Rheology and Rheometry

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What is Rheology?

$\rho\varepsilon\iota\nu =$ flow

Rheology = The Science of Deformation and Flow

Why do we need it?

- measure fluid properties
- understand structure-flow property relations
- modelling flow behaviour
- simulate flow behaviour

of melts under processing conditions

Processing conditions	shear rate [s^{-1}]
Sedimentation	10^{-6} – 10^{-4}
Leveling	10^{-3}
Extrusion	10^{0}-10^{2}
Chewing	10^{1} -10^{2}
Mixing	10^{1}-10^{3}
Spraying, brushing	10^{3} -10^{4}
Rubbing	10^{4} -10^{5}
Injection molding	10^{2} -10^{5}
coating flows	10^{5} -10^{6}

How about Newtonian behaviour?

1. Constant viscosity

2. No time effects

3. No normal stresses in shear flow

4. η(ext)/η(shear) = 3

Symbols: $\varepsilon^{\circ} \Rightarrow$ D

$\sigma \Rightarrow$T

s $\Rightarrow \sigma$

Newton's law: T = -pI +η 2D

Contents

1. Rheological Phenomena:

Do real melts behave according to Newton's law?

Deviation 1:

Mayonnaise: resistance (viscosity) decreases with increasing shear rate: shear thinning

Starch solution: resistance increases with increasing shear rate: shear thickening

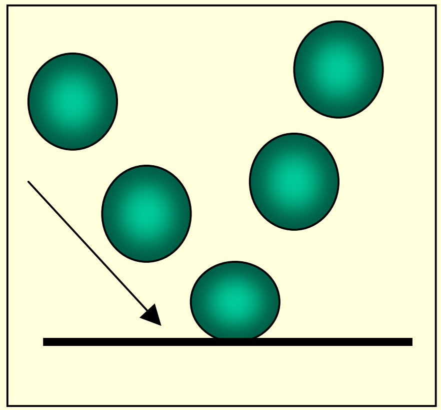
This is a non-linearity:

$$\boxed{\eta(\dot{\gamma})}$$

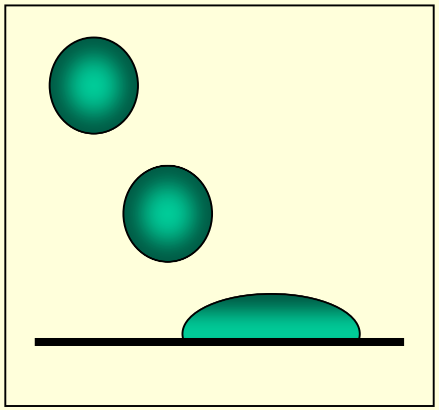
Do real melts behave according to Newton's law?

Deviation 2: example silly putty

$t < \tau$



$t > \tau$



The response of the material depends on the time scale:
* Short times: elastic like behaviour
* Long times: liquid-like behaviour

VISCO-ELASTIC BEHAVIOUR

$G(t)$ or $G(t,\gamma)$

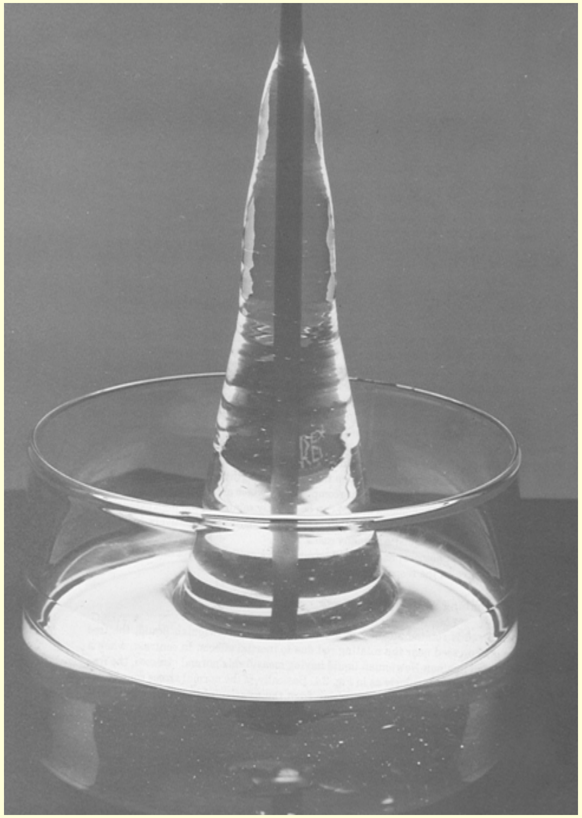
Linear

non-linear

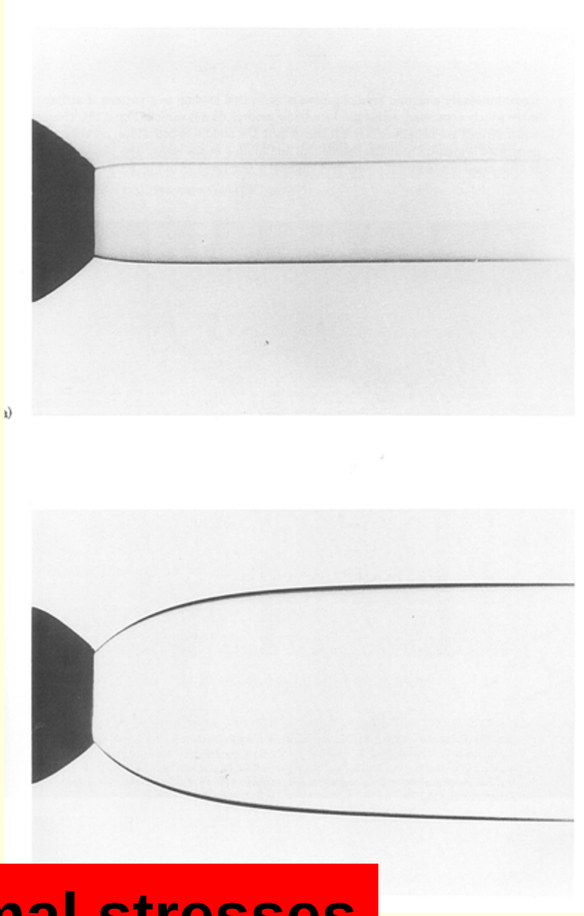
Do real melts behave according to Newton's law?

Deviation 3:

Weissenberg effect



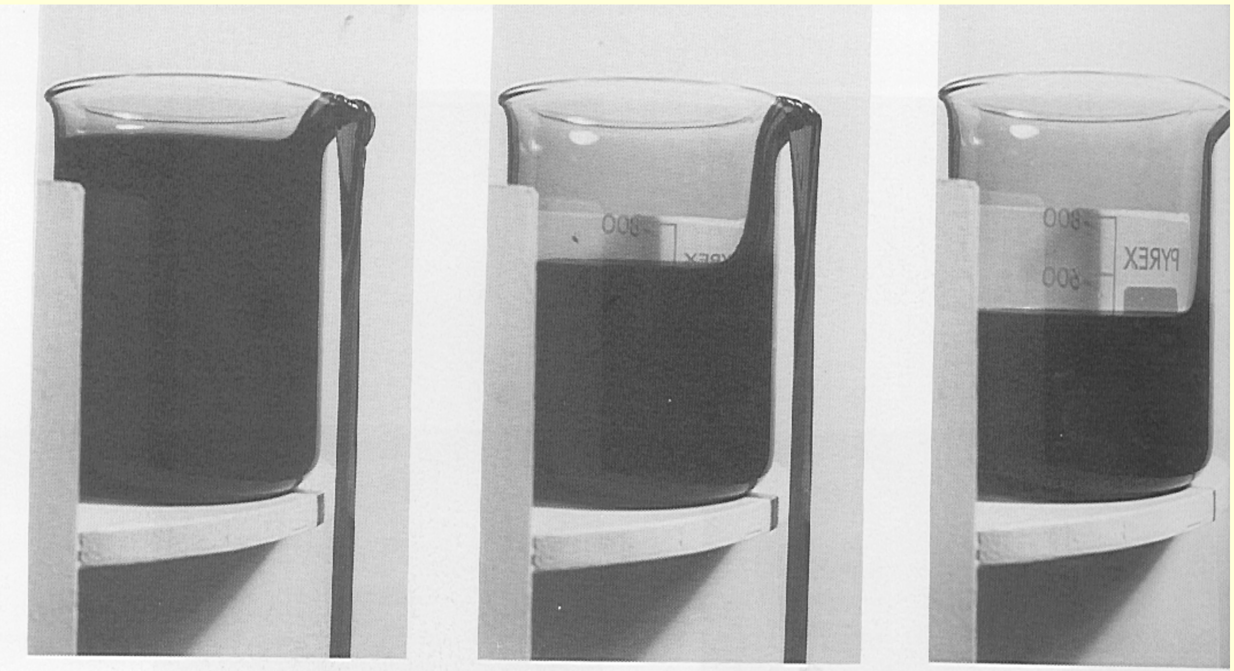
Die Swell



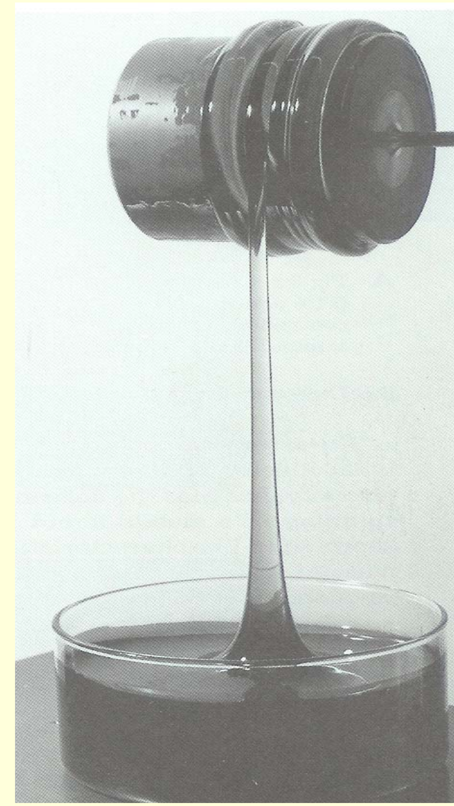
Normal stresses

Do real melts behave according to Newton’s law?

deviation 4: Ductless Syphon



(a) (b) (c)



η(ext) > > η(shear)

In summary:

Newtonian behaviour	real behaviour
1. Constant viscosity	1. Variable viscosity
2. No time effects	2. Time effects
3. No normal stresses in shear flow	3. Normal stresses
4. η(ext)/η(shear) = 3	4. Large η(ext)
3 dim: $T = -pI + \eta\ (2D)$ Simple shear: $\sigma = \eta\ d\gamma/dt$	?

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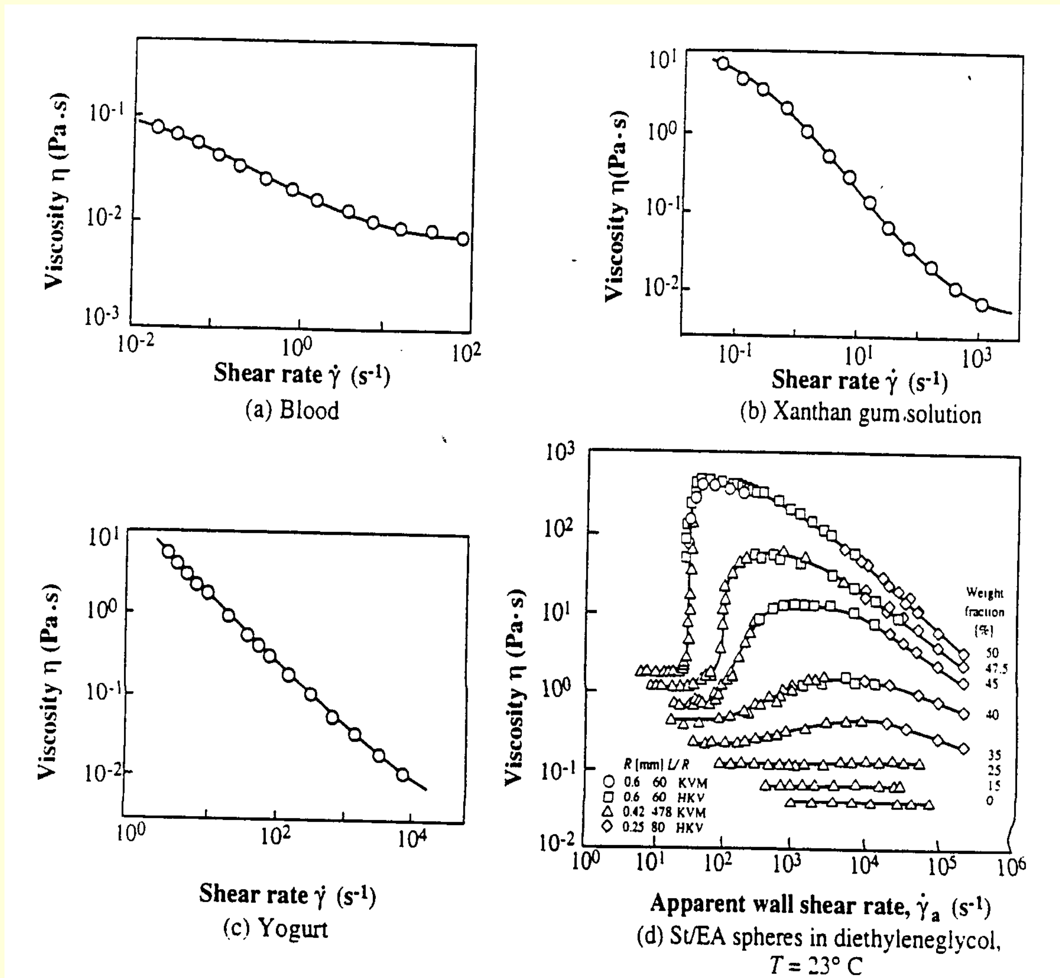
2. Constitutive equations
2.1 Generalized Newtonian fluids

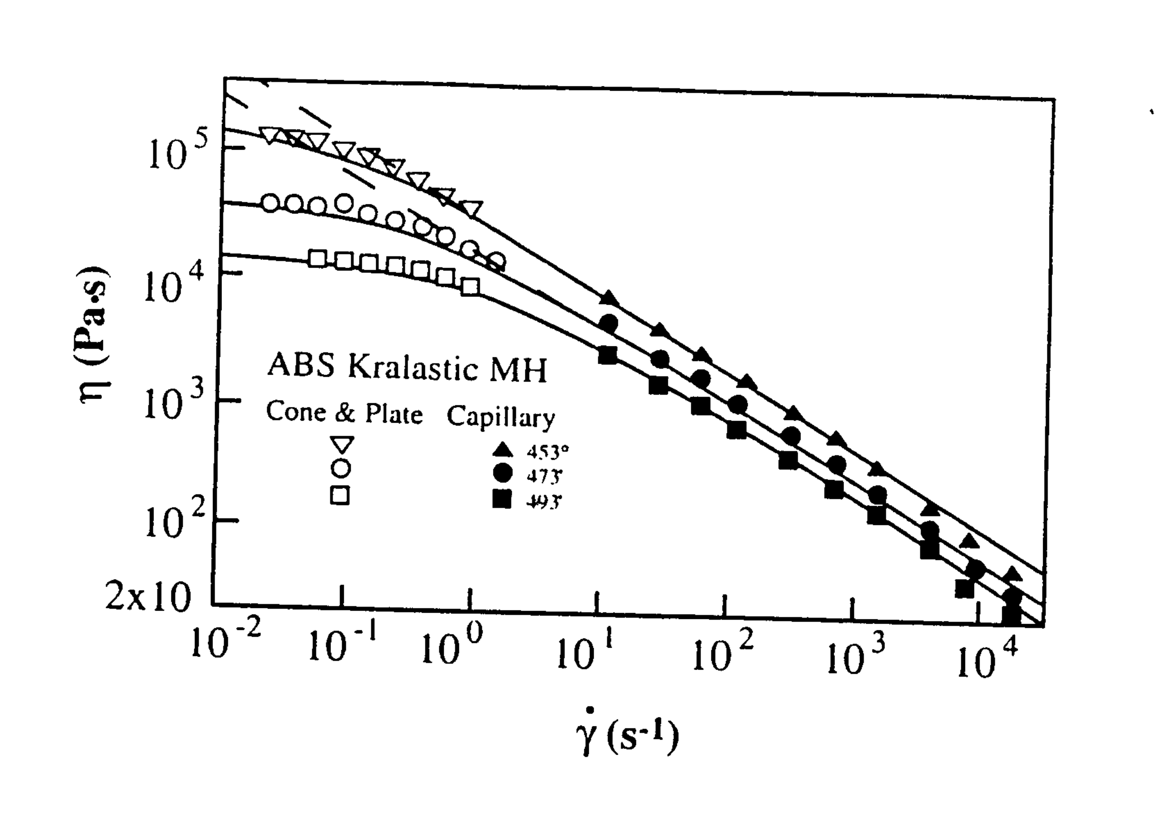
Examples of non-Newtonian behaviour:



