Aalto University
School of Chemical
Engineering

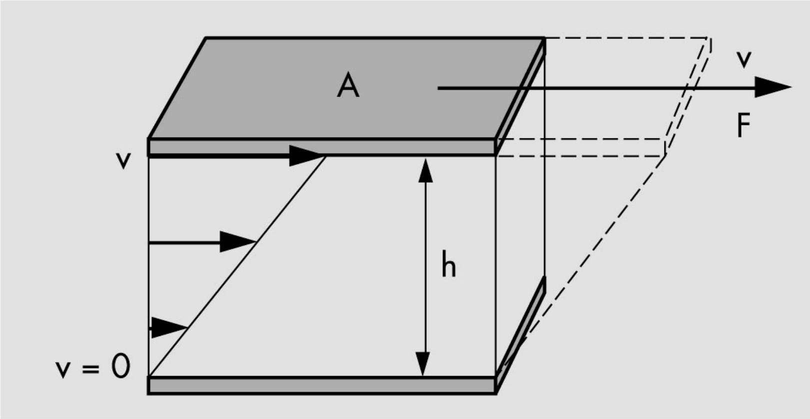
Rheology of cellulose solutions

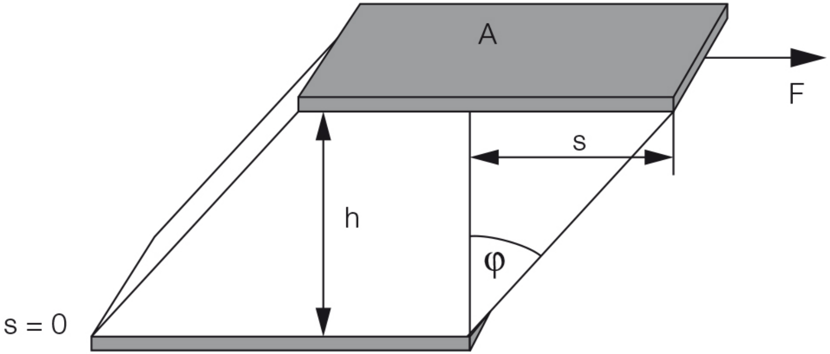
Theory and Practice of Wet Spinning of Cellulose Solutions

Fundamentals

- Anton Paar, Basics of Rheology. Course number: IARBA001
- Gebhard Schramm, A practical approach to rheology and rheometry, Gebrueder Haake GmbH, Karlsruhe (ASIN: B000BWY1WA)
- Thomas G. Mezger, Applied Rheology – With Joe Flow on Rheology Road (ISBN: 978-3-9504016-0-8)

Steady shear tests





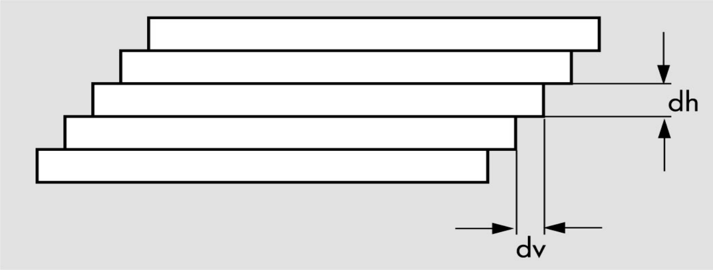
h … plate distance
A … area of upper plate
F … force displacing upper plate sidewards
v … velocity of upper plate (bottom one is fixed)

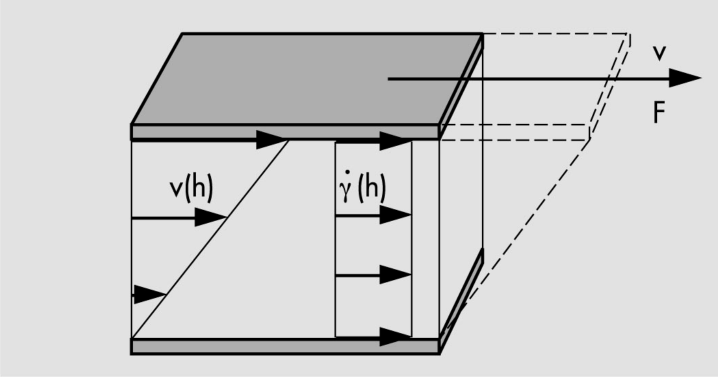
s … deflection path
φ … deflection angle

Shear stress: $\tau = {}^{F}/_{A}$ [Pa]

Shear strain: $\gamma = {}^{s}/_{h}$

Steady shear tests



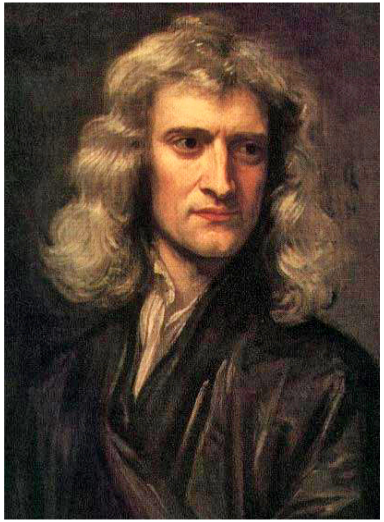


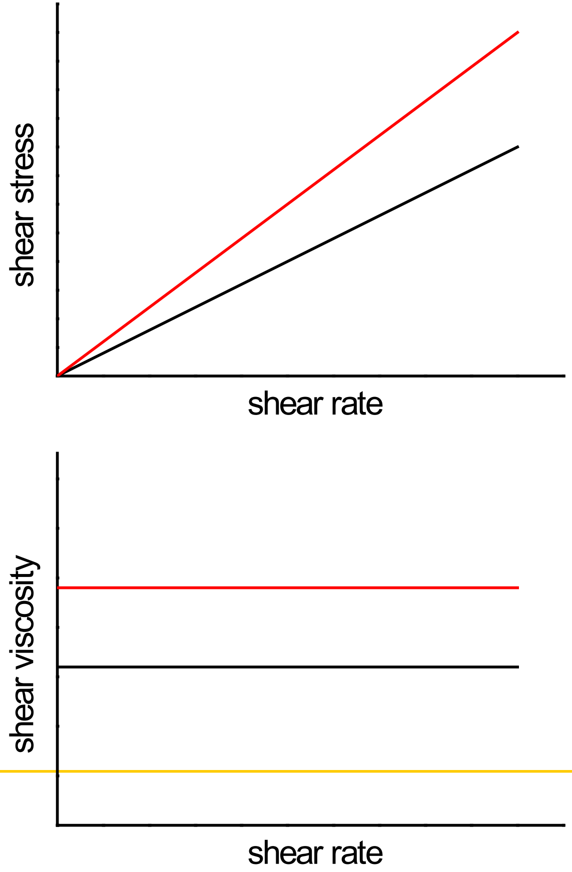
Shear rate: $\dot{\gamma} = {}^{dv}/_{dh}$ $[s^{-1}]$

$$\dot{\gamma} = \frac{d\gamma}{dt} = \frac{{}^{ds}/_{dh}}{dt} = \frac{{}^{ds}/_{dt}}{dh} = \frac{dv}{dh}$$

Newton's law

$$\tau = \eta * \dot{\gamma}$$





Isaac Newton (1642 to 1727); he writes about the flow resistance of fluids (e.g. of air and water).

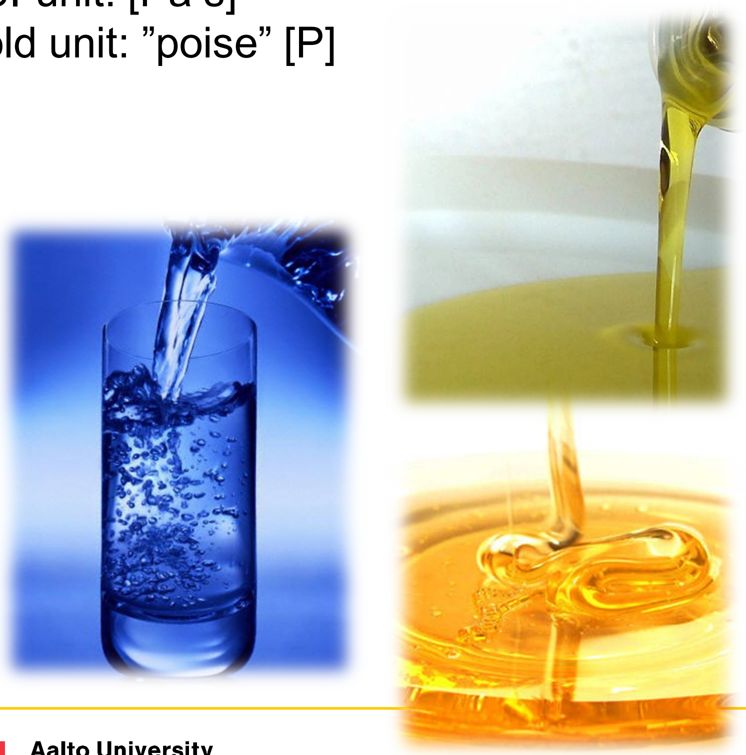
However, this later so-called "Viscosity Law of Newton" was formulated not before the 19 century (e.g. by G.G. Stokes in 1845).

