing precision limits within which the steady-state is to be reached (C >1)

Spinneret geometry

- Irregularities in spinneret capillary
- Flow instabilities



Summary questions

- **What is melt fracture?**
- **What is the difference between cohesive and capillary break?**