Macosko, 1992

2.1 Generalized Newtonian fluids

Non-Newtonian behaviour is typical for polymeric solutions and molten polymers



e.g. ABS polymer melt (Cox and Macosko)

2.1 Generalized Newtonian fluids

$$\mathrm{T} = -\mathrm{p}\mathbf{I} + \mathrm{f}_1(\mathrm{II}_{2\mathbf{D}}) \cdot 2\,\mathbf{D}$$

The viscosity is now replaced by a function of the second invariant of 2**D**

for a shear flow this becomes:

$$\sigma_{xy} = \eta_1\left(\dot{\gamma}^2\right) \cdot \dot{\gamma}$$

and different forms for this function have been proposed

With: $\mathrm{II}_{2D} = 1/\,2\,(\mathrm{tr}^2{}_{2D} - \mathrm{tr}\,(2D)^2)$

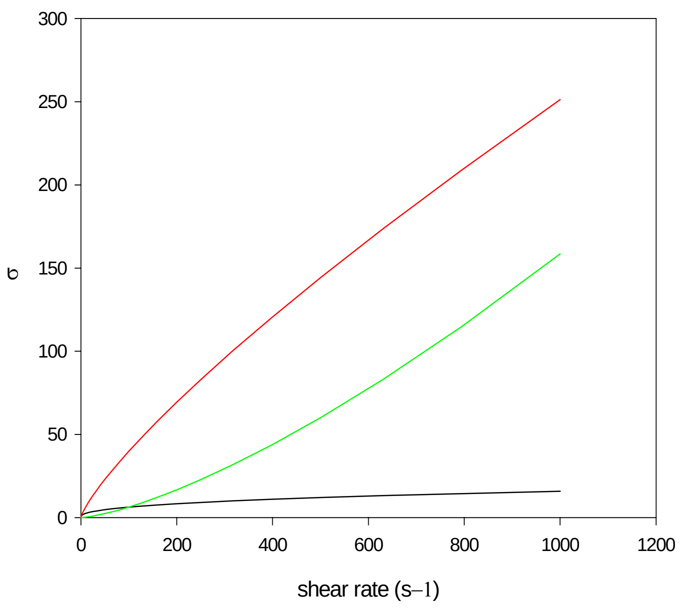
tr = trace = sum of the diagonal elements

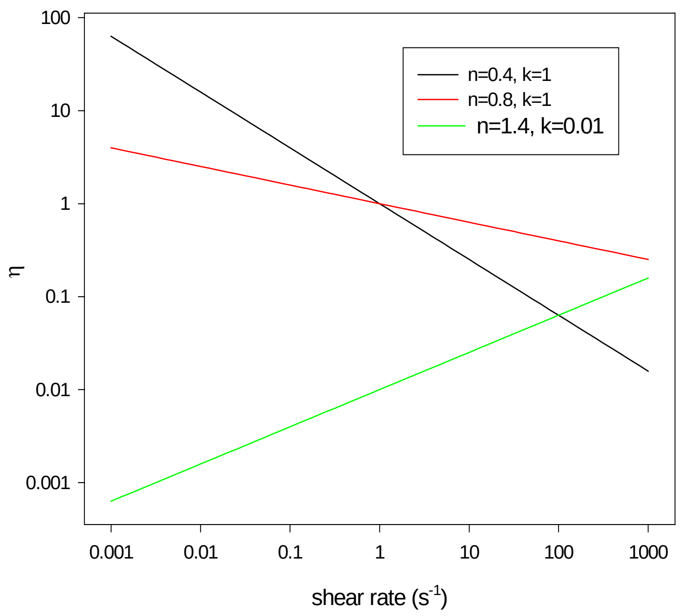
Model 1: Power Law

$$\overline{\overline{T}} = -p\mathbf{I} + k \cdot \left|II_{2\mathbf{D}}\right|^{(n-1)/2} \cdot 2\mathbf{D}$$

$$\sigma_{xy} = k\dot{\gamma}^{n} \qquad \eta = k\dot{\gamma}^{n-1}$$

2 parameters



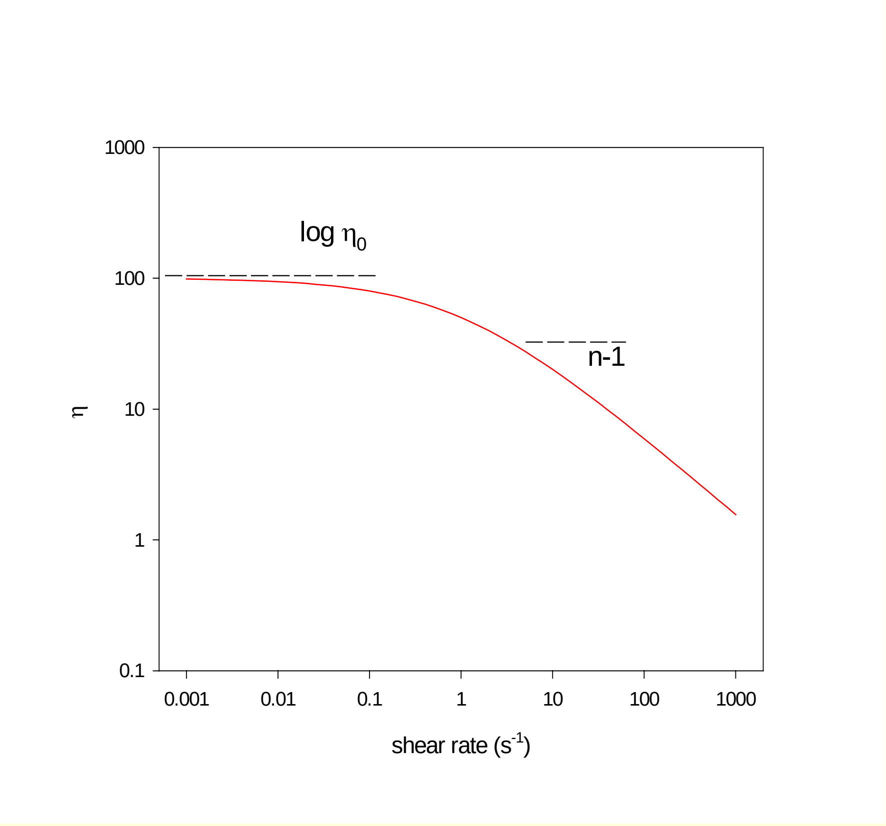


n<1 : shear-thinning
n>1: shear-thickening

Model 2: Ellis model

$$\frac{\eta}{\eta_0} = \frac{1}{1 + k \cdot \dot{\gamma}^{(1-n)}}$$

3 parameters



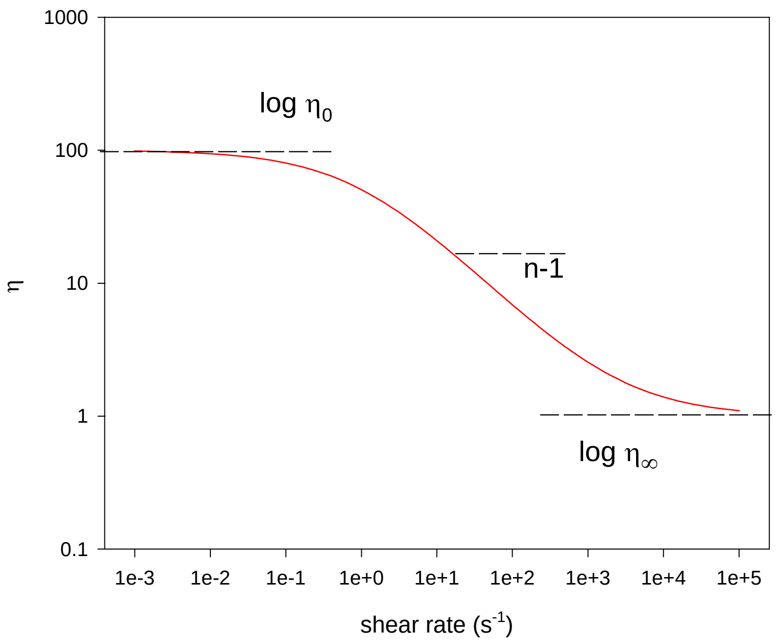
Model 3: CROSS model

$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + k \cdot \dot{\gamma}^{(1-n)}}$$

4 parameters

3D

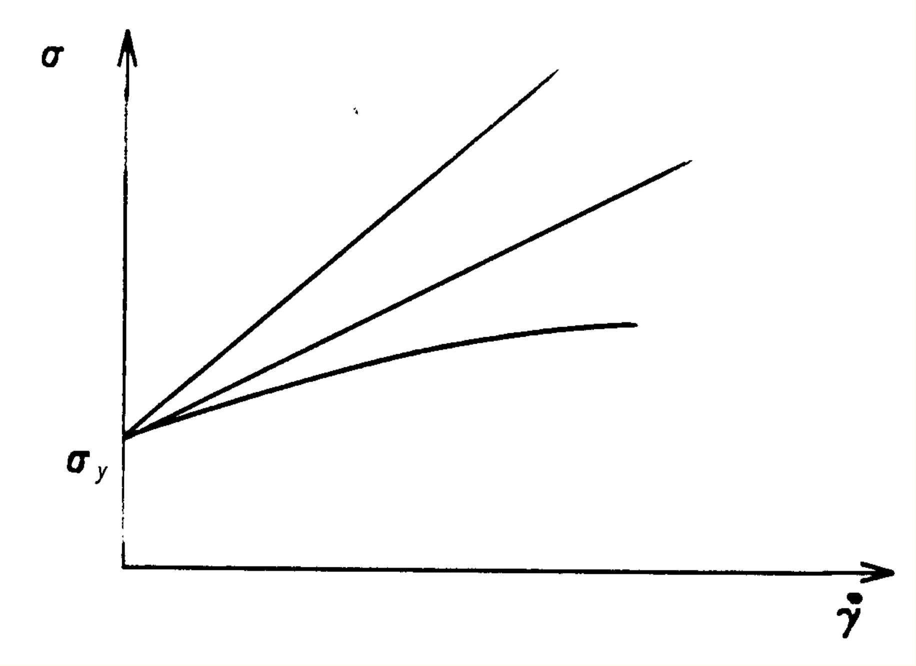
$$\frac{\eta - \eta_\infty}{\eta_0 - \eta_\infty} = \frac{1}{1 + \left(k^2 \cdot II_{2\mathbf{D}}\right)^{(1-n)/2}}$$



Special case: plastic Behaviour

Yield stress $\sigma < \sigma_y \rightarrow \dot{\gamma} = 0 \quad , \quad \sigma = G \cdot \gamma$ No flow, only deformation

$$\sigma > \sigma_y \rightarrow \dot{\gamma} \neq 0$$



What have we gained in generalized Newtonian?

Newtonian behaviour	real behaviour
1. Constant viscosity	1. Variable viscosity
2. No time effects	2. Time effects
3. No normal stresses in shear flow	3. Normal stresses
4. $\eta(\mathrm{ext})/\eta(\mathrm{shear}) = 3$	4. Large $\eta(\mathrm{ext})$
3 dim: $T = -pI + \eta\ (2D)$	$T = -pI + \eta(II_{2D)}\ (2D)$

Simple shear: $\sigma = \eta\ d\gamma/dt$

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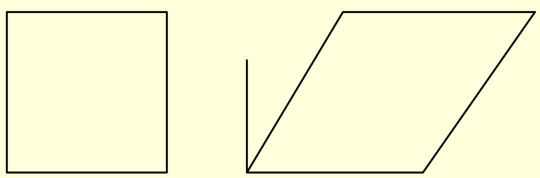
2. Constitutive equations
2.2 Linear visco-elasticity

Reference: 2 extremes

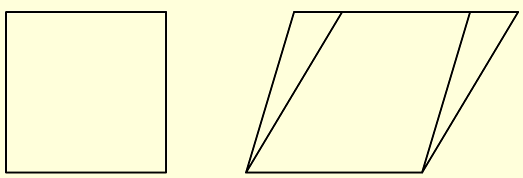
Hooke's Law
(solid mechanics)



$\sigma = G.\gamma$

G = modulus (Pa)
Material property

Newton's Law
(fluid mechanics)

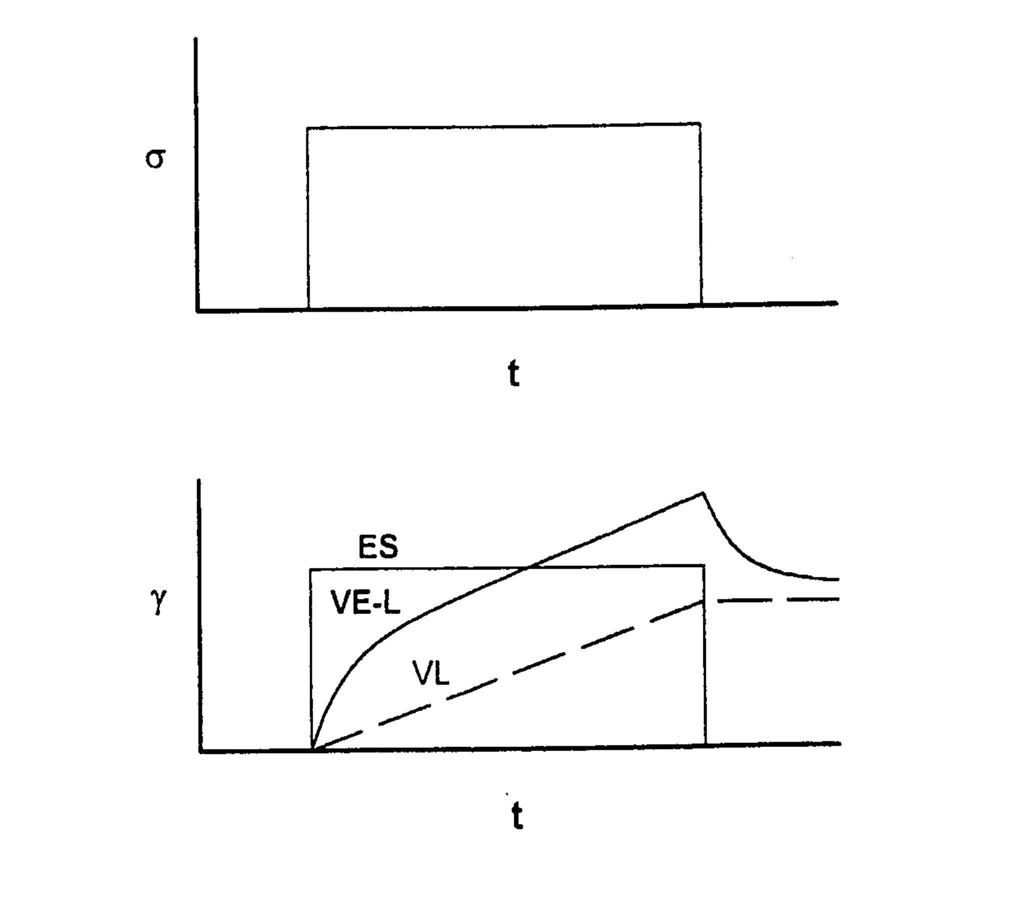


$\sigma = \eta\ .d\gamma/dt$

η = viscosity (Pa.s)
material property

Time effects (linear visco-elastic phenomena):