Viscosity values

$$\tau = \eta * \dot{\gamma}$$

SI-unit: [Pa s]
old unit: ”poise” [P]

viscosity = flow resistance of fluids in motion



Material	Shear viscosity η / mPas (20 °C)
air	0.018
water	1.00
ethanol	1.20
olive oil	100
motor oils	50-1000
honey	10000

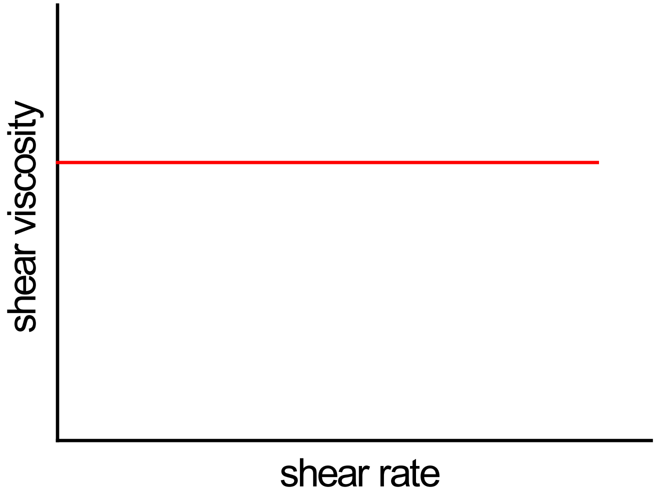
(1P = 0.1 Pas or 1cP = 1mPas)

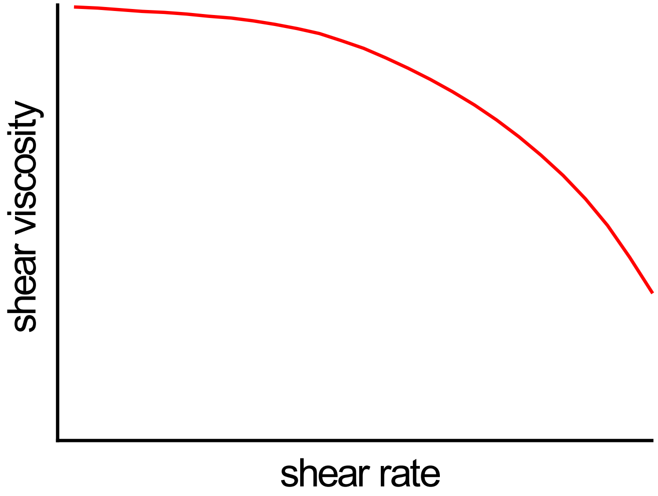
Typical shear rate ranges

Process	**Shear rates (s^{-1})**
Sedimentation	< 0.001 to 0.01
Surface leveling	0.01 to 0.1
Sagging	0.01 to 1
Dip coating	1 to 100
Pipe flow, pumping, filling into containers	10 to 10,000
Mixing, stirring	10 to 10,000
Spinning	10 to 10,000
Coating, painting, brushing	100 to 10,000
Spraying	1000 to 10,000
(High-speed) coating, blade coating	100,000 to 1 mio.

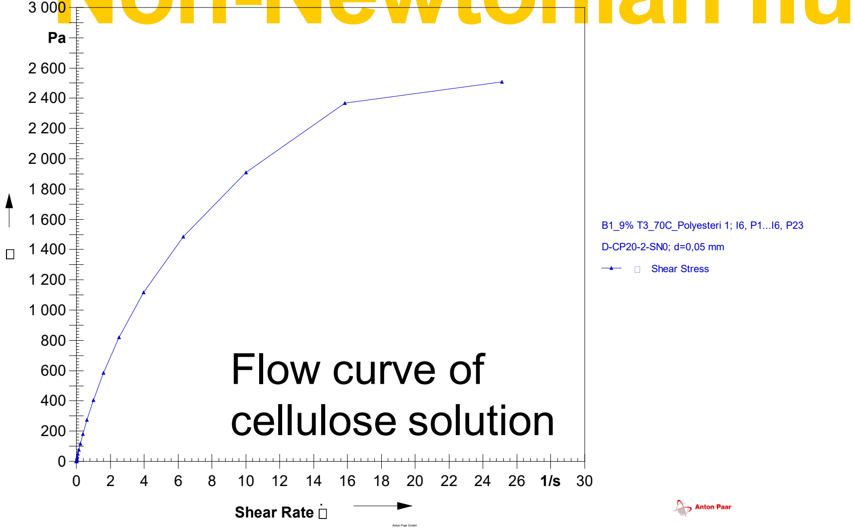
Anton Paar, Rheology of Food. Course number: IARAD002

Non-Newtonian fluid



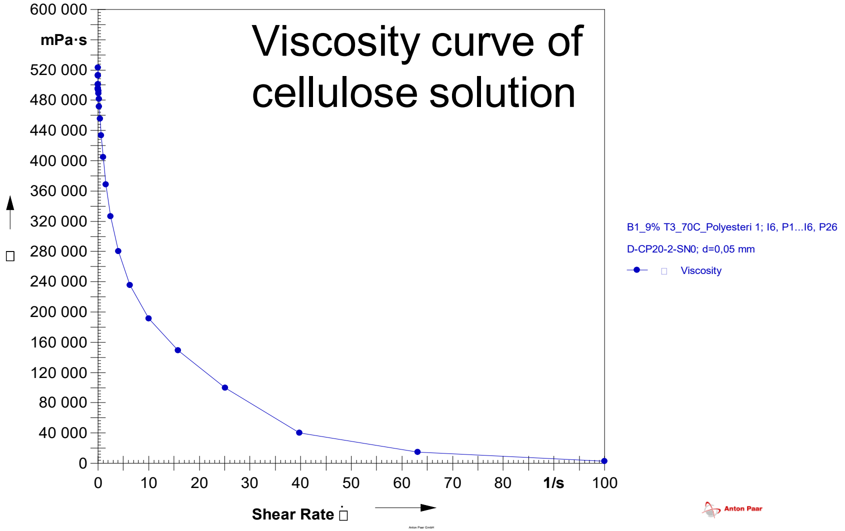


Non-Newtonian fluid

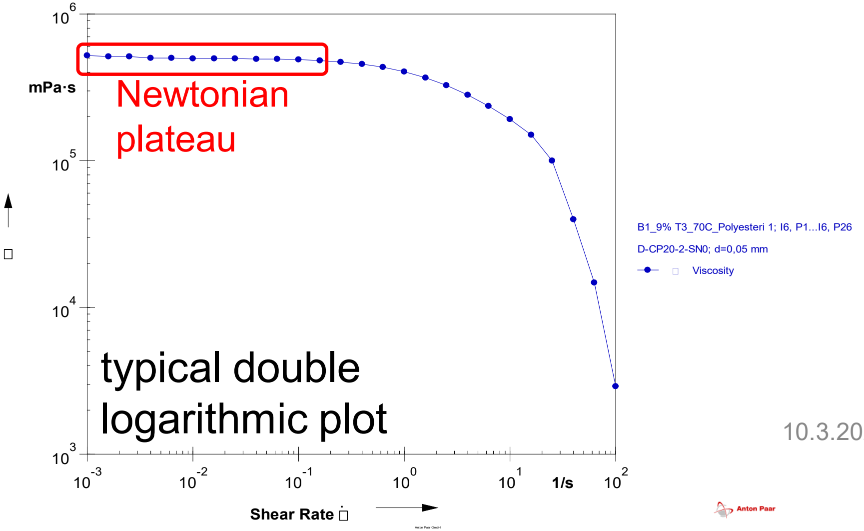


Flow curve of cellulose solution

Polymer melts or solutions show reduced viscosity at high shear rates. This phenomenon is called *shear thinning*



Viscosity curve of cellulose solution

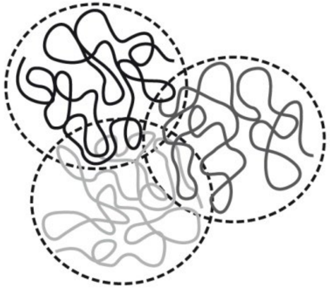


Newtonian plateau

typical double logarithmic plot

Non-Newtonian fluid

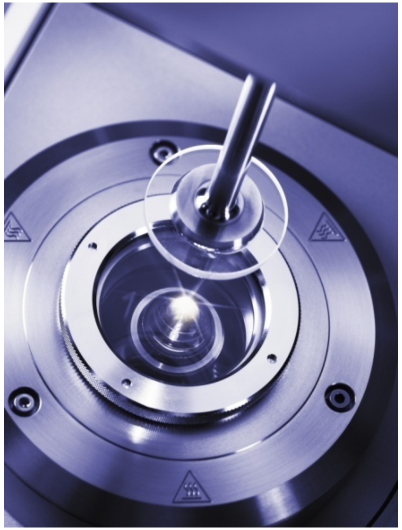
1. Liquids at rest



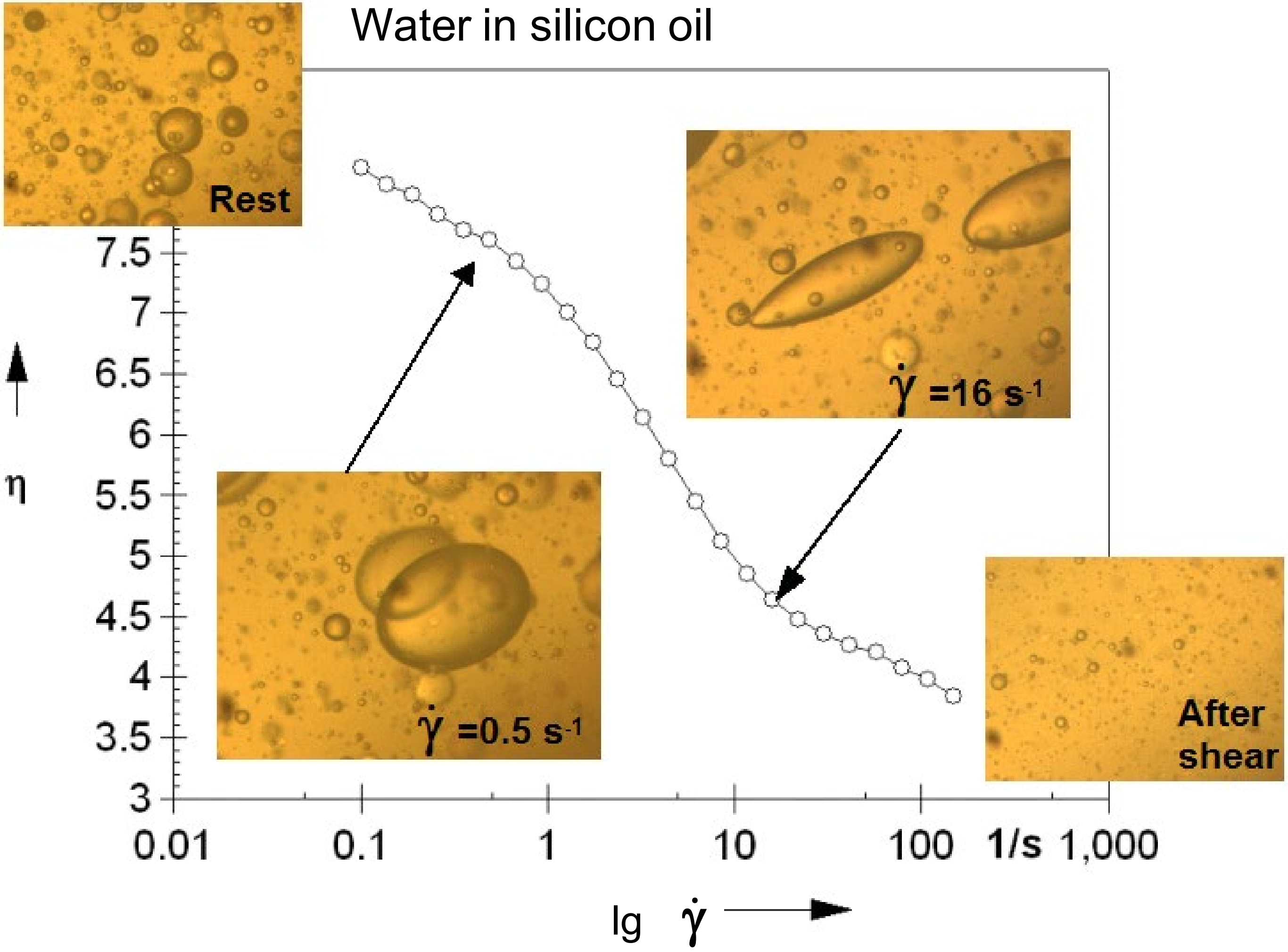
2. Liquids flowing in the direction of the arrows

stretching

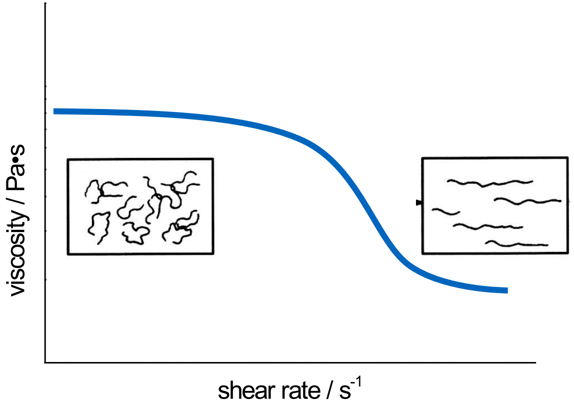
Non-Newtonian fluid

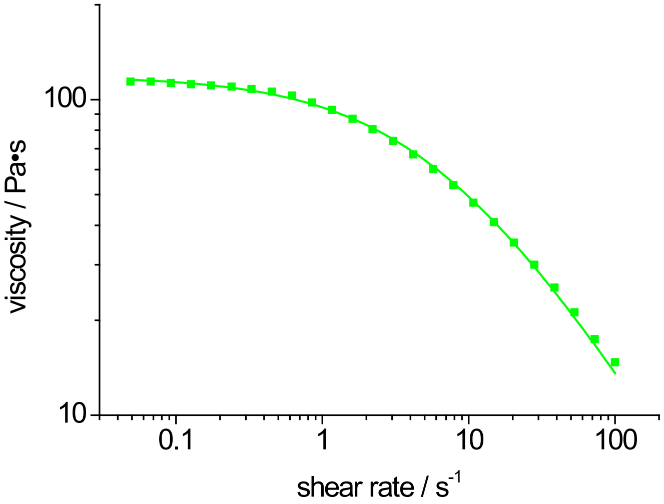


Water in silicon oil



Zero shear viscosity η_0





The viscosity of polymer solutions and melts is dependent on the shear rate. Extrapolation of the viscosity curve to $\dot{\gamma} = 0$ affords the so called *zero shear viscosity* η_0

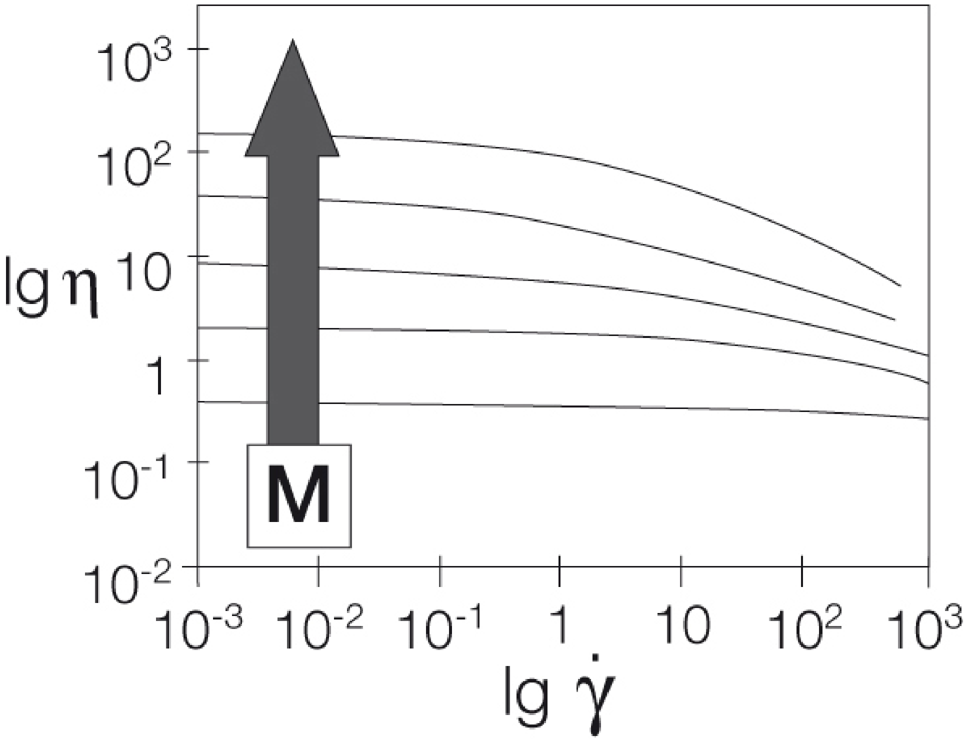
Suitable model functions for concentrated polymer solutions and melts to determine η_0:

$$\eta(\dot{\gamma}) = \frac{\eta_0}{1 + (c * \dot{\gamma})^p}$$ Cross

$$\eta(\dot{\gamma}) = (c * \dot{\gamma})^p$$ Power law (for $\eta(\dot{\gamma}) << \eta_0$)

$$\eta(\dot{\gamma}) = \frac{\eta_0}{(1 + (c * \dot{\gamma})^{p_1})^p}$$ Carreau/Gahleitner

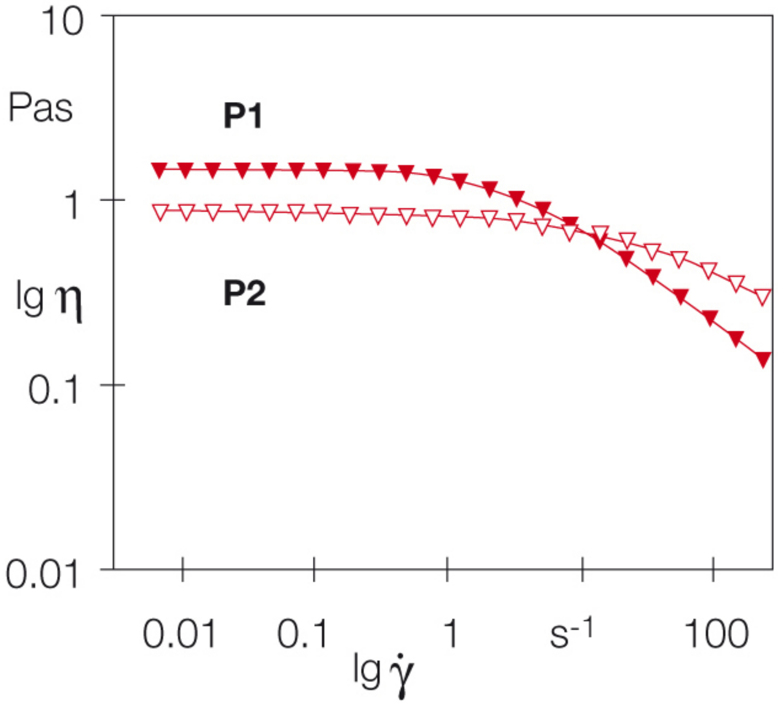
Polymer solution



For solutions containing unlinked polymers

An increasing average molar mass M results in a higher zero shear viscosity value (for a constant polymer concentration)

Polymer solution



Polymer solutions

Unlinked polymers and zero shear viscosity

P1: narrower MMD, with a steeper decrease of the curve

P2: wider MMD

MMD: molar mass distribution

Non-Newtonian behaviors

Phenomenon*	Description
Shear thinning	Viscosity decrease upon shear rate increase
Shear thickening	Viscosity increase upon shear rate increase
Thixotropic behavior	**Time dependent** viscosity decrease upon constant shear load
Rheopectic behavior	**Time dependent** viscosity increase upon constant shear load

*these terms are only applicable if the solute (molecules) are not degraded, i.e. the fluid displays the initial viscosity level after a certain rest phase.