Example 1: creep



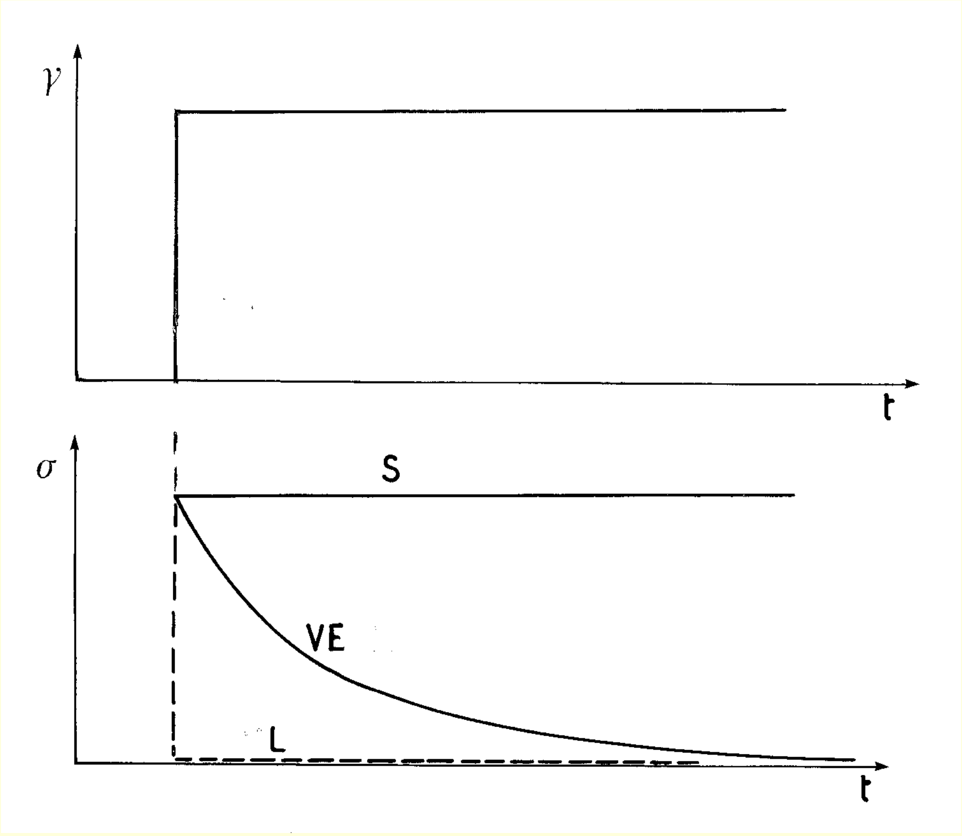
Apply constant stress σ

Compliance

$$J(t) = \frac{\gamma(t)}{\sigma_0}$$

Time effects (linear visco-elastic phenomena):

Example 2: stress relaxation upon step strain

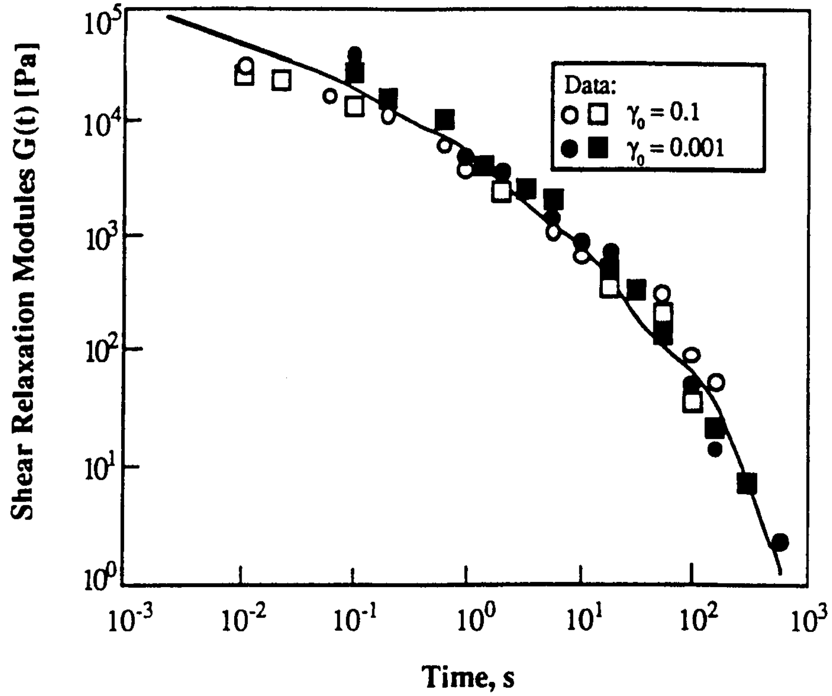


Apply constant strain

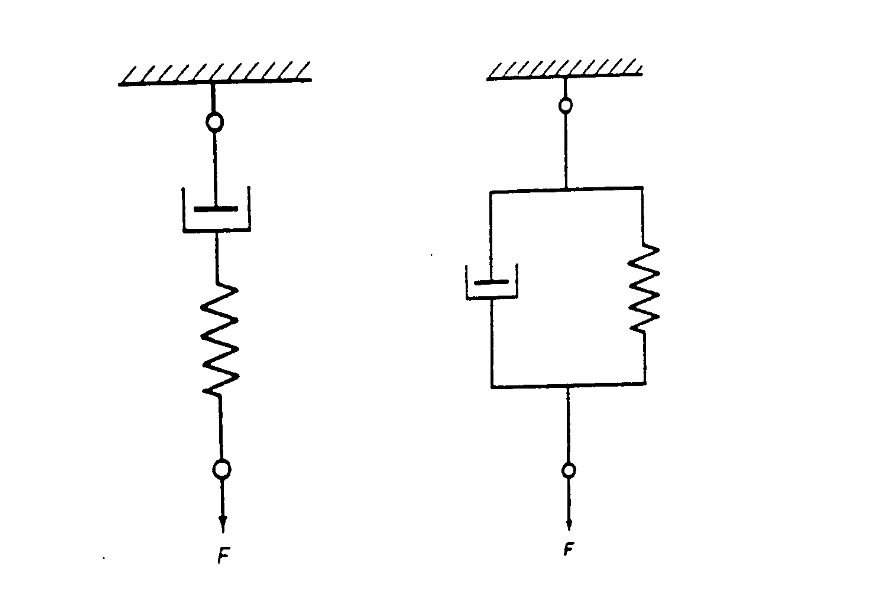
Modulus

$$G(t) = \sigma(t)/\gamma$$

Example for molten LDPE [Laun, Rheol. Acta, **17**,1 (1978)]



How to descibe this behaviour?
Example: differential models



Maxwell Kelvin-Voigt

Phenomenological models

Hookean spring

$$\sigma_1 = G_0 \gamma_1$$

Newtonian dashpot

$$\sigma_2 = \eta_0 \cdot \dot{\gamma}_2$$

Maxwell model:

$$\gamma = \gamma_1 + \gamma_2$$

$$\sigma = \sigma_1 = \sigma_2$$

$$\dot{\gamma} = \dot{\gamma}_1 + \dot{\gamma}_2$$

$$\dot{\gamma} = \frac{\dot{\sigma}_1}{G_0} + \frac{\sigma_2}{\eta_0}$$

$$\sigma + \left(\frac{\eta_0}{G_0}\right)\dot{\sigma} = \eta_0\dot{\gamma}$$

$$\boxed{\sigma + \tau\dot{\sigma} = \eta_0\dot{\gamma}}$$

τ = relaxation time

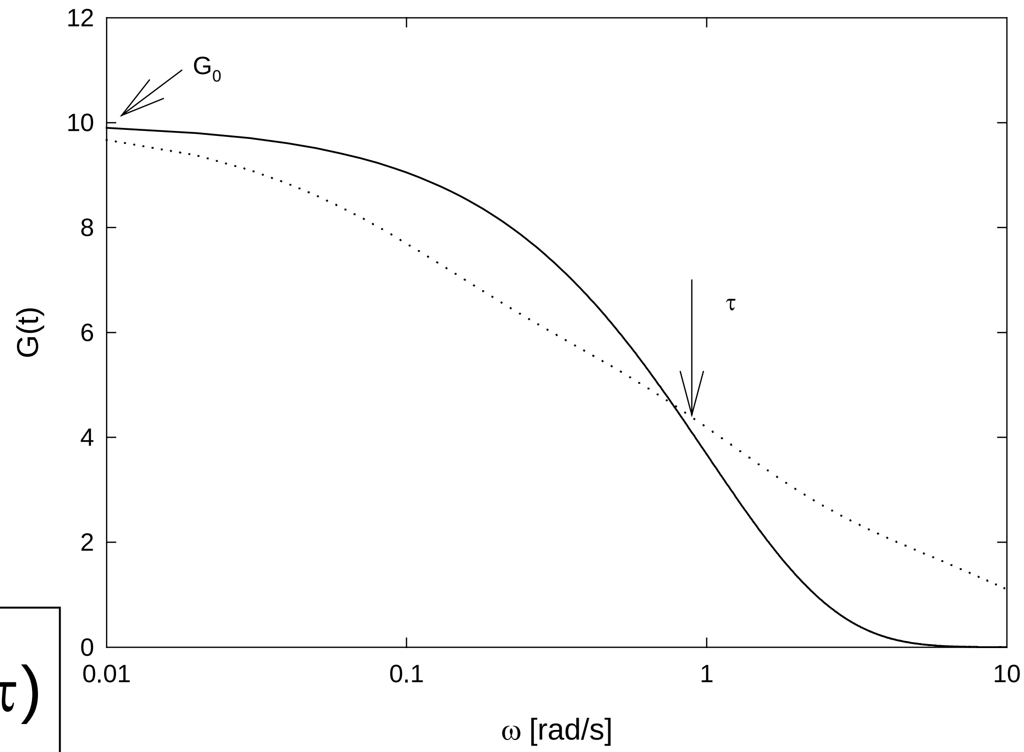
Example: Stress relaxation upon step strain for a Maxwell element

$$\gamma = \gamma_0 \quad t \geq 0$$

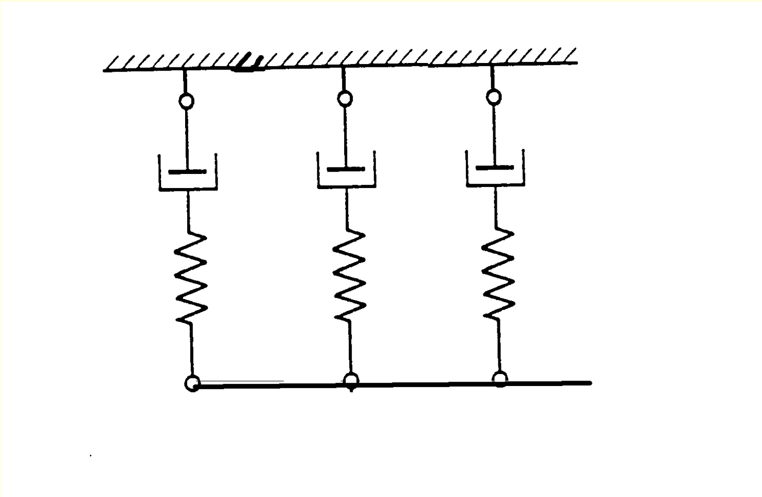
$$\sigma + \tau \frac{d\sigma}{dt} = 0$$

$$t = 0; \sigma = G_0 \gamma_0$$

$$\boxed{\frac{\sigma(t)}{\gamma} = G(t) = G_0 \cdot \exp(-t / \tau)}$$



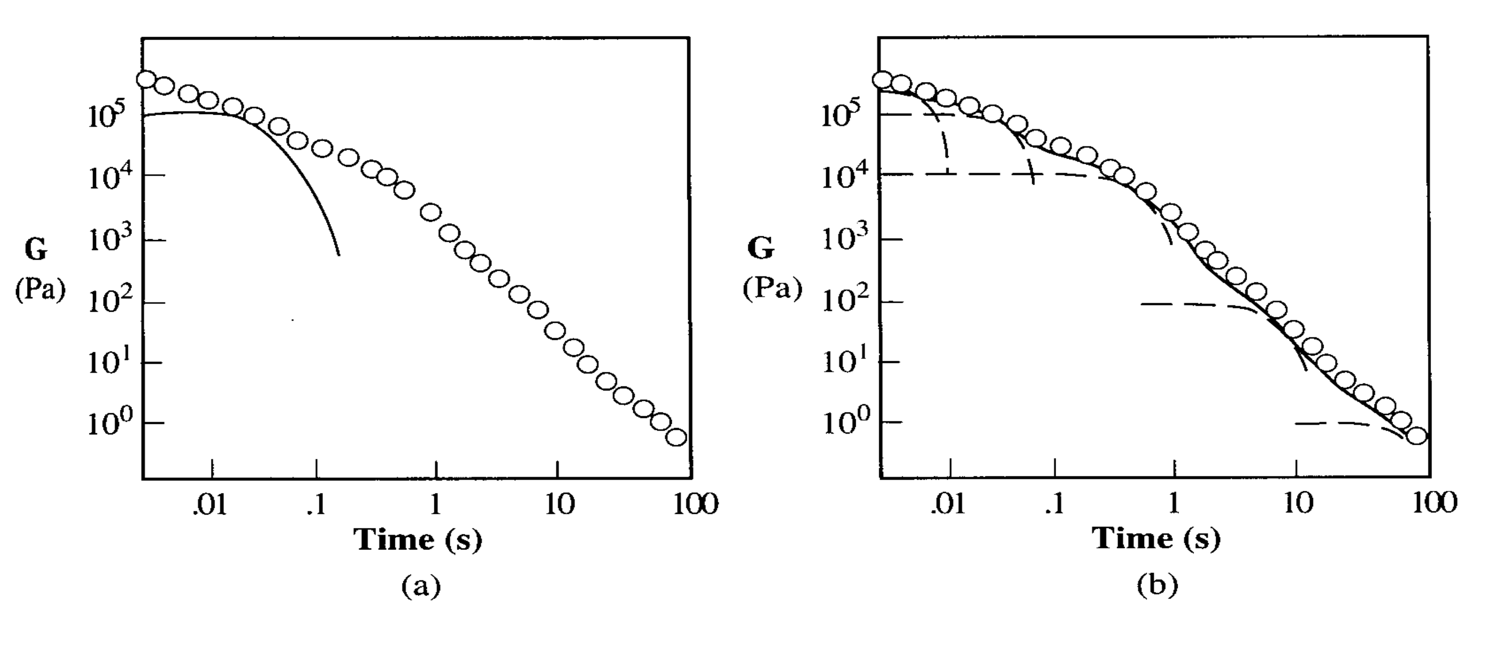
Generalized Maxwell model to describe molten polymers:



$$\sigma_{TOT} = \sum_i \sigma_i$$

$$\sigma_i + \tau_i \dot{\sigma}_i = \eta_i \dot{\gamma}$$

$$G(t) = \sum_i G_{0i} \exp(-t/\tau_i)$$



Relaxation functions:

For a simple Maxwell model: single exponential (single relaxation time τ):

$$G(t) = G_0 \exp(-t / \tau)$$

For a generalized Maxwell fluid (discrete number of relaxation times τ_I:

$$G(t) = \sum G_i \exp(-t / \tau_i)$$

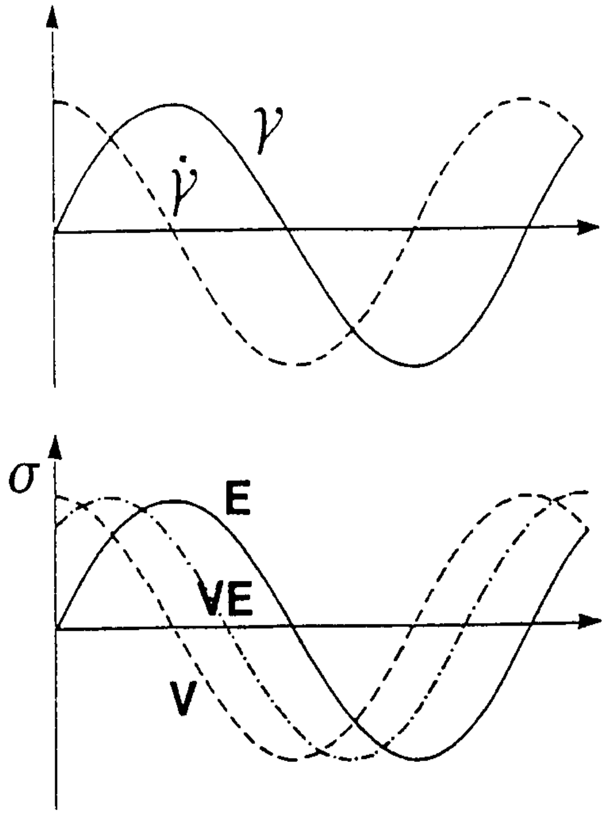
We can replace the discrete relaxation times by a continuous spectrum:

$$G(t) = \int_0^\infty F(\tau) \exp\left(\frac{-t}{\tau}\right) d\tau$$

Or based on a logaritmic time scale : the **relaxation spectrum** is defined by:

$$G(t) = \int_0^\infty H(\tau) \exp\left(\frac{-t}{\tau}\right) \frac{d\tau}{\tau}$$

Time effects (linear visco-elastic phenomena):
Example 3: Oscillatory experiments



STRAIN:

$\gamma = \gamma_0 \sin(\omega t)$

$\gamma = \gamma_0 \exp(i\omega t)$

STRAIN RATE

$\dot{\gamma} = \gamma_0 \omega \cos(\omega t) = \gamma_0 \sin(\omega t + 90°)$

$\dot{\gamma} = \mathrm{i}\omega\gamma_0 \exp(i\omega t)$

HOOKEAN SOLID

$\sigma = G\gamma = G\gamma_0 \sin(\omega t)$
$\sigma = G\gamma_0 \exp(i\omega t)$

NEWTONIAN FLUID

$\sigma = \eta\dot{\gamma} = \eta\gamma_0\omega \sin(\omega t + 90°)$
$\sigma = \eta i\gamma_0\omega \exp(i\omega t) = \eta i\gamma\omega$

VISCOELASTIC MATERIAL

$$\sigma = \sigma_{el} + \sigma_{visc}$$

$$\sigma = G\gamma + i\omega\eta\gamma$$

$$\sigma = (G + i\omega\eta)\gamma$$

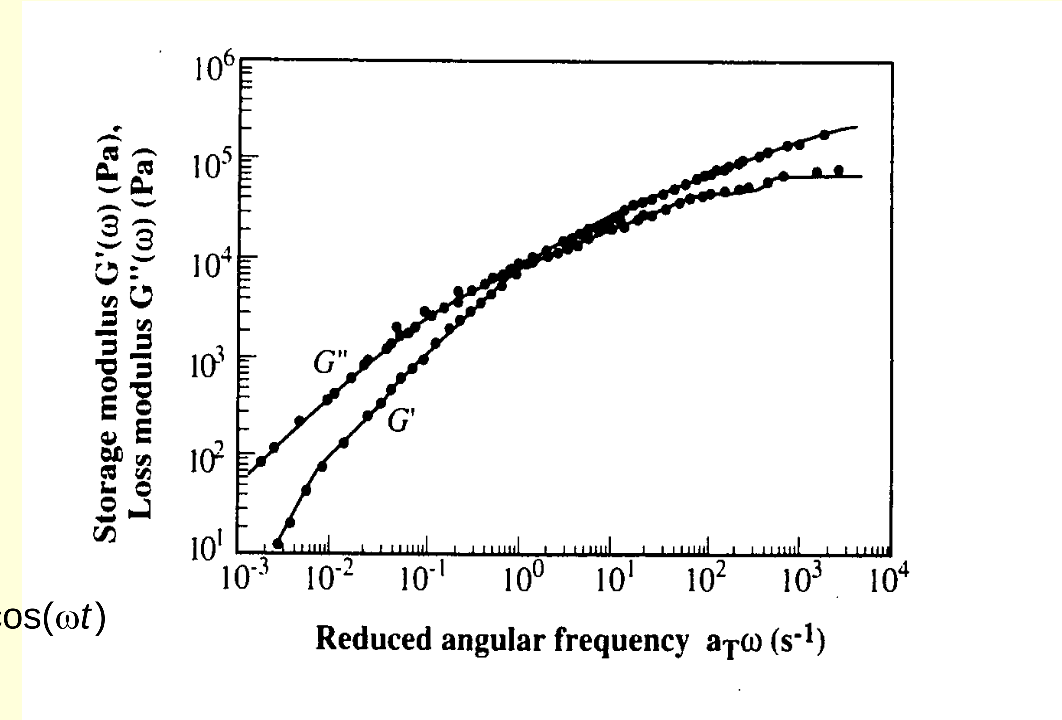
complex mod*ulus*:

$$\sigma = G^*\gamma$$

$$\sigma = G^*\gamma_0 \sin(\omega t + \delta)$$

$$\sigma = G^*\gamma_0[\sin(\omega t).\cos(\delta) + \cos(\omega t).\sin(\delta)]$$
$$\sigma = \left(G^* \cos(\delta)\right)\cdot\gamma_0 \sin(\omega t) + \left(G^* \sin(\delta)\right)\cdot\gamma_0 \cos(\omega t)$$

$$\sigma = [G'\cdot\sin(\omega t) + G''\cdot\cos(\omega t)]\gamma_0$$



$$\sigma = (G' + iG'')\gamma$$

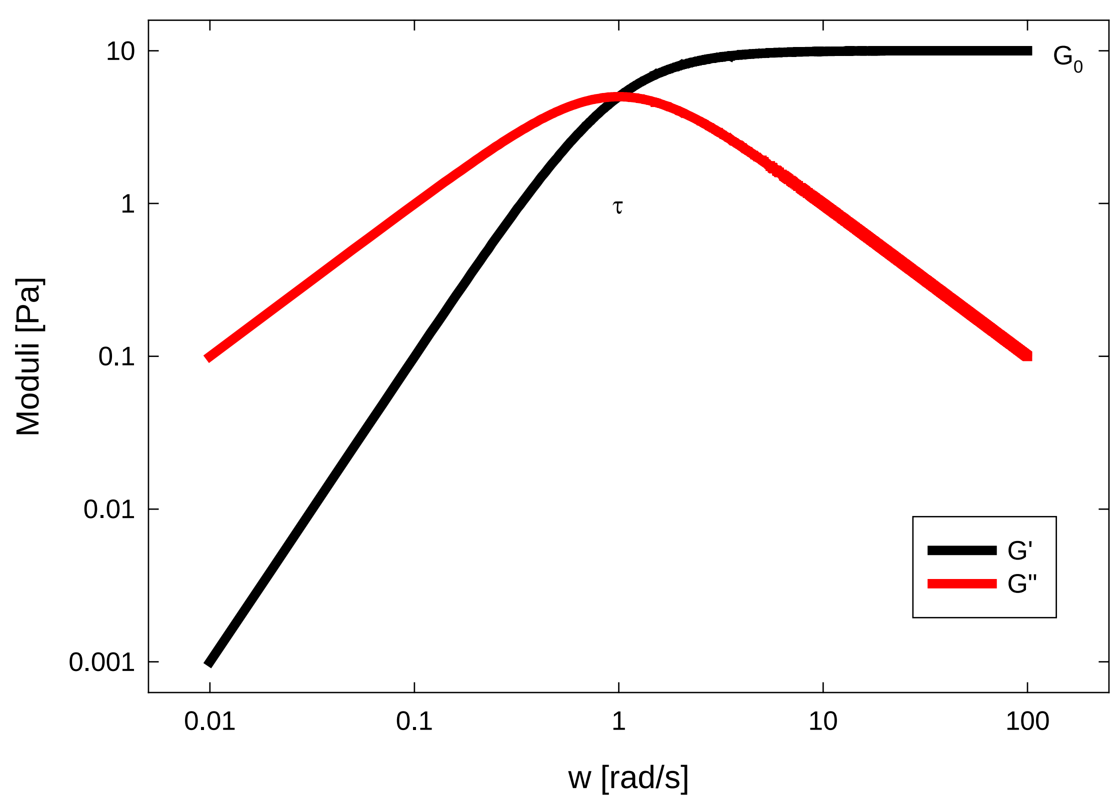
Storage and Loss modulus

$$\tan\delta = \frac{G''}{G'}$$

Dynamic moduli of a Maxwell fluid

$$G'(\omega) = \frac{G_0 \omega^2 \tau^2}{1 + \omega^2 \tau^2}$$

$$G''(\omega) = \frac{G_0 \omega \tau}{1 + \omega^2 \tau^2}$$



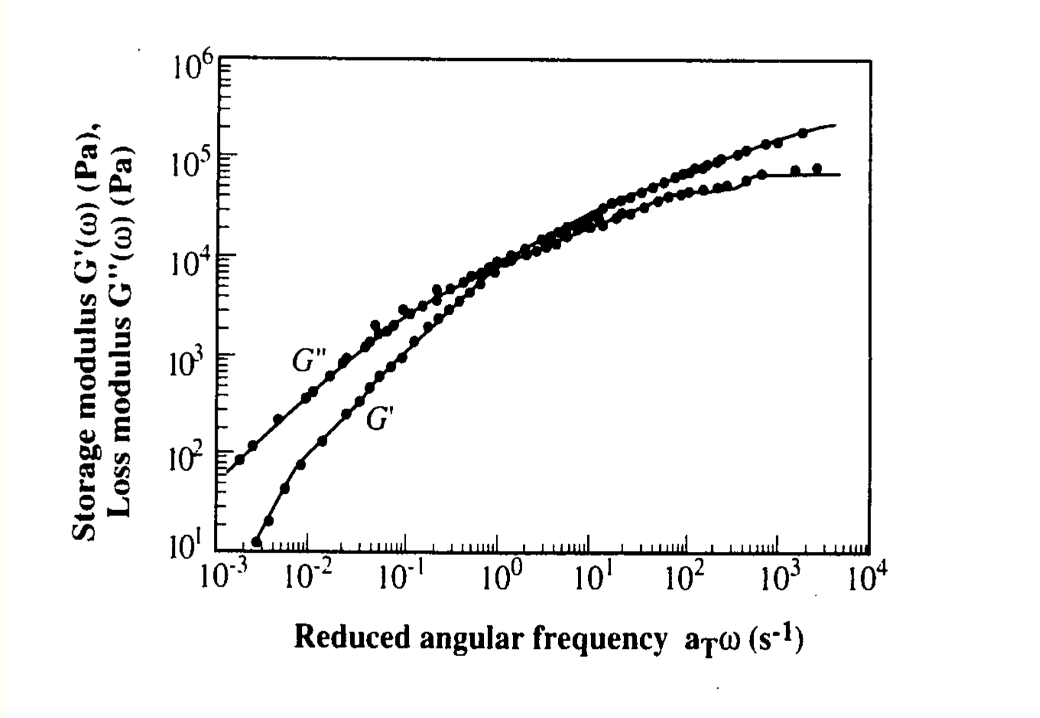
G' and G" for a generalized Maxwell fluid:

$$G'' = \omega \int_0^\infty G(s)\cdot\cos(\omega s)ds = \omega \int_0^\infty \left(\sum_{i=1}^{N} G_i e^{-\tau_i s} \right)\cdot \cos(\omega s) ds$$

$$\boxed{= \sum_{i=1}^{N} G_i \frac{\omega\tau_i}{1+(\omega\tau_i)^2}}$$

$$G' = \omega \int_0^\infty G(s)\cdot\sin(\omega s)ds$$

$$\boxed{= \sum_{i=1}^{N} G_i \frac{(\omega\tau_i)^2}{1+(\omega\tau_i)^2}}$$



What have we gained in linear visco-elasticity?

Newtonian behaviour	real behaviour
1. Constant viscosity	1. Variable viscosity
2. No time effects	2. Time effects
3. No normal stresses in shear flow	3. Normal stresses
4. η(ext)/η(shear) = 3	4. Large η(ext)
3 dim: $T = -pI + \eta\ (2D)$ Simple shear: $\sigma = \eta\ d\gamma/dt$	$G(t)$, $H(\tau)$,… fully descibes linear VE

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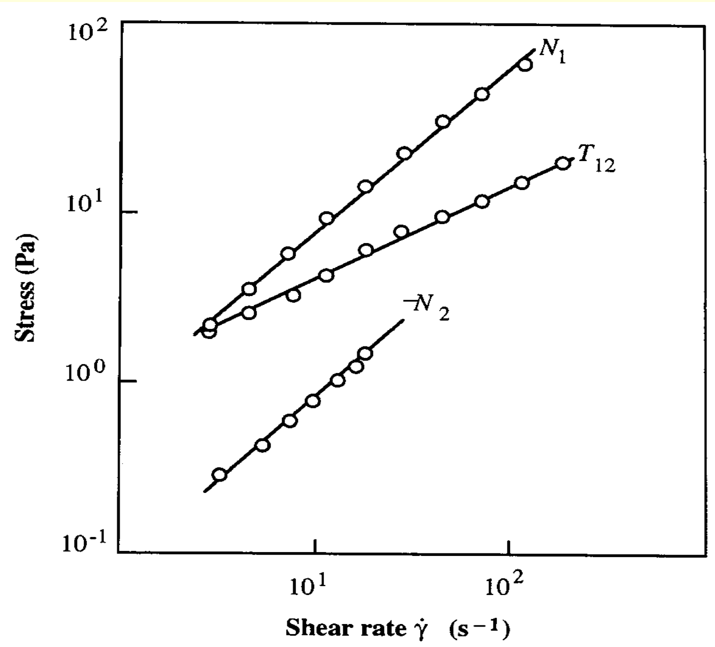
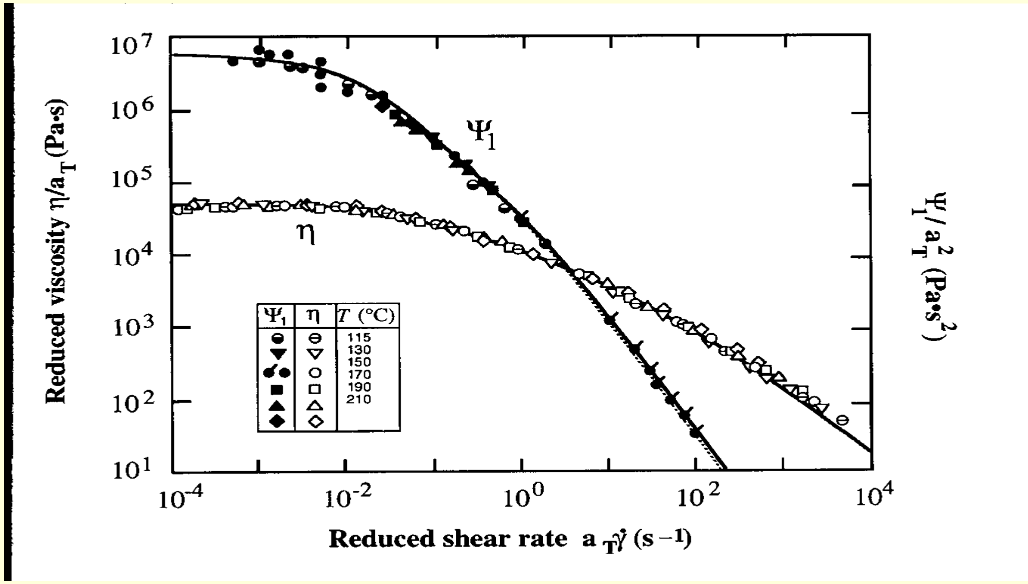
2. Constitutive equations
2.3. Non-linear visco-elasticity
Example 1: Steady state shear flow