Shear test – Continuous rotation

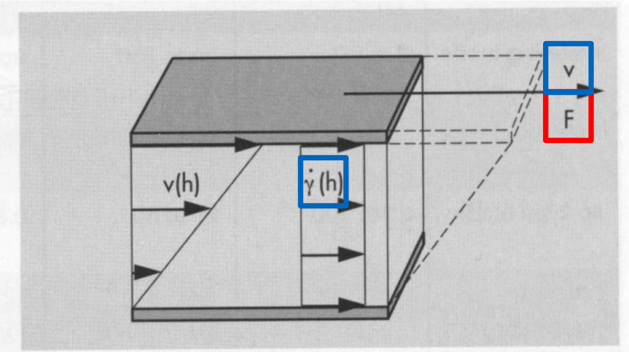
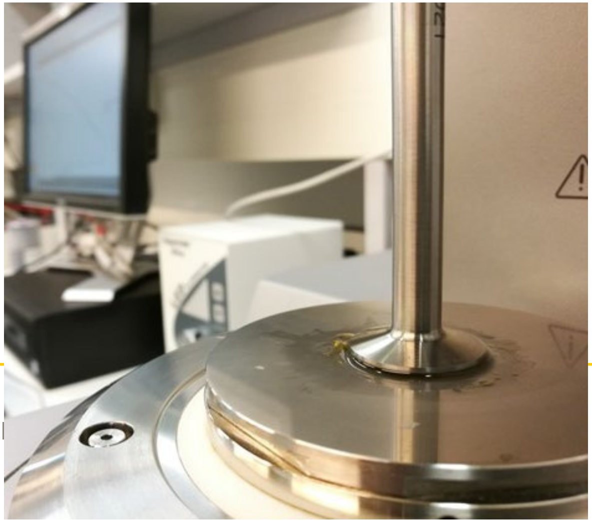


Figure 2.3: Velocity distribution and shear rate in the shear gap of a Two-Plates-Model



Controlled shear rate (CSR): Shear rate (velocity) is set and controlled and shear stress is measured

Controlled shear stress (CSS): Shear stress is set and controlled and shear rate is measured

Shear test – Continuous rotation

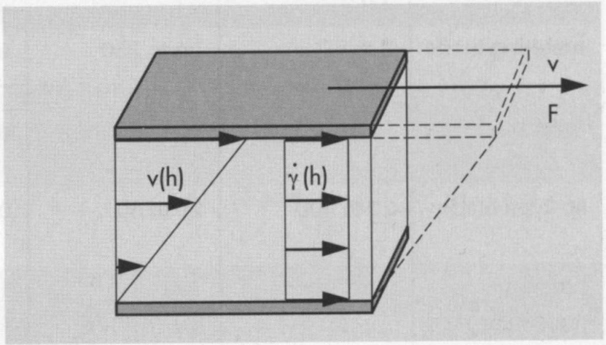


Figure 2.3: Velocity distribution and shear rate in the shear gap of a Two-Plates-Model

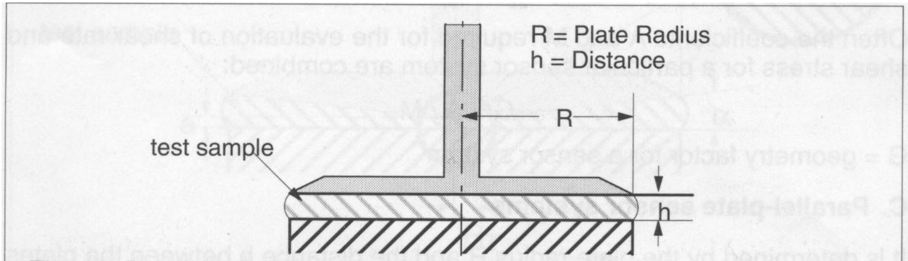


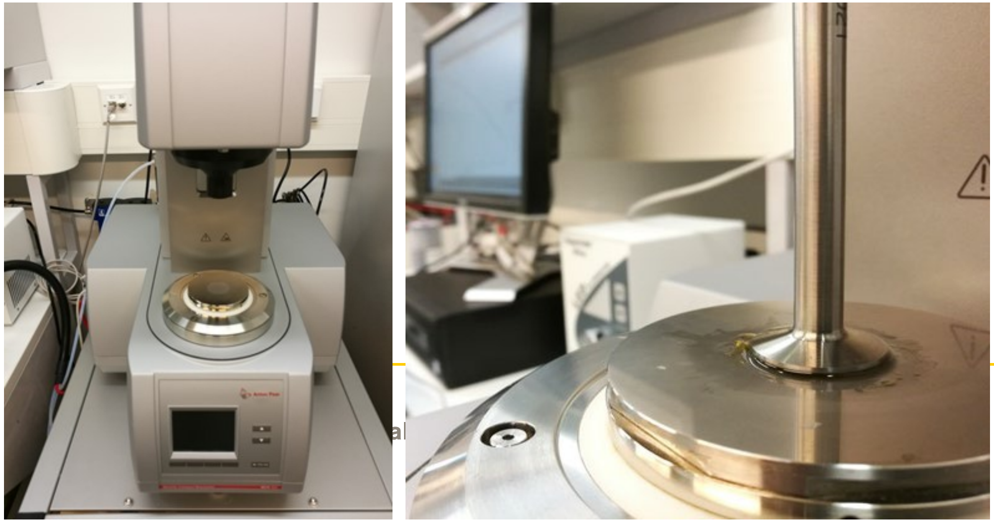
Fig. 28 Parallel-plate sensor system

$$\boldsymbol{\tau} = \frac{2}{\pi R^2} M = C_1 \boldsymbol{M}$$

M…torque [Nm]

$$\dot{\gamma} = \frac{v}{h} = \frac{\omega R}{h} = \frac{2\pi R}{60h} n = C_2 n$$

$$\eta = \frac{\tau}{\dot{\gamma}} = \frac{2\boldsymbol{M}h}{\pi R^4 \omega}$$



ω…angular frequency [rad s^{-1}]

n…rotational speed [min^{-1}]

Shear test

Weissenberg effect

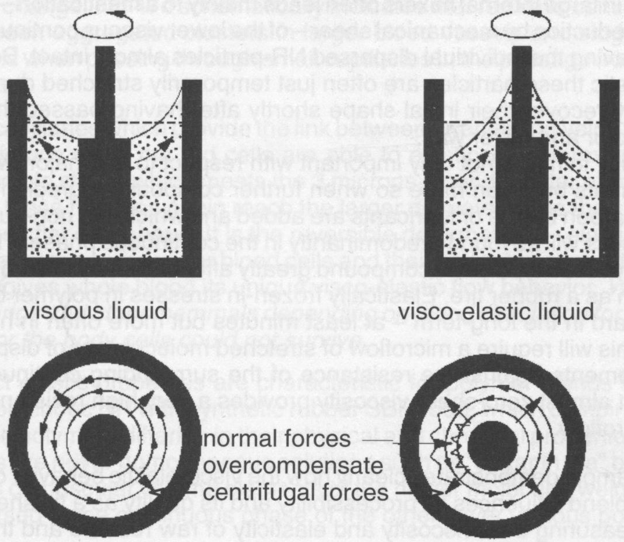


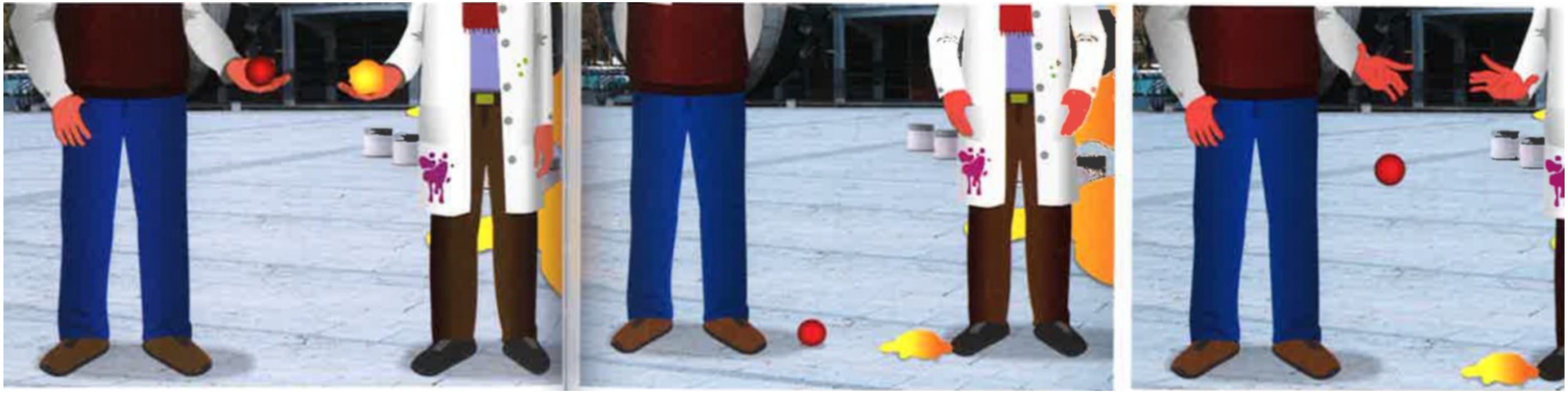
Fig.49 Elastic molecules are stretched more on outer layers and try to escape inwards to a lower energy level

Rotational velocity increases with the radius ($v = \omega r$). Hence, polymer chains are subjected to higher shear stress at the outer layers. To ”escape” this stress they try to move inwards and, subsequently, upwards. This generate a ”normal (perpendicular) stress”

Weissenberg effect

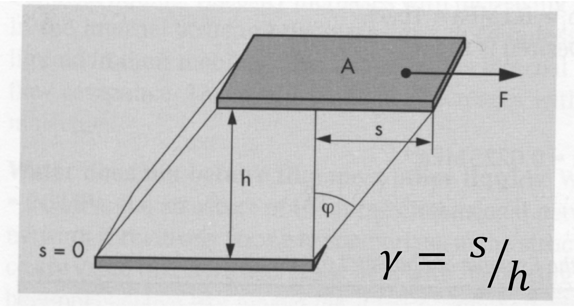
YouTube: https://www.youtube.com/watch?v=npZzlgKjs0I

Visco-elasticity



Metzger – Applied Rheology **2015**, Anton Paar.

Elastic behavior and shear modulus



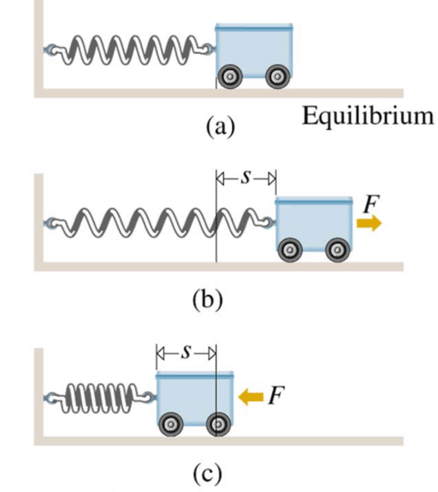
$$\gamma = {}^{s}/_{h}$$

within the linear-elastic range

$$\tau = G * \gamma$$

G… shear modulus [Pa]

Hooke's law:



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within the Hookean range

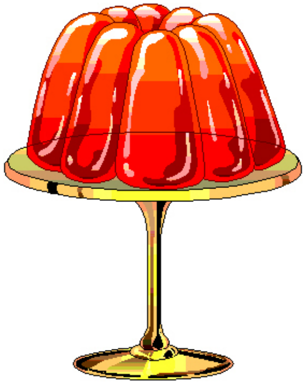
$$F = -k * s$$

k… spring constant [N m^{-1}]

Robert Hooke (1635 to 1703); in 1676 he describes **for solids proportionality of force and deformation**.

However, the laterly so-called **“Elasticity Law of Hooke”** was formulated not before the 19. century (e.g. by T. Young in 1807, or A.L. Cauchy in 1827).

Elastic behavior and shear modulus



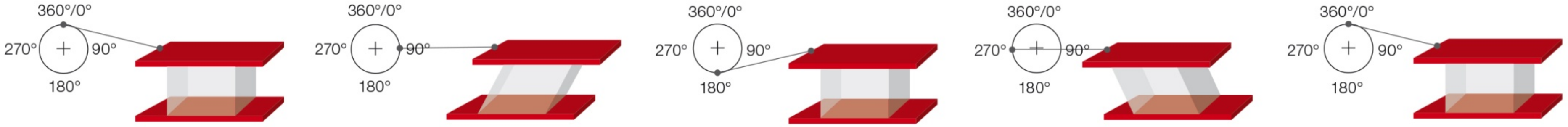
Material	Shear modulus G / Pa (20 °C)
salad dressing	≈10
cosmetics	≈500
puddings	≈5 000
gummi bears	≈100 000
PE-LD	≈100 000 000
PE-HD	≈500 000 000
window glass	≈30 000 000 000
steel	≈80 000 000 000

Elastic behavior and shear modulus

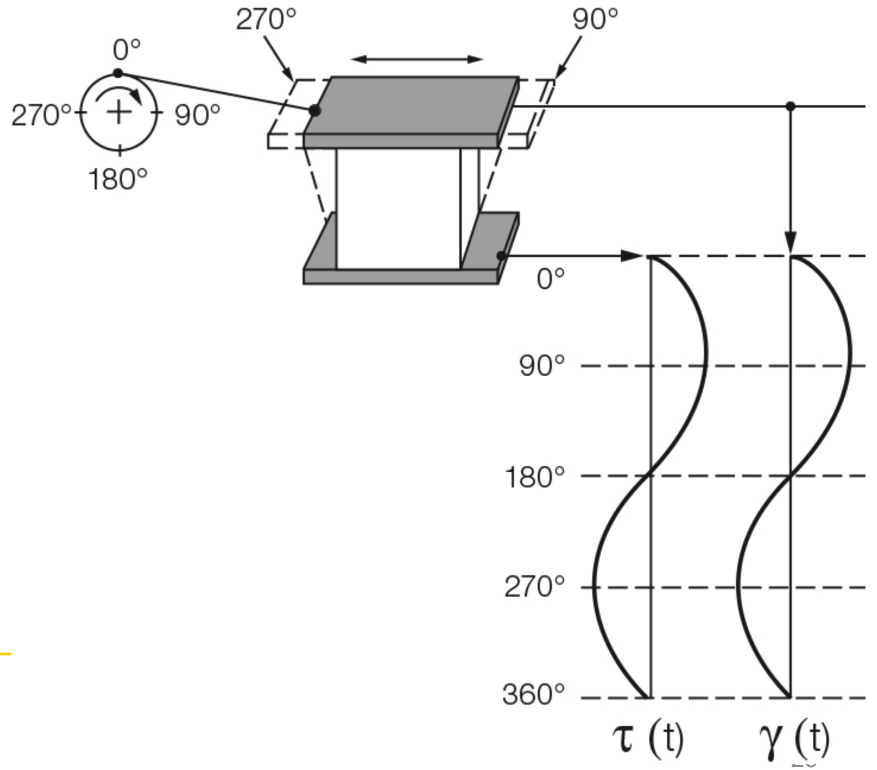
Cheese type	**Example**	**Shear modulus** (around)
1 cream	Philadelphia	1 kPa
2 soft	French Camembert	10 kPa
3 semi-hard	Holland Gouda (young)	0.1 MPa
4 hard	Swiss Emmentaler	0.5 MPa
5 extra hard	Italian Parmigiano	1 MPa

Anton Paar, Rheology of Food. Course number: IARAD002

Oscillatory tests



Two plates model, equipped with two sensors, on top: preset of deflection path (strain or deformation) bottom: measurement of resulting force (shear stress)



Sinusoidal preset

For ideally elastic behavior of a totally stiff sample (e.g. a stone or steel):

- There is no time shift between the sine curves of preset strain and resulting shear stress:
- The curves of γ and τ are “in phase”

$$G^* = \frac{\tau(t)}{\square\, t)}$$

$i = \sqrt{-1}$…imaginary unit

G'…**storage modulus** [Pa]: refers to stress energy that is stored upon deformation and completely recovered after removal of the external stress

G''…**loss modulus** [Pa]: refers to energy that is lost during shear induced flow (energy dissipation)

$$G^* = G' + iG''$$

$$G' = \frac{\tau_A}{\gamma_A} * \cos(\delta)$$

$$G'' = \frac{\tau_A}{\gamma_A} * \sin(\delta)$$

$$|G^*| = \sqrt{(G')^2 + (G''^2)}$$

$$\frac{G''}{G'} = \frac{\sin(\delta)}{\cos(\delta)} = \tan(\delta)$$

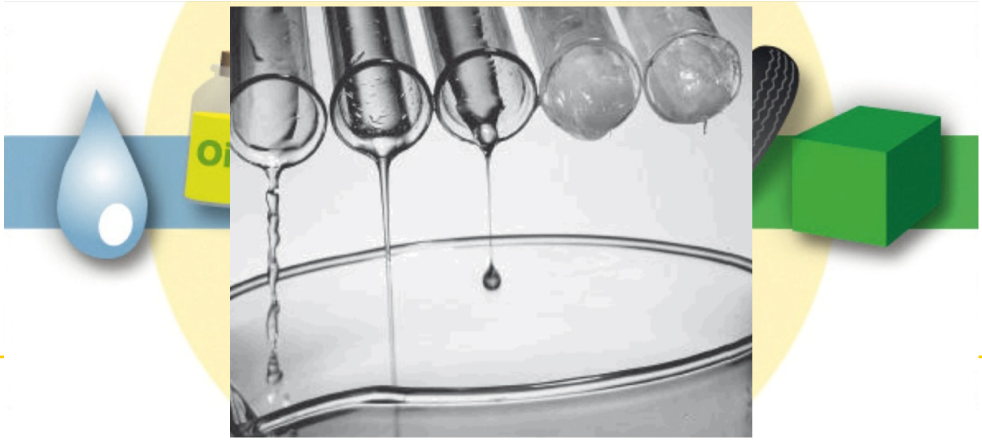
$$|G^*| = \omega * |\eta^*|$$

$|\eta^*|$…**complex (dynamic) viscosity**

Note: G', G'', η^*, and δ are frequency dependent! Therefore, a test requires to measure a whole frequency range (ω) = frequency sweep.

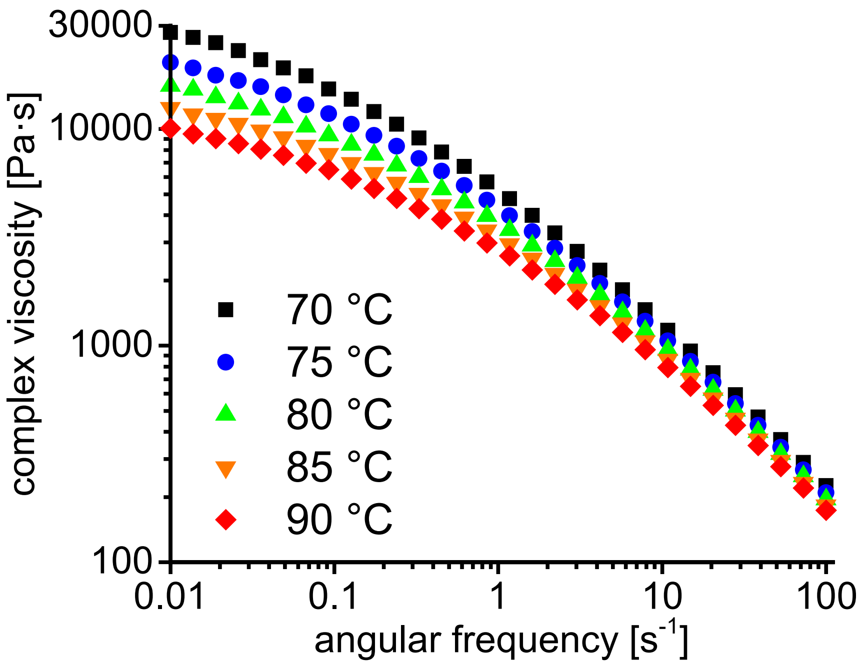
Viscoelasticity: summary

Idealviscous flow behavior	Behavior of a viscoelastic liquid (sol)	Sol/gel transition point	Behavior of a viscoelastic solid (gel)	Idealelastic deformation behavior
$\delta = 90^\circ$	$90^\circ > \delta > 45^\circ$	$\delta = 45^\circ$	$45^\circ > \delta > 0^\circ$	$\delta = 0^\circ$
$\tan(\delta) \to \infty$	$\tan(\delta) > 1$	$\tan(\delta) = 1$	$\tan(\delta) < 1$	$\tan(\delta) \to 0$
$G' \to 0$	$G'' > G'$	$G' = G''$	$G' > G''$	$G'' \to 0$