$$\sigma_{xy}$$

$$N_1 = \sigma_{xx} - \sigma_{yy}$$

$$N_2 = \sigma_{yy} - \sigma_{zz}$$

$$\eta = \frac{\sigma_{xy}}{\dot{\gamma}}$$

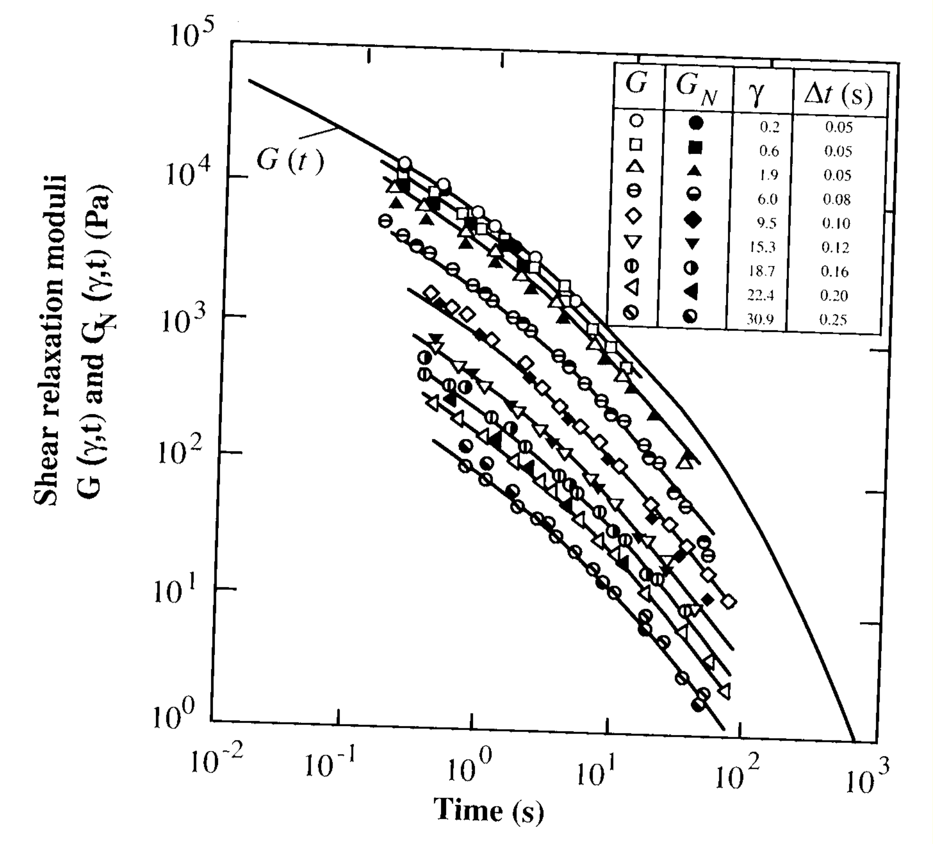
$$\Psi_1 = \frac{\sigma_{xx} - \sigma_{yy}}{\dot{\gamma}^2}$$

$$\Psi_2 = \frac{\sigma_{yy} - \sigma_{zz}}{\dot{\gamma}^2}$$

PIB in decalin, Keentok et al.

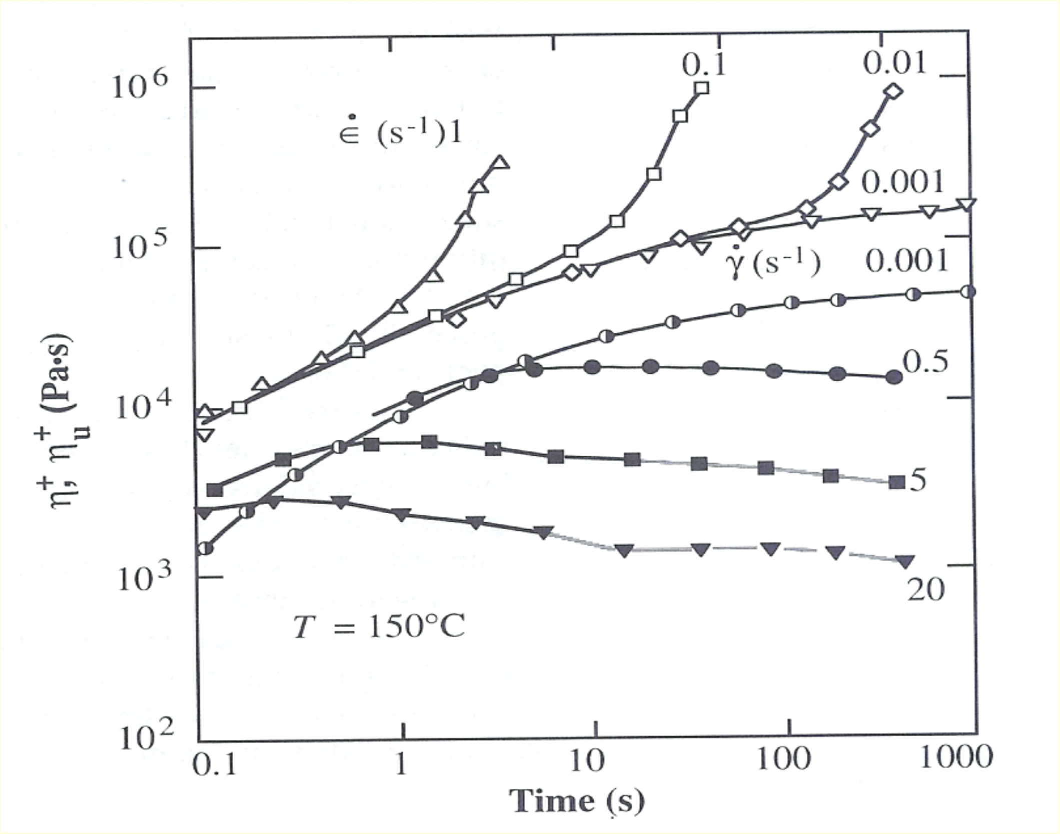
LDPE, Laun et al.

Example 2: Non-linear stress relaxation upon step strain



LDPE, Laun et al.

Example 3: Stress evolution upon inception of shear or elongational flow



What have we gained in non-linear visco-elasticity?

Newtonian behaviour	real behaviour
1. Constant viscosity	1. Variable viscosity
2. No time effects	2. Time effects
3. No normal stresses in shear flow	3. Normal stresses
4. η(ext)/η(shear) = 3	4. Large η(ext)
3 dim: $T = -pI + \eta\ (2D)$	no universal model
Simple shear: $\sigma = \eta\ d\gamma/dt$	

Contents

3. Rheometry

Why ?

1. Input for Constitutive Equations
2. Quality control
3. Simulate industrial flows

A rheometer is an instrument that measures both stress and deformation.

⇔ indexer

⇔ viscometer

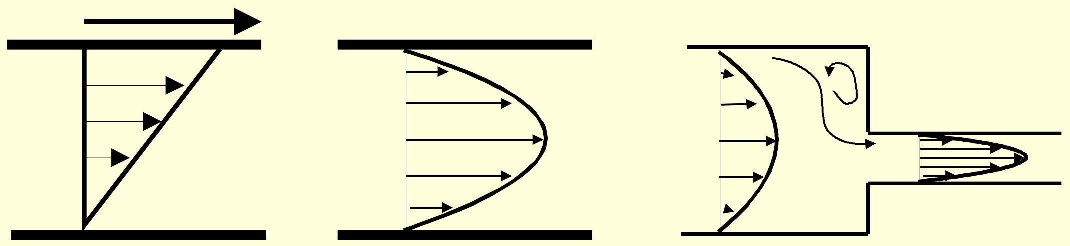
What do we want to measure?

- steady state data
- small strain (LVE) functions
- large strain deformations

Introduction: classifications

➔Kinematics : shear vs elongation

➔homogeneous vs non-homogeneous vs complex flow fields



➔ type of straining:

- small : $G'(\omega)$, $G''(\omega)$, $\eta^{+}(t)$, $\eta^{-}(t)$, $G(t)$, σ_y
- large : $G'(\omega,\gamma)$, $G''(\omega,\gamma)$, $\eta^{+}(t,\gamma)$, $\eta^{-}(t,\gamma)$, $G(t,\gamma)$, $\eta(t,\varepsilon)$
- steady : $\eta(\dot{\gamma})$, $\Psi_1(\dot{\gamma})$

➔ shear rheometry : Drag or pressure driven flows.

Shear flow geometries

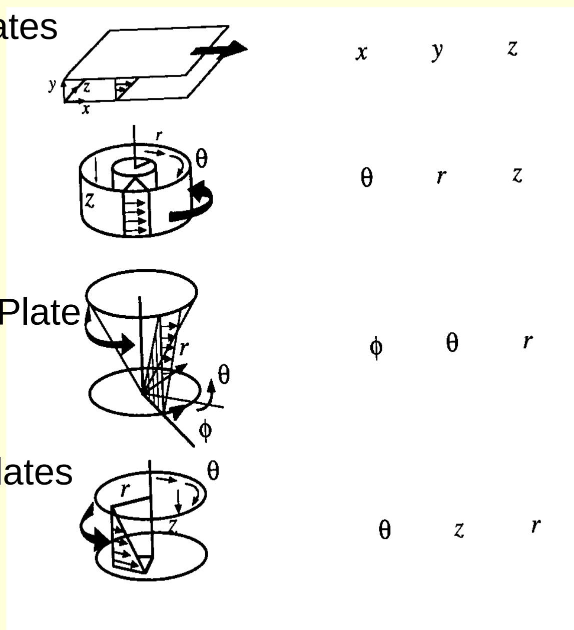
Drag flows

Sliding plates

Couette

Cone and Plate

Parallel plates

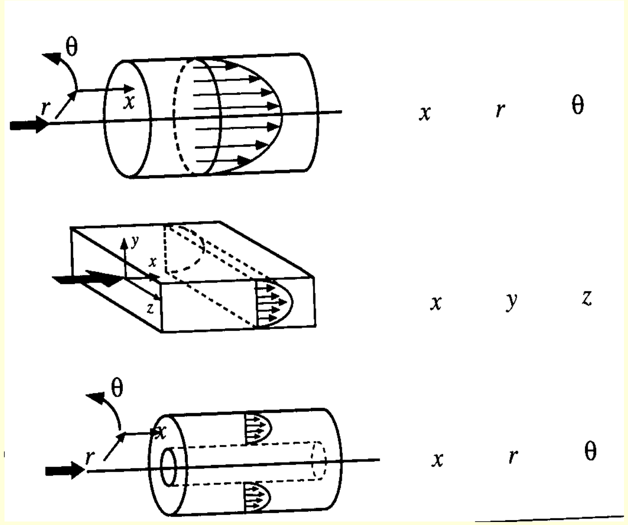


Pressure driven flows

Capillary

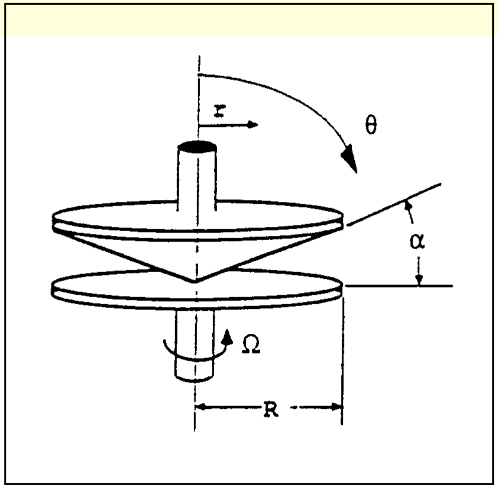
Slit

Annulus



Macosko, 1992

Drag flows : Cone and plate



Probably most popular geometry Mooney (1934)

1. Steady, laminar, isothermal flow
2. Negligible gravity and end effects
3. Spherical boundary liquid
4. $v_r = v_z = 0$ and $v_\phi(r,\theta)$
5. Angle $\alpha < 0.1$ radians

Equations of motion:

$$r: \quad \frac{1}{r^2}\frac{\partial\left(r^2\sigma_{rr}\right)}{\partial r} - \frac{\sigma_{\theta\theta}+\sigma_{\phi\phi}}{r} = -\rho\frac{v_\theta^2}{r}$$

$$\theta: \quad \frac{1}{r\sin\theta}\frac{\partial\left(\sigma_{r\theta}\sin\theta\right)}{\partial r} - \frac{\cot\theta}{r}\cdot\sigma_{\theta\theta} = 0$$

$$\phi: \quad \frac{1}{r}\frac{\partial\sigma_{\theta\phi}}{\partial\theta} + \frac{2}{r}\cot\theta\cdot\sigma_{\theta\phi} = 0$$

Drag flows : Cone and plate geometry

Boundary conditions

1. $v_\phi(\pi/2) = 0$
2. $v_\phi(\pi/2-\alpha)=\omega r\sin(\pi/2-\alpha)\approx\omega r$

Shear stress

$$\phi: \quad \frac{1}{r}\frac{d\left(\sigma_{\theta\phi}\right)}{d\theta}+\frac{2}{r}\cot\phi\cdot\sigma_{\theta\phi}=0 \quad \rightarrow \quad \sigma_{\theta\phi}=\frac{C}{\sin^2\theta}\cong Cte$$

$$M=\int_0^{2\pi}\int_0^{R} r^2\sigma_{\theta\phi}\,dr\,d\phi$$

$$\boxed{\sigma_{\theta\varphi}=\frac{3M}{2\pi\cdot r^3}}$$

Independent of fluid characteristics because of small angle!