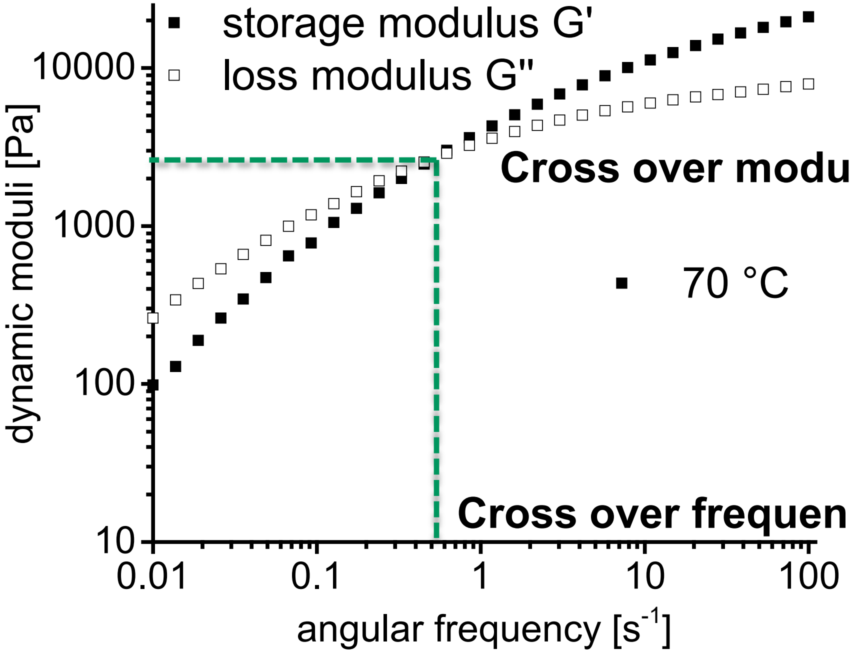
Solutions with direct solvents

Frequency sweep



Oscillatory frequency sweep measurements provides complex viscosity as function of angular frequency

Frequency sweep

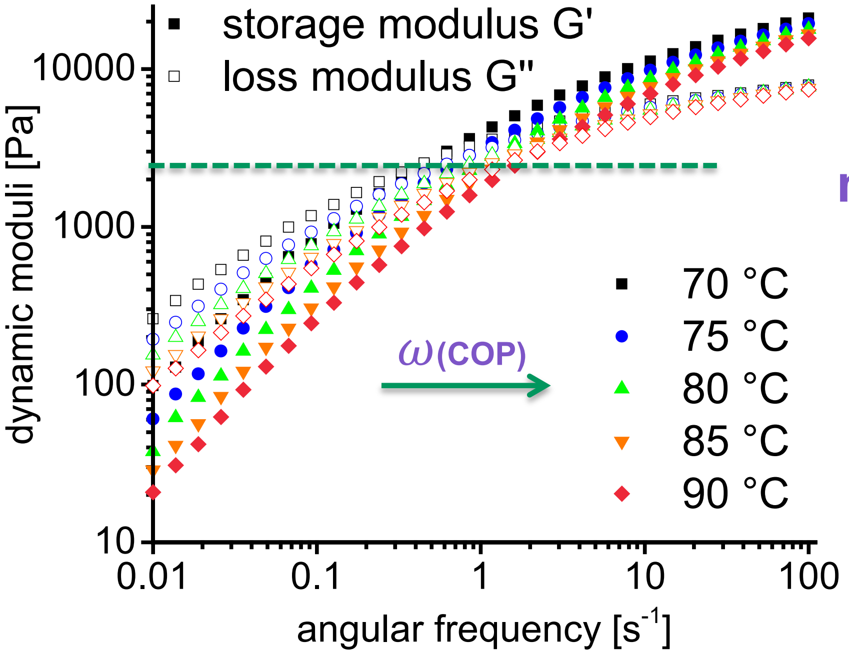


Cross over modulus

Cross over frequency $\omega = {}^{1}/_{\tau}$

Visco-elasticity described by storage and loss moduli

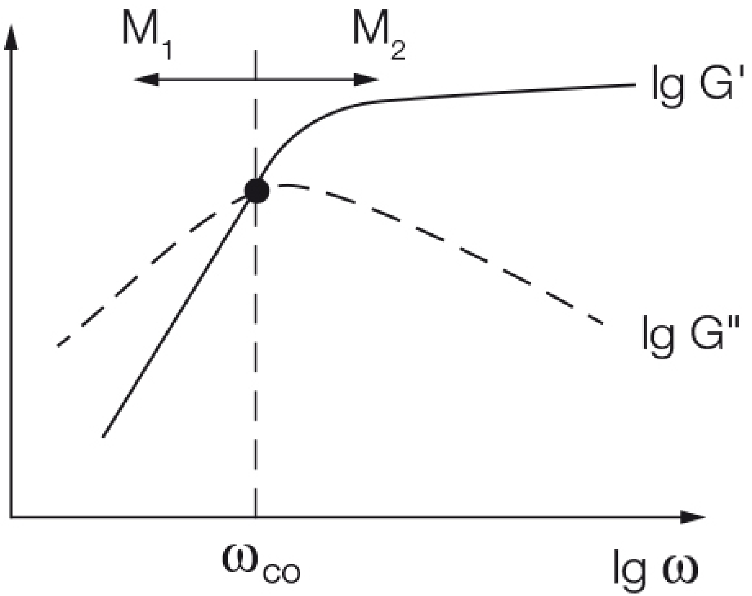
Frequency sweep

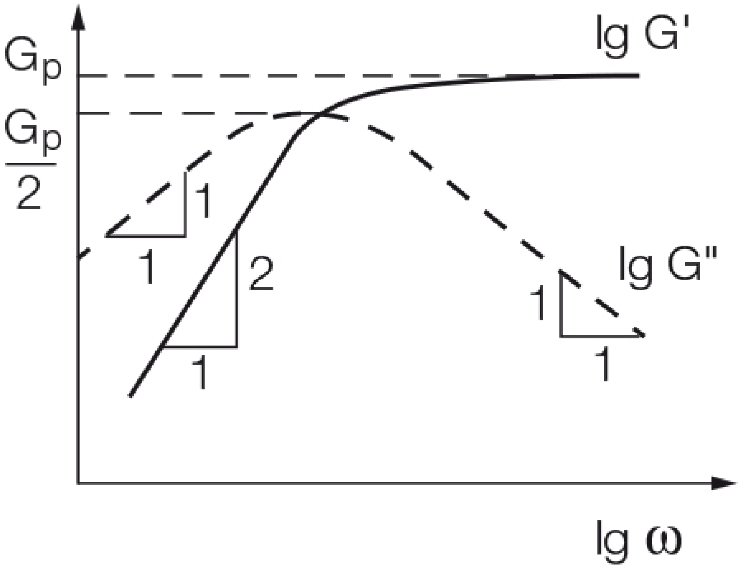


G_{COP} does not change much

Visco-elasticity affected by the temperature

Frequency sweep





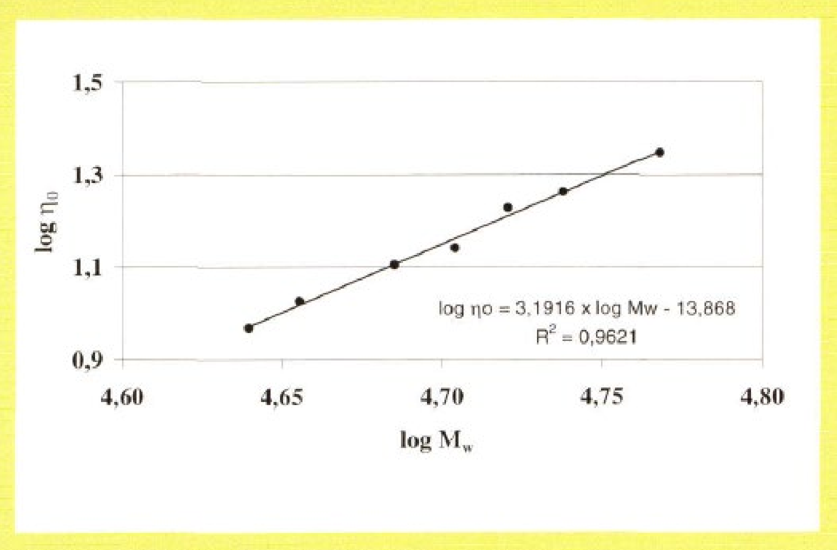
Average molar mass M

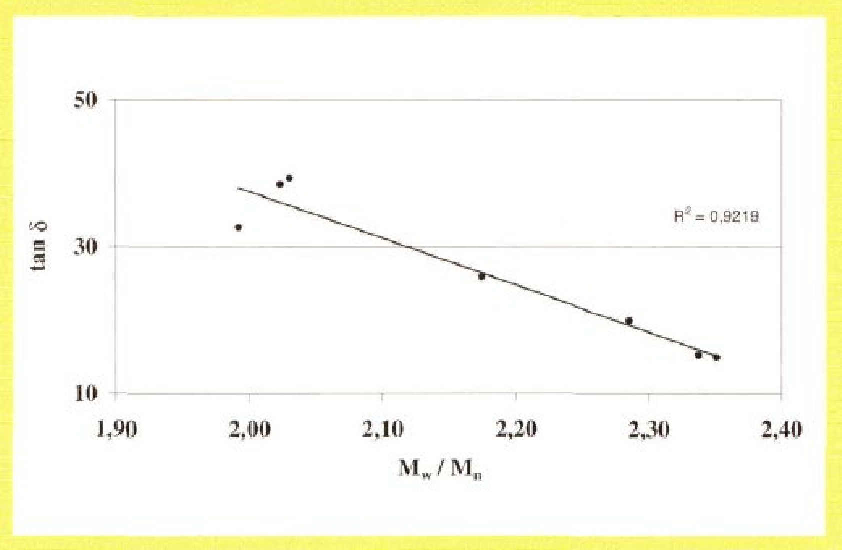
Position of the
crossover point G' = G",
depends on M (here: $M_1 > M_2$)

Maxwellian behavior

In the range of low frequencies
G"(ω) and G'(ω) show the
slopes of 1:1 and 2:1

Determination of molar mass



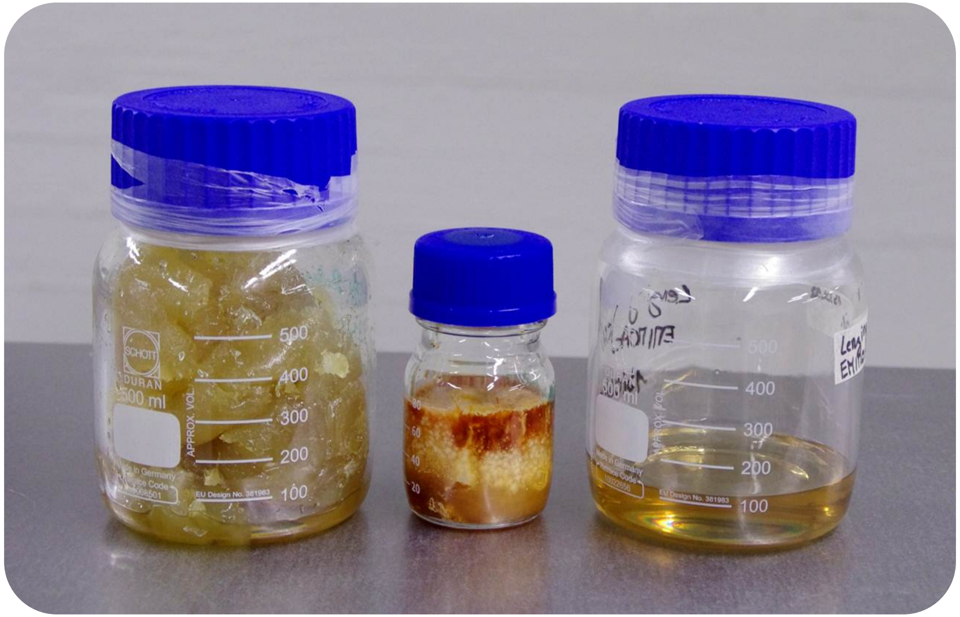


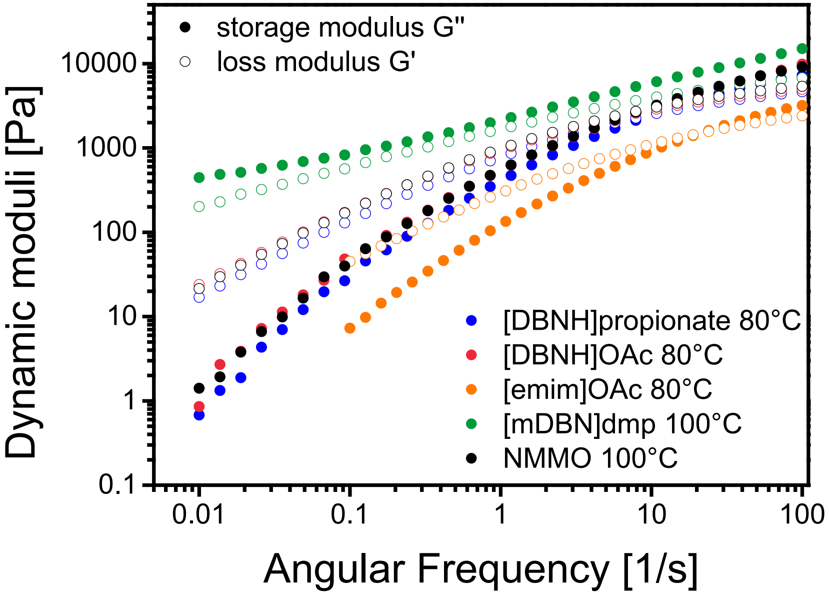
Correlation between zero shear viscosity η_0 and weight average molar mass M_w

Correlation between tan(δ) and polydispersity index M_w/M_n

Schausberger and Möslinger, *Das Papier.* **1999**, 12, 715-721.