Drag flows : Cone and plate geometry

Shear rate: is also constant throughout the sample: homogeneous!

$$\dot{\gamma} = \frac{v_r}{h(r)} = \frac{\omega \cdot r}{r \cdot tg(\alpha)} = \frac{\omega}{tg(\alpha)} \cong \frac{\omega}{\alpha}$$

Normal stress differences: total trust on the plate is measured **Fz**

$$F_z = \frac{\pi R^2}{2}\left(\sigma_{\theta\theta} - \sigma_{\phi\phi}\right)$$

$$N_1 = \frac{2F_z}{\pi R^2}$$

Drag flows : Cone and plate geometry

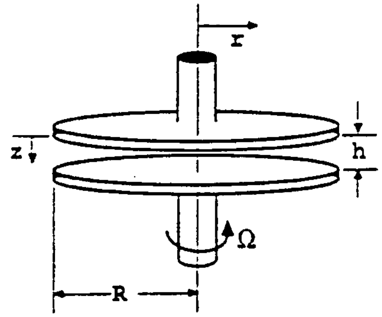
+

- constant shear rate, constant shear stress -homogeneous!
- most useful properties can be measured
- both for high and low viscosity fluids
- small sample
- easy to fill and clean

-

- high visc: shear fracture - limits max. shear rate
-(low visc : centrifugal effects/inertia - limits max. shear rate)
- (settling can be a problem)
- (solvent evaporation)
- stiff transducer for normal stress measurements
- viscous heating

Drag flows : Parallel plates



Again proposed by Mooney (1934)

1. Steady, laminar, isothermal flow
2. Negligible gravity and end effects
3. cylindrical edge
4. $v_r = v_z = 0$ and $v_\phi(r,z)$

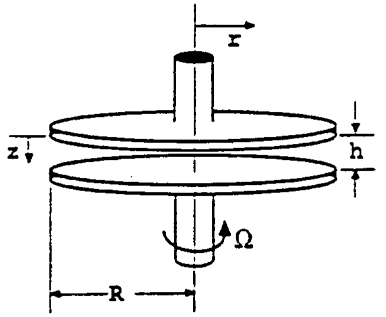
Equations of motion:

$$r: \quad \frac{1}{r}\frac{\partial(r\sigma_{rr})}{\partial r} - \frac{\sigma_{\theta\theta}}{r} = -\rho\frac{v_\theta^2}{r}$$

$$\theta: \quad \frac{\partial(\sigma_{\theta z})}{\partial z} = 0$$

$$z: \quad \frac{\partial(\sigma_{zz})}{\partial z} = 0$$

Drag flows : Parallel plates



Shear rate: is not constant throughout the sample

$$\dot{\gamma} = \frac{v_r}{h} = \frac{\omega \cdot r}{h}$$

Shear stress

$$\sigma = \frac{M}{2\pi R^3}\left[1 + \frac{d \ln M}{d \ln \dot{\gamma}_R}\right]$$

Normal stresses

$$N_1 - N_2 = \frac{F_z}{\pi R^2}\left[2 + \frac{d \ln Fz}{d \ln \dot{\gamma}_R}\right]$$

Drag flows : Parallel plate geometry

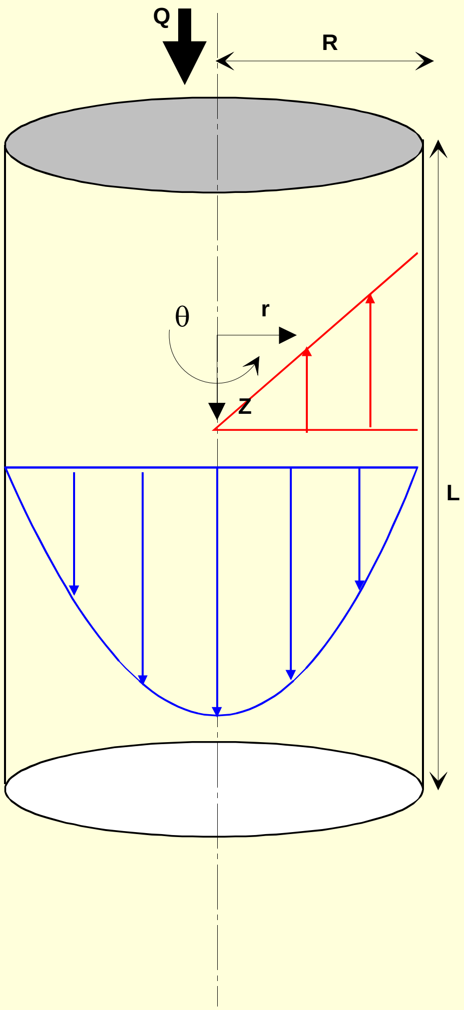
+

- preferred geometry for viscous melts - small strain functions
- sample preparation is much simpler
- shear rate and strain can be changed also by changing h
- determination of wall slip easy
- N_2 when N_1 is known
- edge fracture can be delayed

-

- non-homogeneous flow field (correctable)
- inertia/secondary flow - limits max. shear rate
- edge fracture still limits use
- (settling can be a problem)
- (solvent evaporation)
- viscous heating

Pressure driven flows : capillary rheometry



1. Steady, laminar, isothermal flow
2. No slip at the wall, v_x =0 at R=0
3. $v_r = v_\theta = 0$
4. Fluid is incompressible, $\eta \neq f(p)$

Equation of motion:

$$z: \quad \frac{1}{r}\frac{\partial (r\sigma_{rz})}{\partial r} - \frac{\partial p}{\partial z} = 0$$

Only a function of r

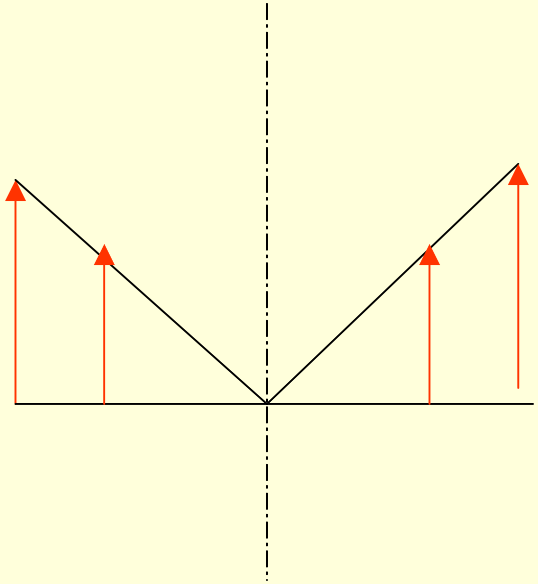
Only a function of z

$$\frac{1}{r}\frac{d(r\sigma_{rz})}{dr} = \frac{dp}{dz}$$

$$\frac{1}{r}\frac{d(r\sigma_{rz})}{dr} = \frac{P_o - P_L}{L}$$

$$\sigma_{rz} = \frac{P_o - P_L}{L} \cdot \frac{r}{2} + \frac{C_2}{r}$$

$C_2 = 0$ *because* $\sigma_{rz} \neq \infty$ @ $r = 0$



$$\sigma_{rz}(R) = \sigma_w = \frac{P_o - P_L}{L} \cdot \frac{R}{2}$$

$$\boxed{\sigma_{rz}(r) = \sigma_w \frac{r}{R}}$$

Note : independent of fluid properties

$$\boxed{Q = 2\pi \int_0^R v_z(r) r dr}$$

Shear rate calculation from Q

$$Q = 2\pi v_z r \Big|_0^R - 2\pi \int_0^R r^2 \frac{dv_z}{dr} dr$$

Integration by parts + assume :no slip

$$r = \frac{R}{\sigma_w}\sigma \quad and \quad dr = \frac{R}{\sigma_w} d\sigma$$

substitute r and dr

$$Q = -2\pi \int_0^R r^2 \frac{dv_z}{dr} dr = -2\pi \int_0^{\sigma_w} \left(\frac{R}{\sigma_w}\sigma \right)^2 \frac{dv_z}{dr} \frac{R}{\sigma_w} d\sigma$$

Typical "trick" to deal with inhomogeneous flows: changing of variables

$$\frac{Q\sigma_w{}^3}{\pi R^3} = -\int_0^{\sigma_w} (\sigma)^2 \frac{dv_z}{dr} d\sigma \longrightarrow \frac{3Q\sigma_w{}^2}{\pi R^3} + \frac{\sigma_w{}^3}{\pi R^3} \cdot \frac{dQ}{d\sigma_w} = -\sigma_w{}^2 \frac{dv_z}{dr}\Big|_{\sigma_w}$$

Differentiate with respect to σ_w using Leibnitz's rule

$$\dot{\gamma}_w = -\frac{dv_z}{dr}\Big|_{\sigma_w} = \frac{3Q}{4\pi R^3} + \frac{3Q}{4\pi R^3} \cdot \frac{d \ln Q}{d \ln \sigma_w}$$

$$\boxed{\dot{\gamma}_w = \frac{\dot{\gamma}_a}{4}\left(3 + \frac{d \ln Q}{d \ln \sigma_w} \right)}$$

Weissenberg-Rabinowitsch "Correction"

$$\gamma_w = \frac{\dot{\gamma}_a}{4}\left(3 + \frac{d \ln Q}{d \ln \sigma_w}\right)$$

"Correction" factor accounts for material behaviour

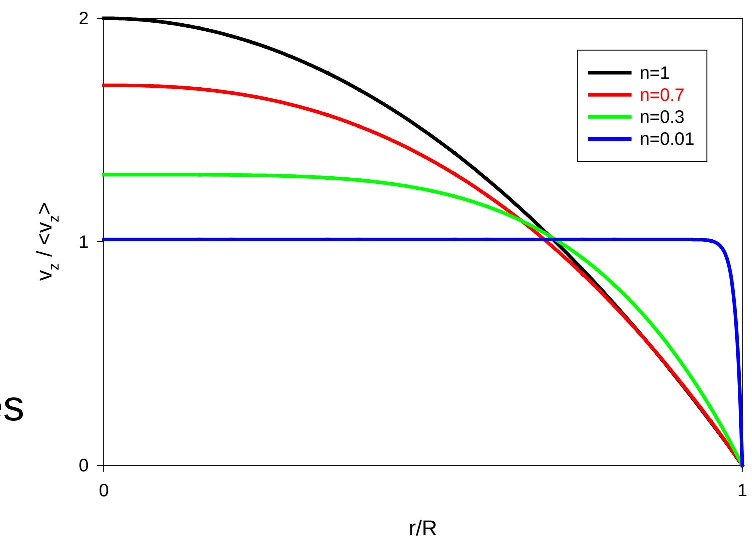
Physical meaning:

e.g. power law fluid

$$\gamma_w = \frac{\dot{\gamma}_a}{4}\left(3 + \frac{1}{n}\right)$$

Steepness of the velocity profile changes
Shear rate is increased with respect to the Newtonian case:

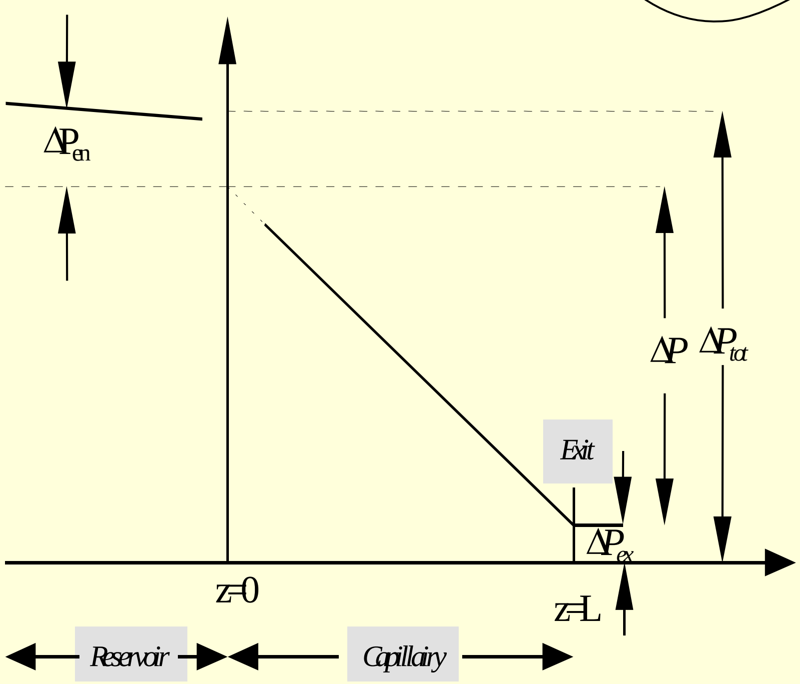
$$\dot{\gamma}_a = \frac{4Q}{\pi R^3}$$

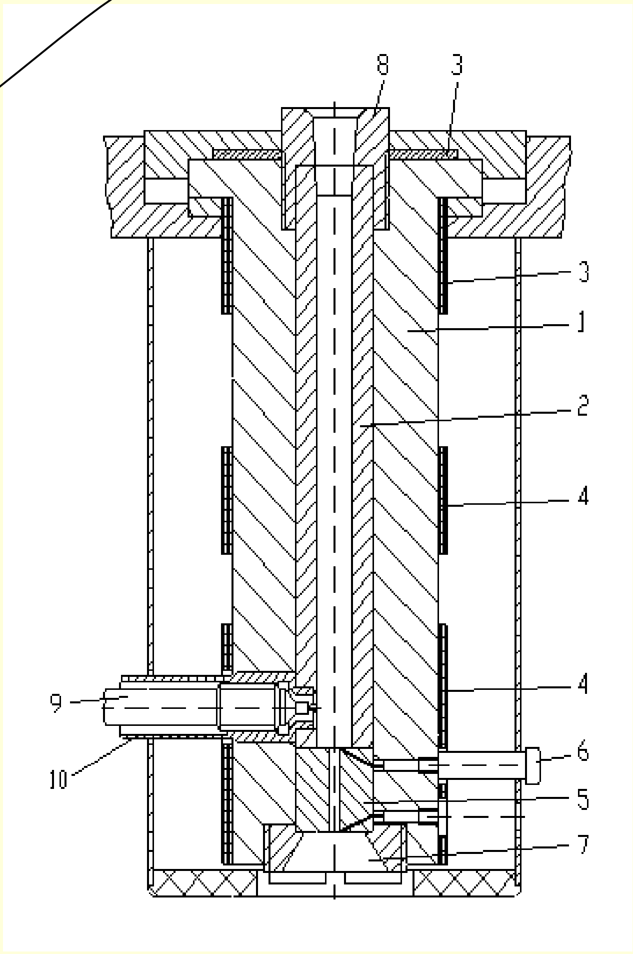


What pressure drop do we really measure?

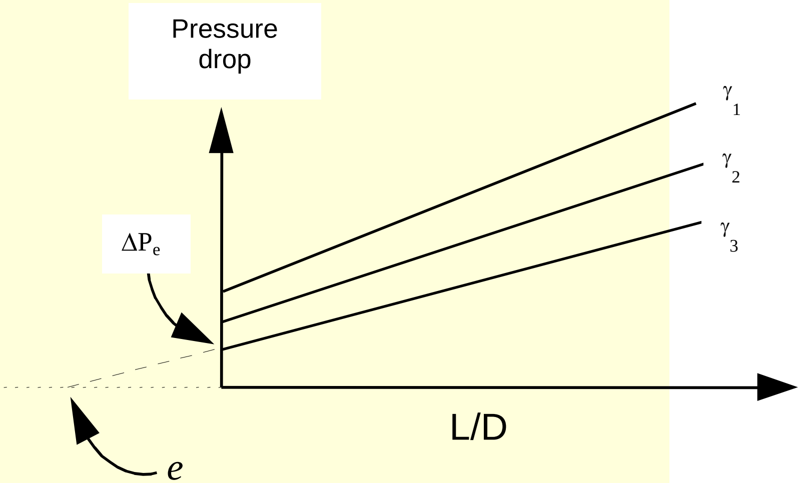
$$\sigma_w = \frac{P_o - P_L}{L} \cdot \frac{R}{2}$$

Cannot be measured!



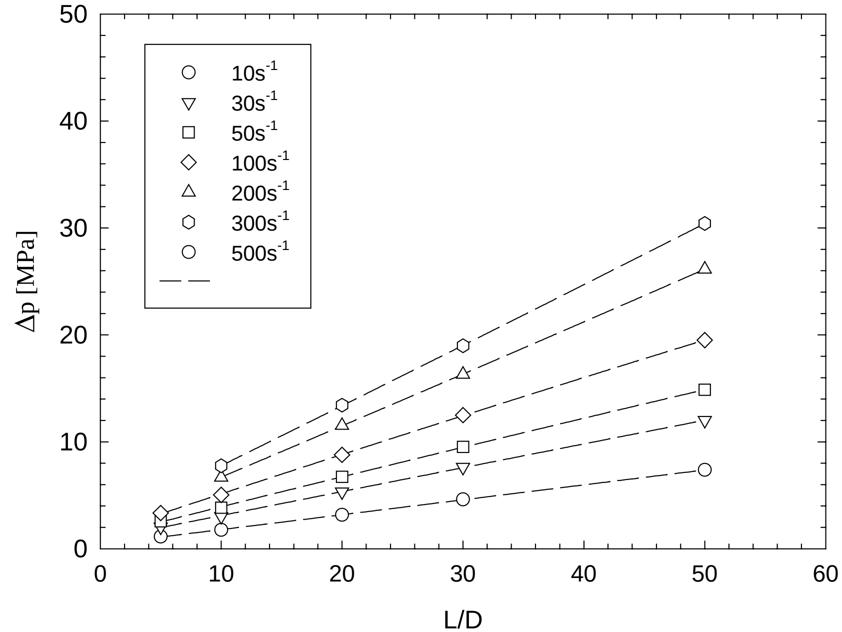


BAGLEY plots



$$\sigma_w = \frac{\Delta P \cdot R}{2(L + eR)}$$

LDPE @190°C

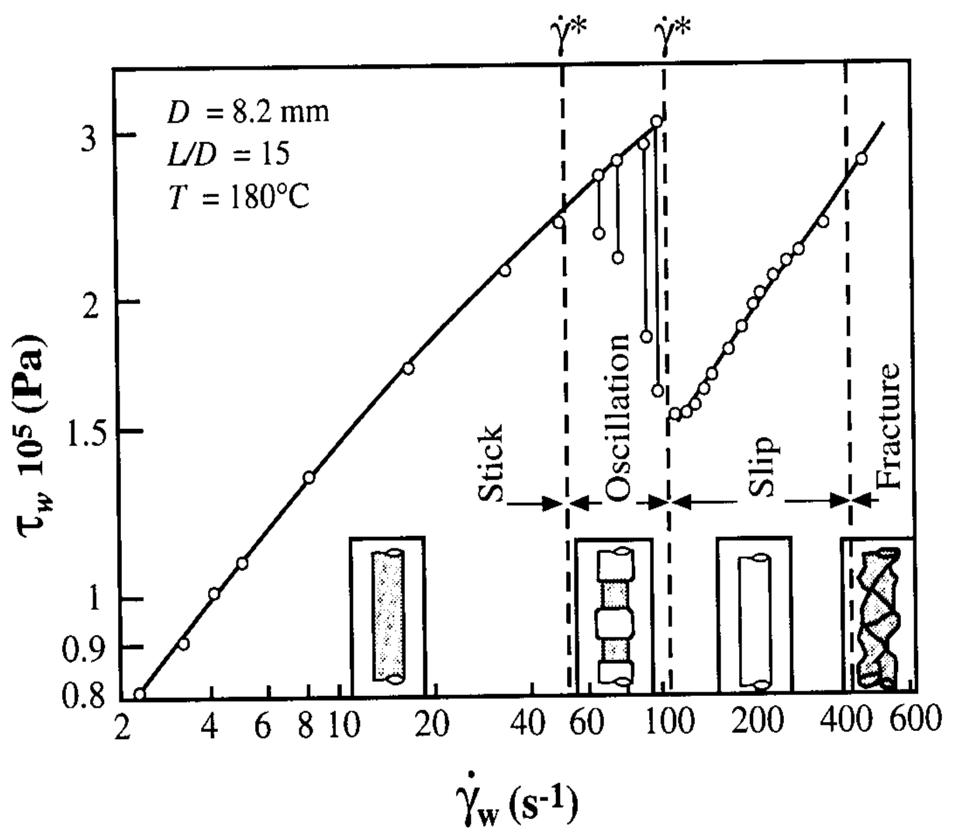


Δp_e can be used to estimate
the elongational viscosity (contraction flow)

Are these conditions met ?

1. Steady, laminar, isothermal flow
2. No slip at the wall, $v_x = 0$ at $R=0$
3. $v_r = v_\theta = 0$
4. Fluid is incompressible, $\eta \neq f(p)$

Problem 1: Melt distortion



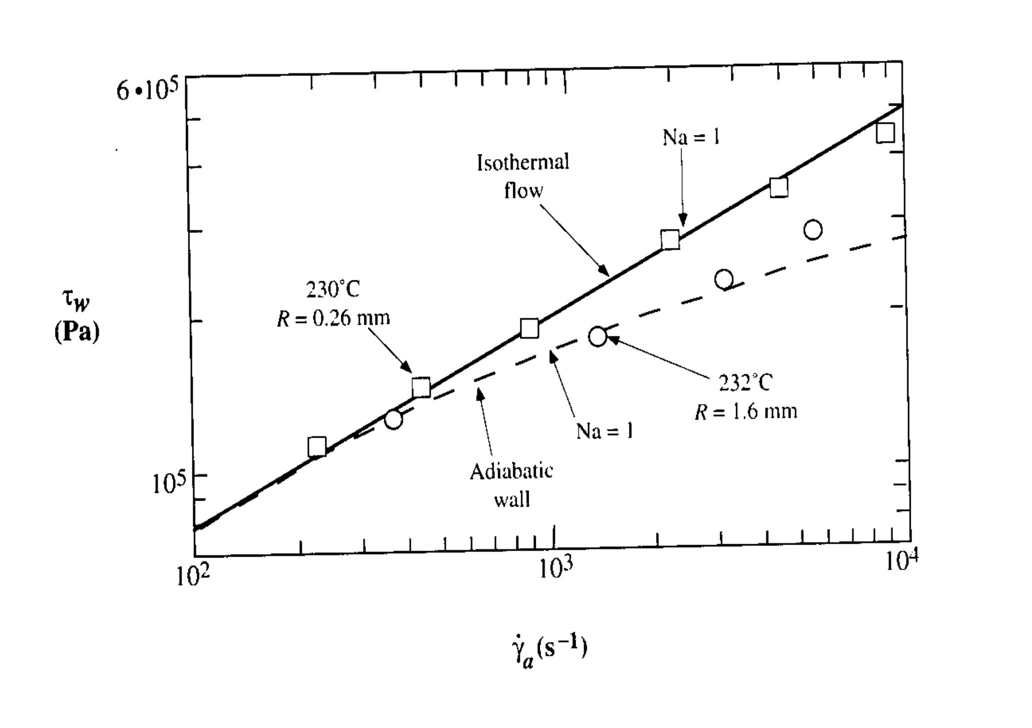
Melt fracture typically occurs at σ_w 10^5 Pa

Are these conditions met ?

1. Steady, laminar, isothermal flow
2. No slip at the wall, $v_x = 0$ at R=0
3. $v_r = v_\theta = 0$
4. Fluid is incompressible, $\eta \neq f(p)$

Problem 2: Viscous heating

$$N_a = \frac{\alpha \tau R^2 \dot{\gamma}}{4k}$$

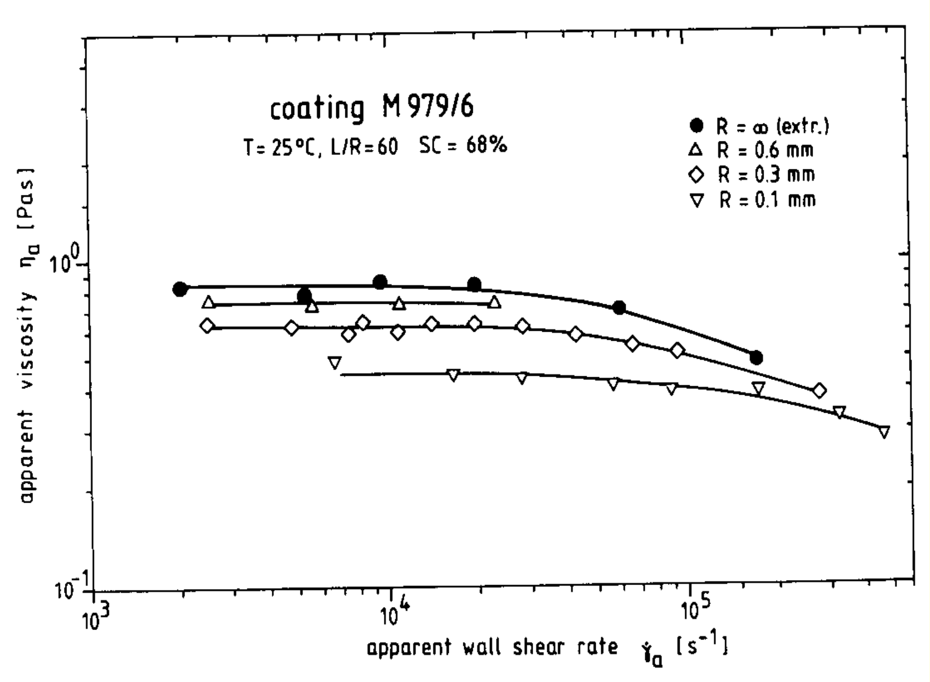


Are these conditions met ?

1. Steady, laminar, isothermal flow
2. No slip at the wall, v_x =0 at R=0
3. v_r=v_θ=0
4. Fluid is incompressible, $\eta \neq f(p)$

Problem 3: Wall slip

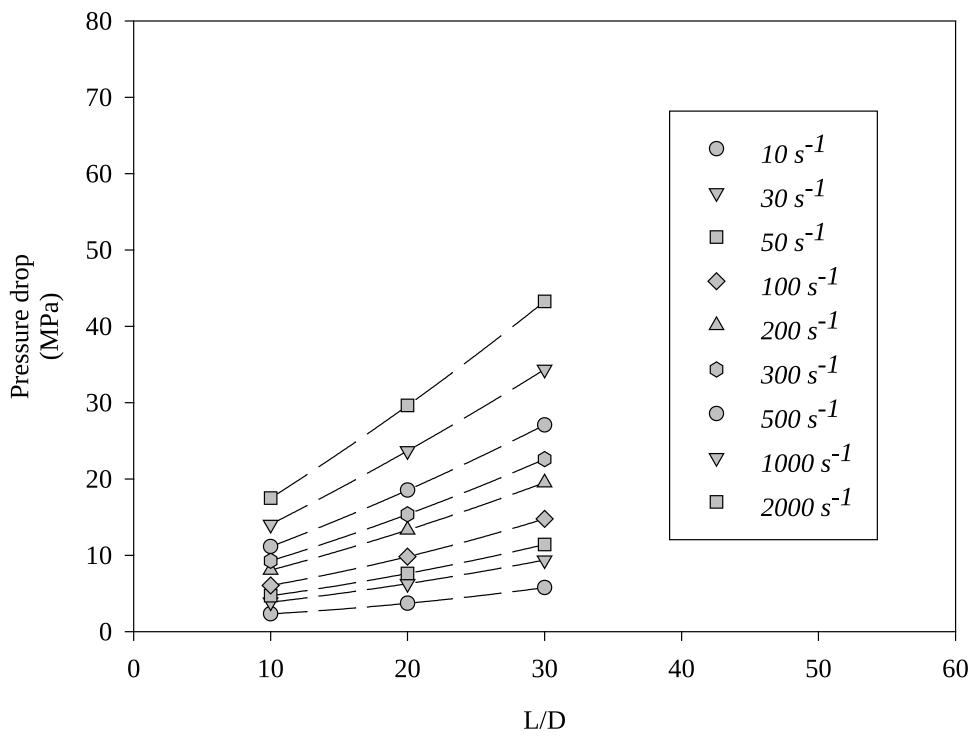
$$\dot{\gamma}_a = \dot{\gamma} + \frac{4v_s}{R} \quad @ \quad \sigma = cst$$



Are these conditions met ?

1. Steady, laminar, isothermal flow
2. No slip at the wall, v_x =0 at R=0
3. $v_r = v_\theta = 0$
4. Fluid is incompressible, $\eta \neq f(p)$

Problem 4: Melt compressibility, $\eta = f(p)$



Capillary rheometry : conclusions

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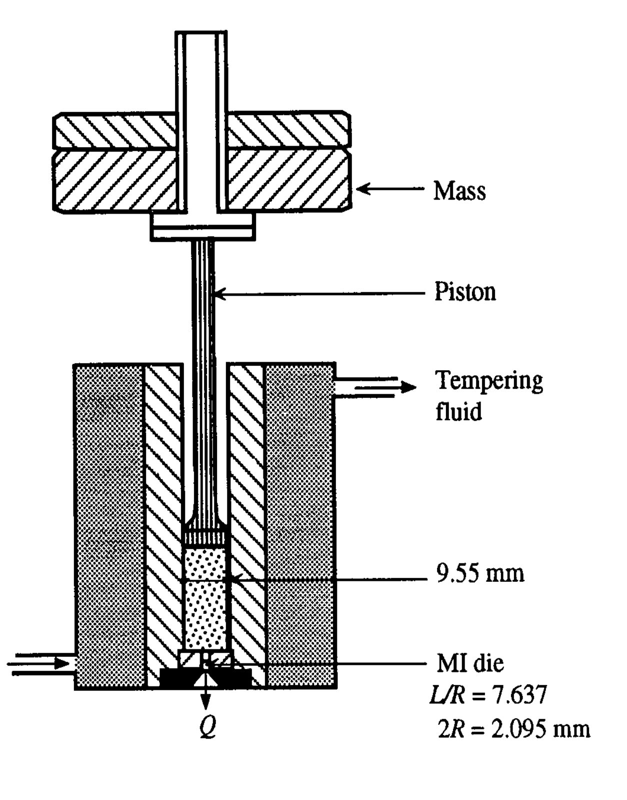
- Simple yet accurate!
- High shear rates possible
- Sealed system, can be pressurized
- Process simulator
- Entrance flows and exit flows can be used
- MFI

-

- Non-homogeneous flow field (correctable)
- Only viscosity data, some indications for N_1, η_e
- Lot of data required (Bagley plots)
- Melt fracture limits shear rate
- Wall slip can be a problem
- Viscous heating
- Shear history / degradation

Melt Flow index



Shear rheometers: the verdict

Couette	+ low η, high rates + can be homogeneous + settling	- end corrections - high visc. : too difficult - no N_1
Cone and Plate	+ best for N_1 + homogeneous + transient meas.	- edges, low shear rate - free surface - alignment
Parallel Plate	+ easy to load + G',G" for melts + vary h!	- edges - non-homogenous - free surface
Capillary	+ high rates + accuracte + sealed	- corrections: - non-homogenous - no N_1

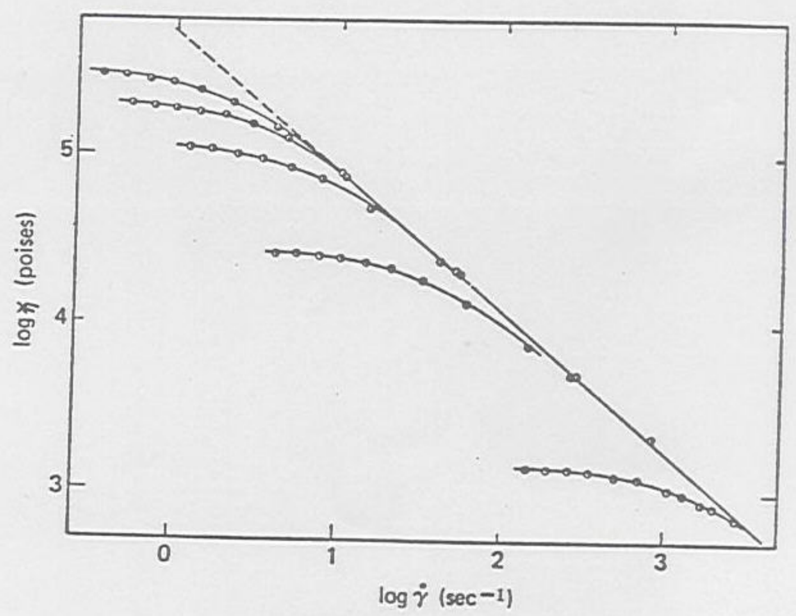
Contents

4. Parameters affecting rheology

- Chemistry
- Molecular weight
- Molecular weight distribution
- Molecular architecture (branching)
- Fillers/additives
- Temperature
- Pressure
- …