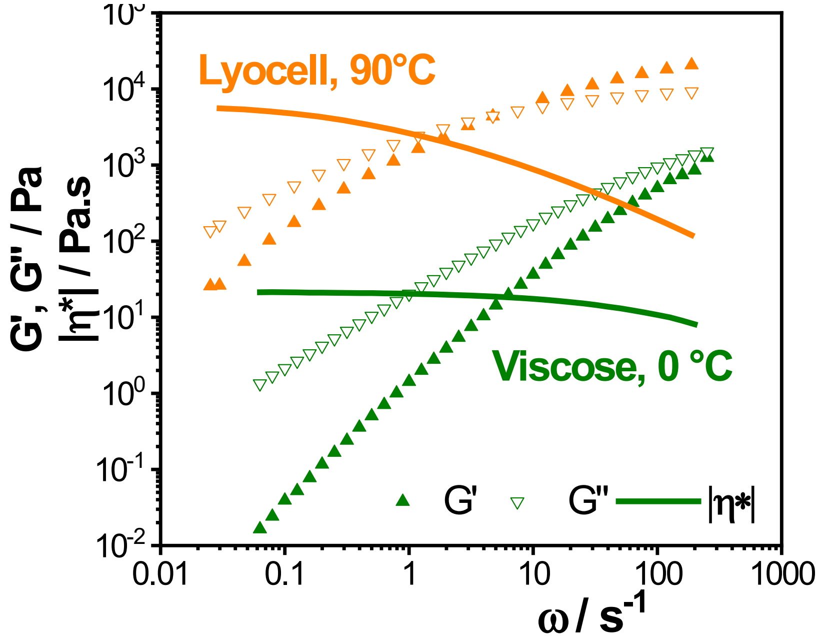
Pulp solutions





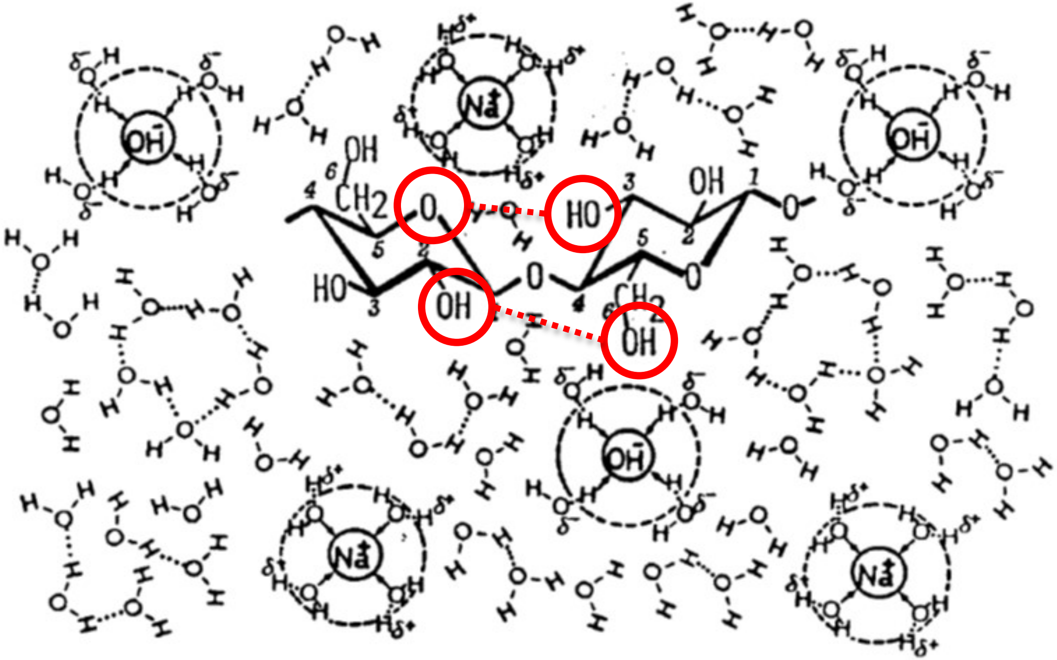
Eucalyptus PHK pulp, 10 wt-%

Viscose vs Lyocell vs Ionic liquids



Aqueous solutions

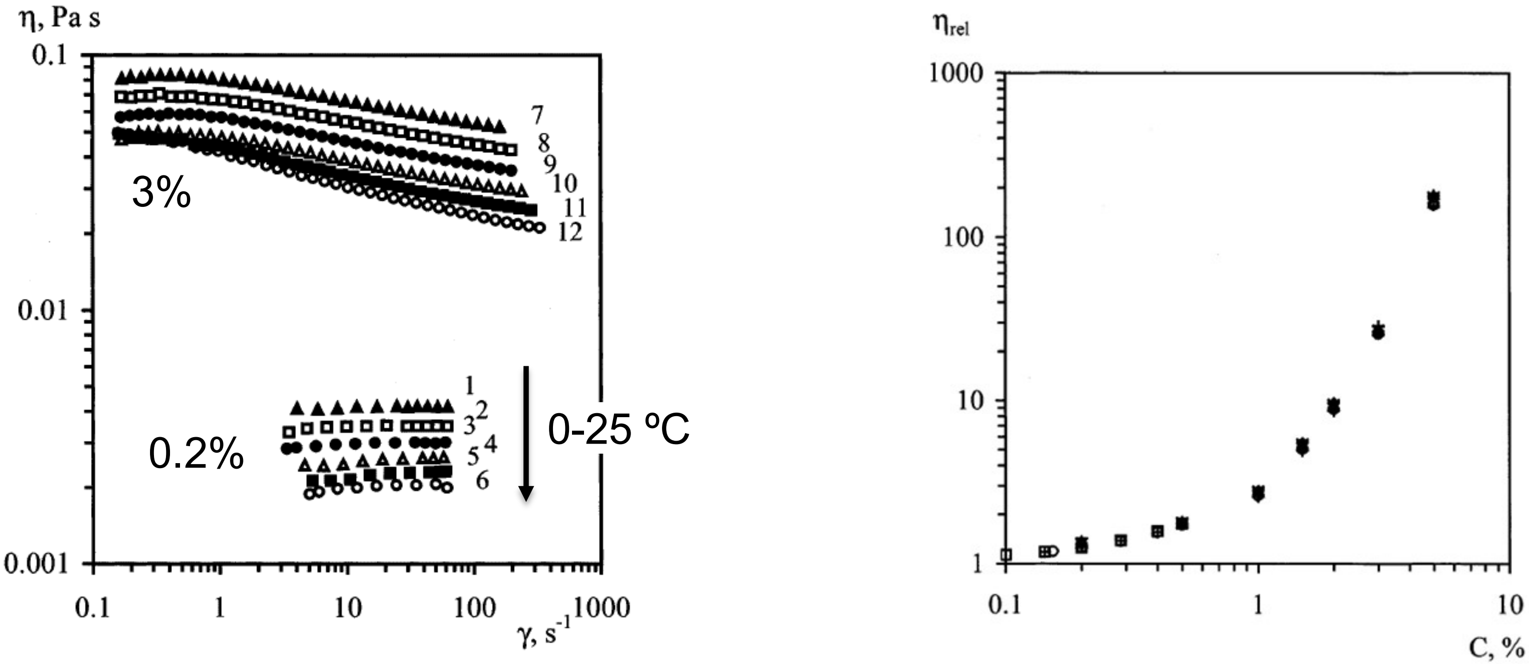
NaOH solutions



Deconstruction of intramolecular O_3-H…O_5' and O_2-H…O_6' H-bonds

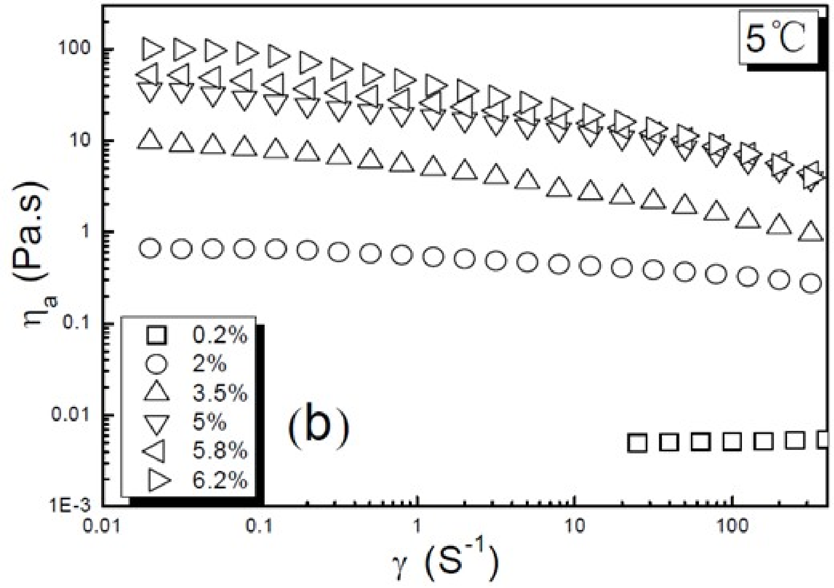
Yamashiki *et al. Polym. J.* 1988, 20, 447-457
Kamide *et al. Cell. Chem. Technol.* 1990, 24, 23-31

NaOH solutions



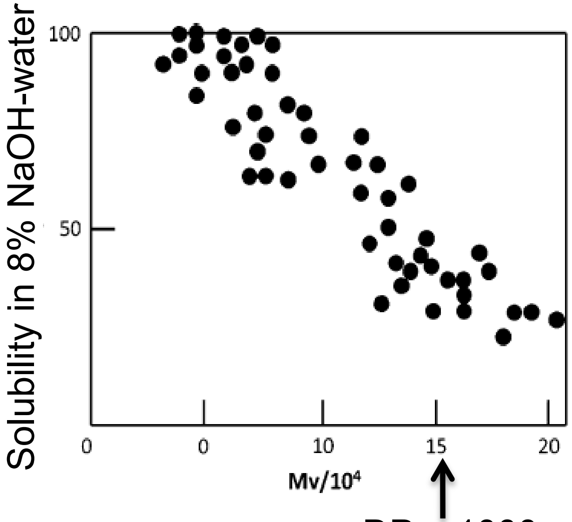
Roy, Budtova, Navard *Biomacromolecules* 2003, 4, 259-264

NaOH solutions



Zhang, Li, Yu *Cellulose Chem. Technol.* 2011, 45, 313-320

NaOH solutions



DP ~ 1000

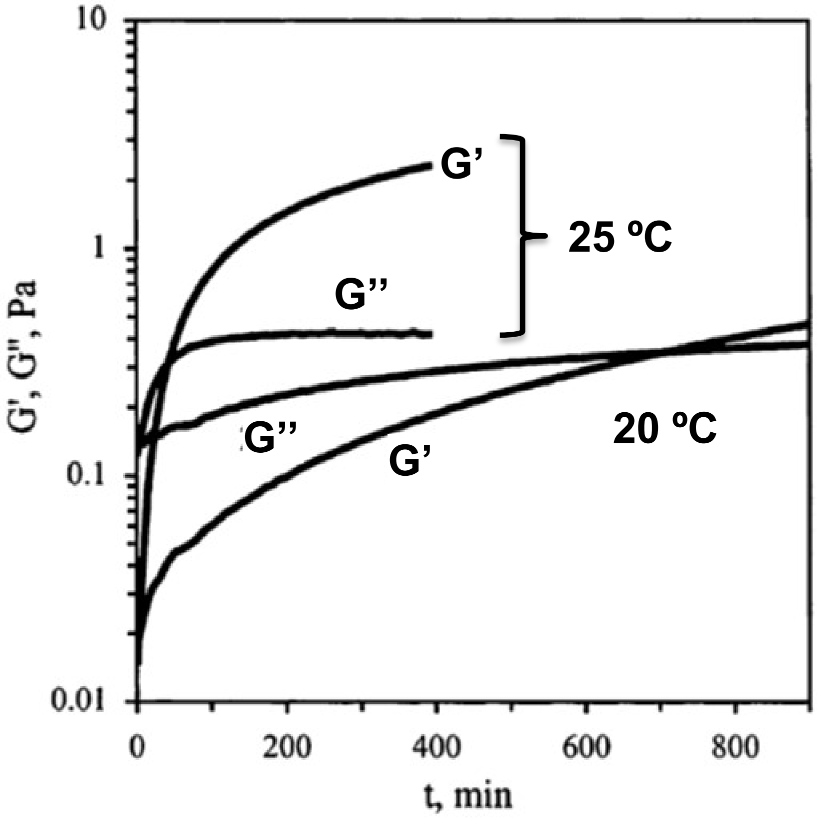
- Major limitation of NaOH as solvent: solubility of cellulose strongly dependent on DP
- Upper limit for cellulose concentration;
- Limited mechanical properties of regenerated products

Aalto University
School of Chemical Engineering

Budtova, Navard *Cellulose* 2016, 23, 5-55
Kamide *et al. Polym. J.* 1992, 24, 71-96

NaOH solutions

- tendency of solutions to gel irreversibly
- Gelling over time
- Pronounced gelling upon temperature increase



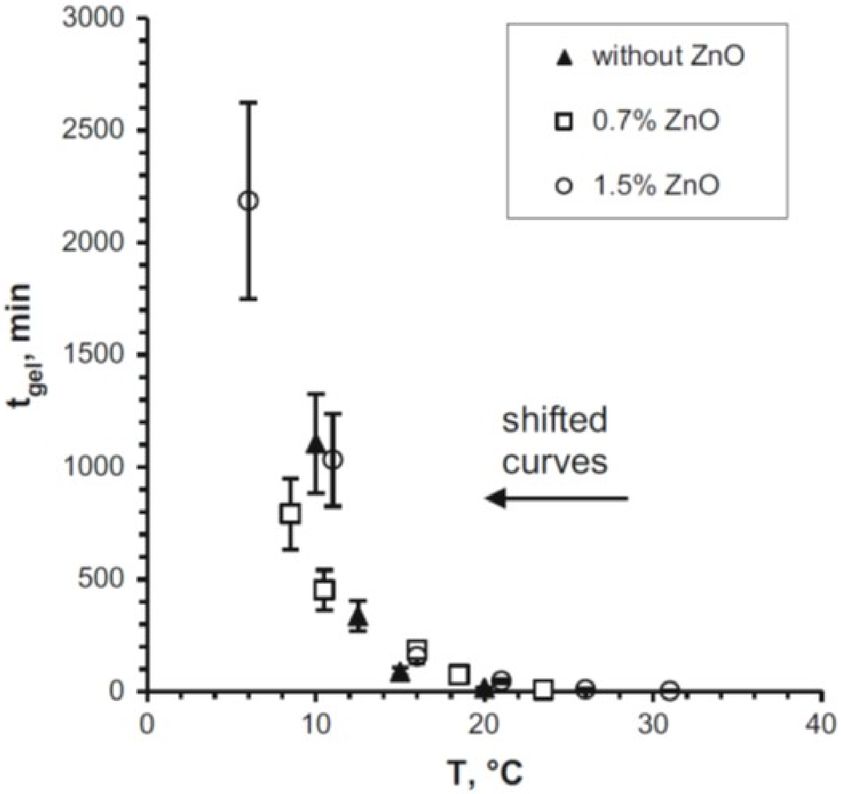
Roy *et al. Biomacromolecules* 2003, 4, 259-264

NaOH solutions – additives

Various additives tested:

- amongst longest know: ZnO
- also urea and thiourea

No confirmed effect on solubility maximum; but stabilization of solution state and hampering of gelation



Liu *et al. Cellulose* 2011, 18, 663-673

Summary questions

- What is viscoelasticity?
- How does the temperature affect viscoelasticity?
- How does the polymer molecular weight affect viscoelasticity?
- Compare aqueous and direct cellulose solutions in terms of their viscoelastic properties