Effect of molecular weight on the viscosity curve

Example: narrow MW polystyrenes

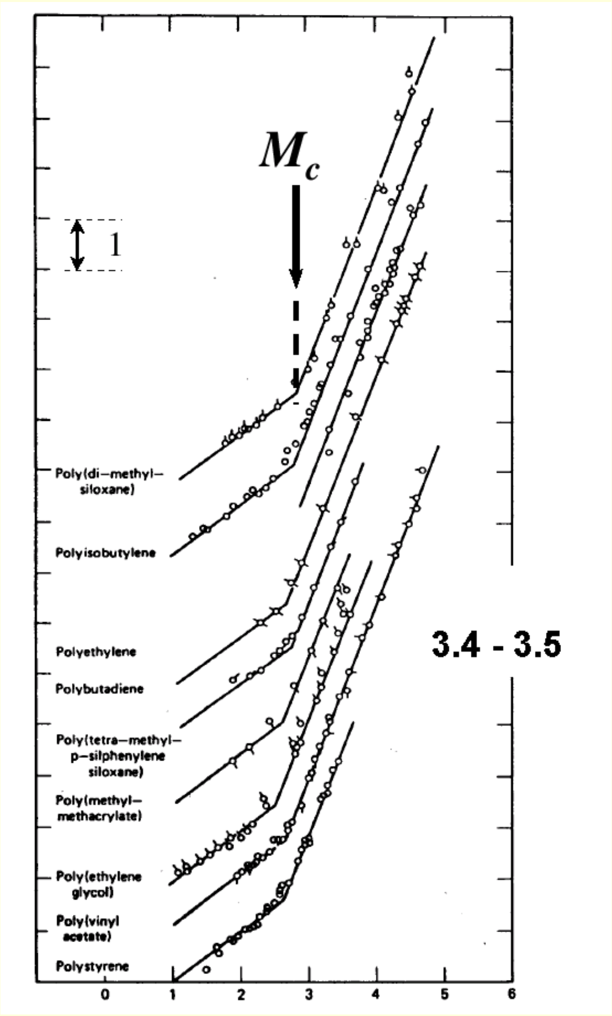


η/η_0 vs $\dot{\gamma}\tau_0$: single curve

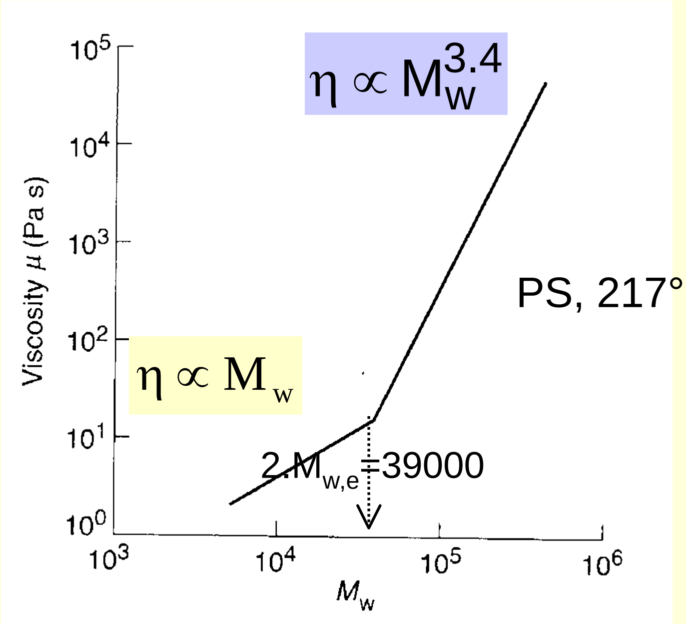
From Stratton

Effect of the MW on the zero shear viscosity for linear molten polymers

Log η + ct

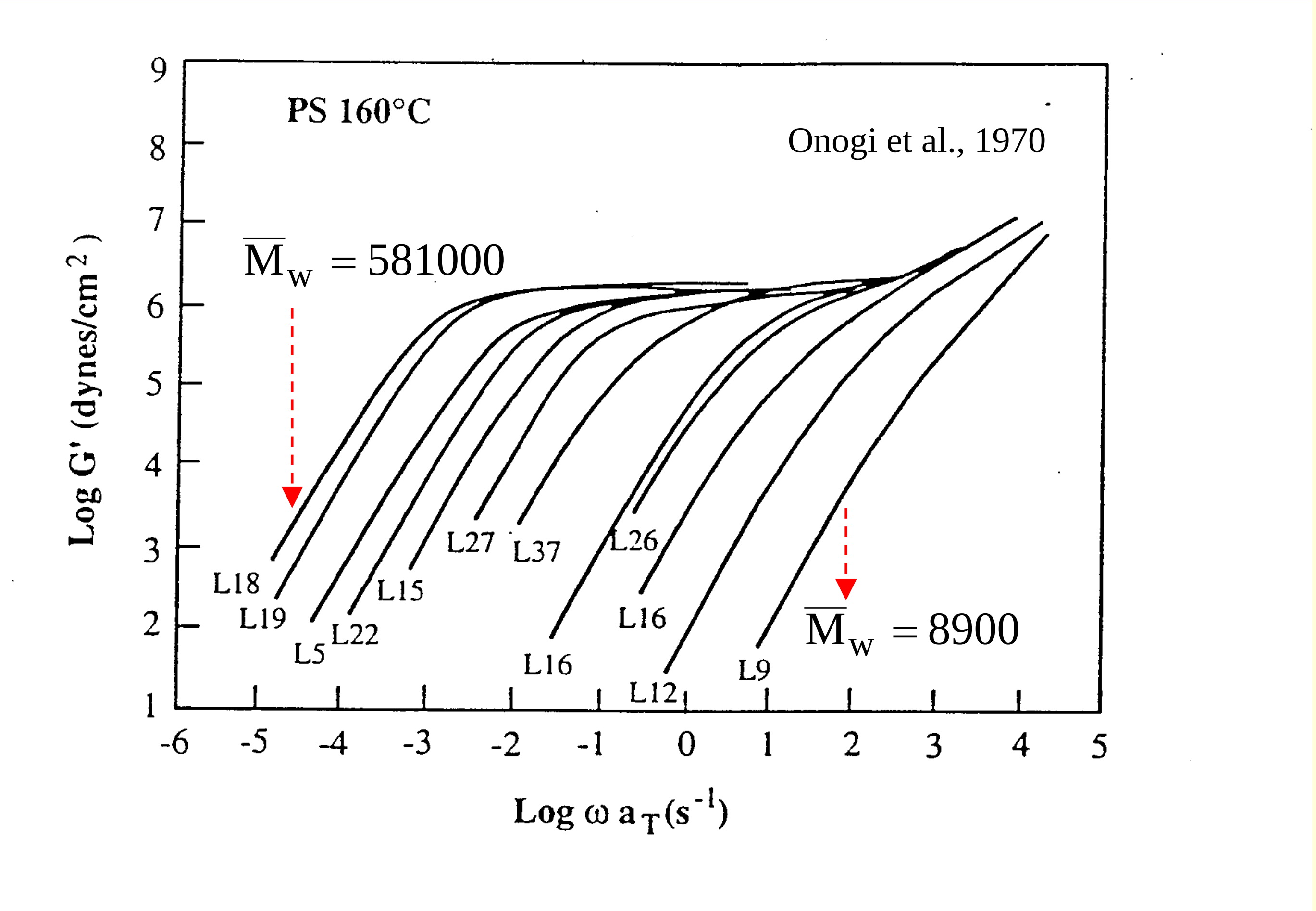


Log Mw + ct



Berry and Fox

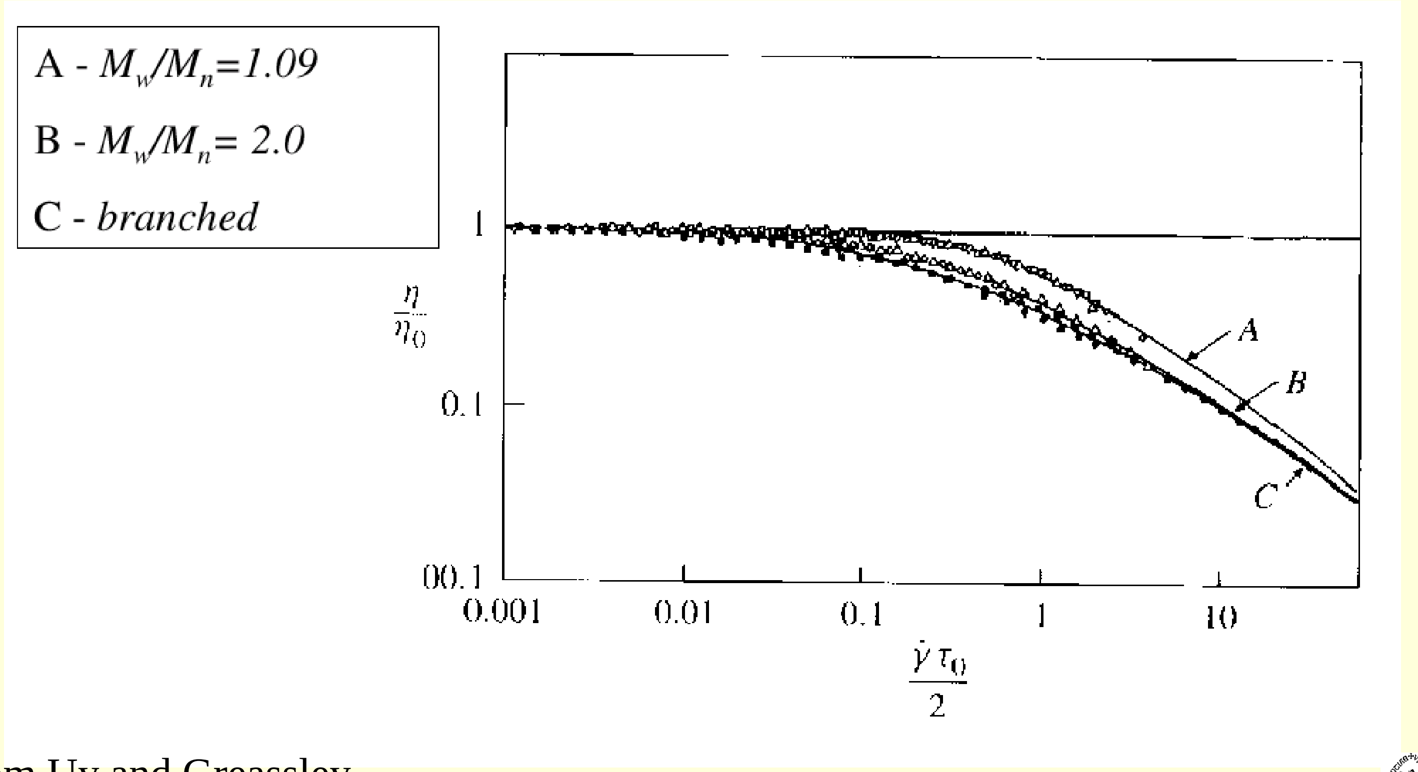
Effect of molecular weight on moduli



Effects of molecular weight distribution

Viscosity:

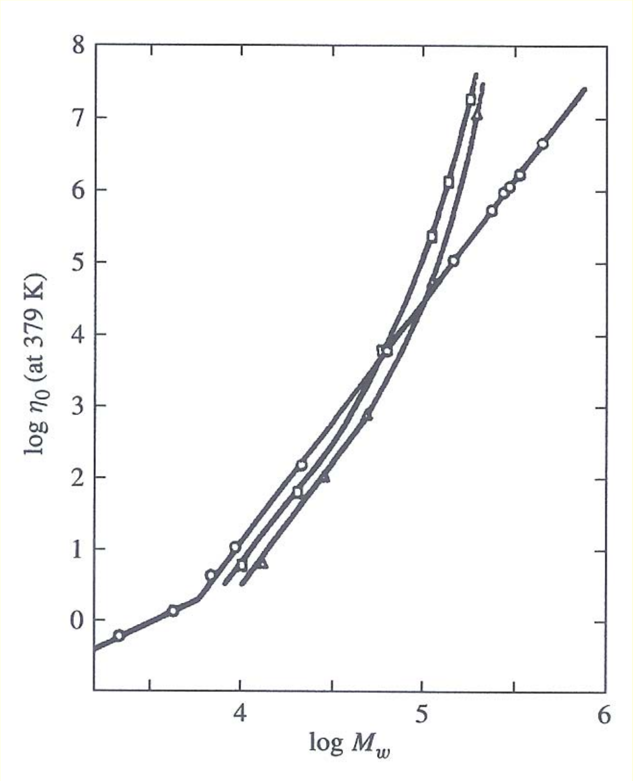
Shear thinning sets in earlier with increasing molecular weight distribution



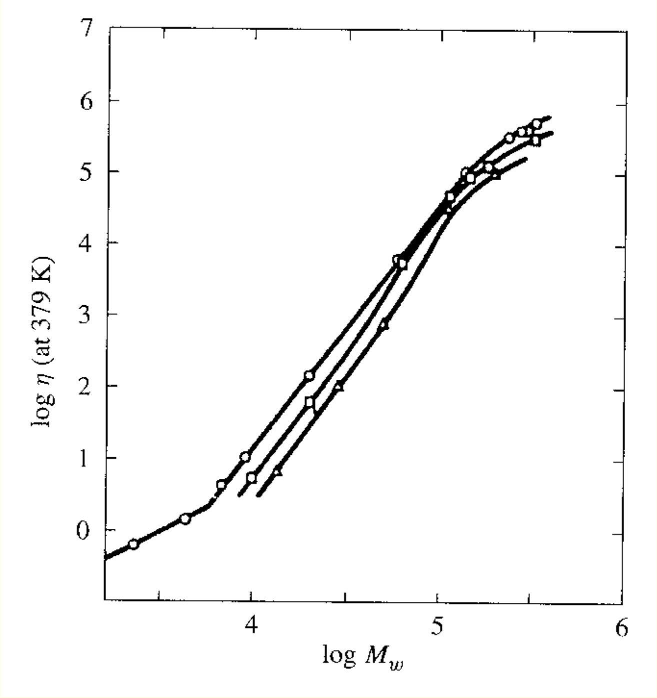
From Uy and Greassley

Effect of chain architecture (branching)

Low shear rates



higher shear rates

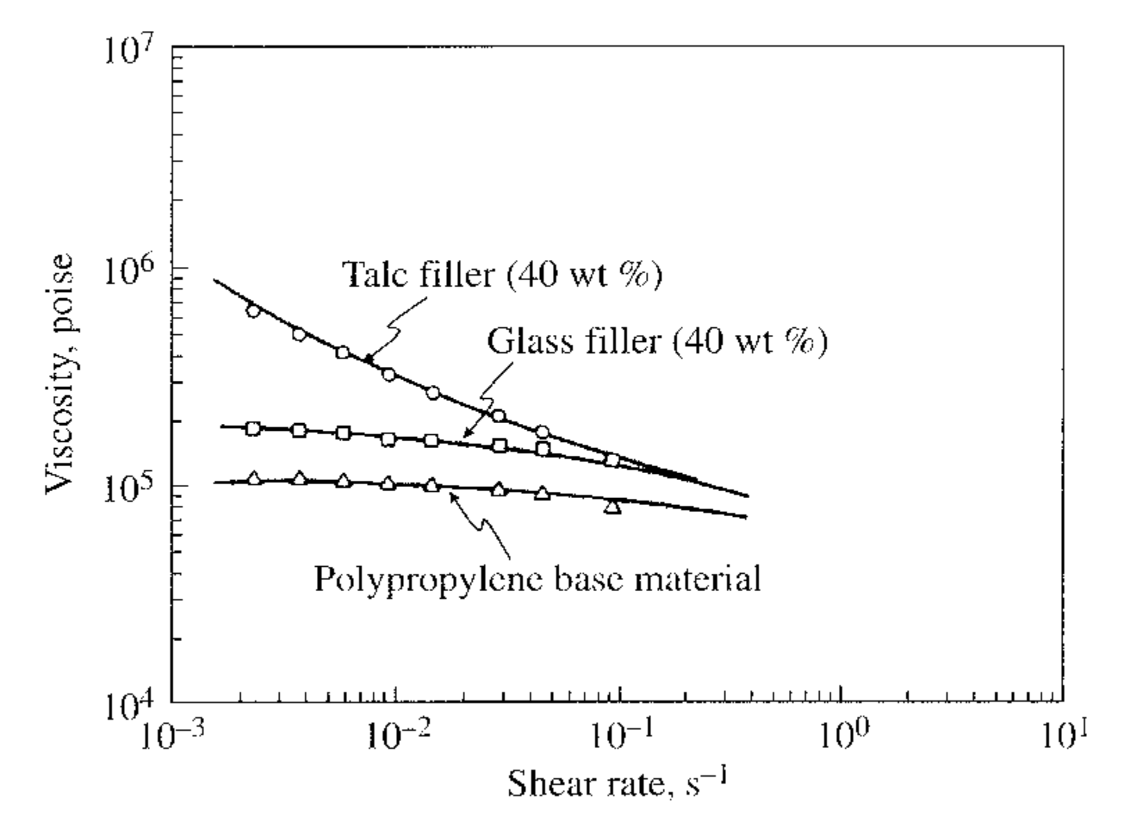


O = linear

□ and Δ = branched

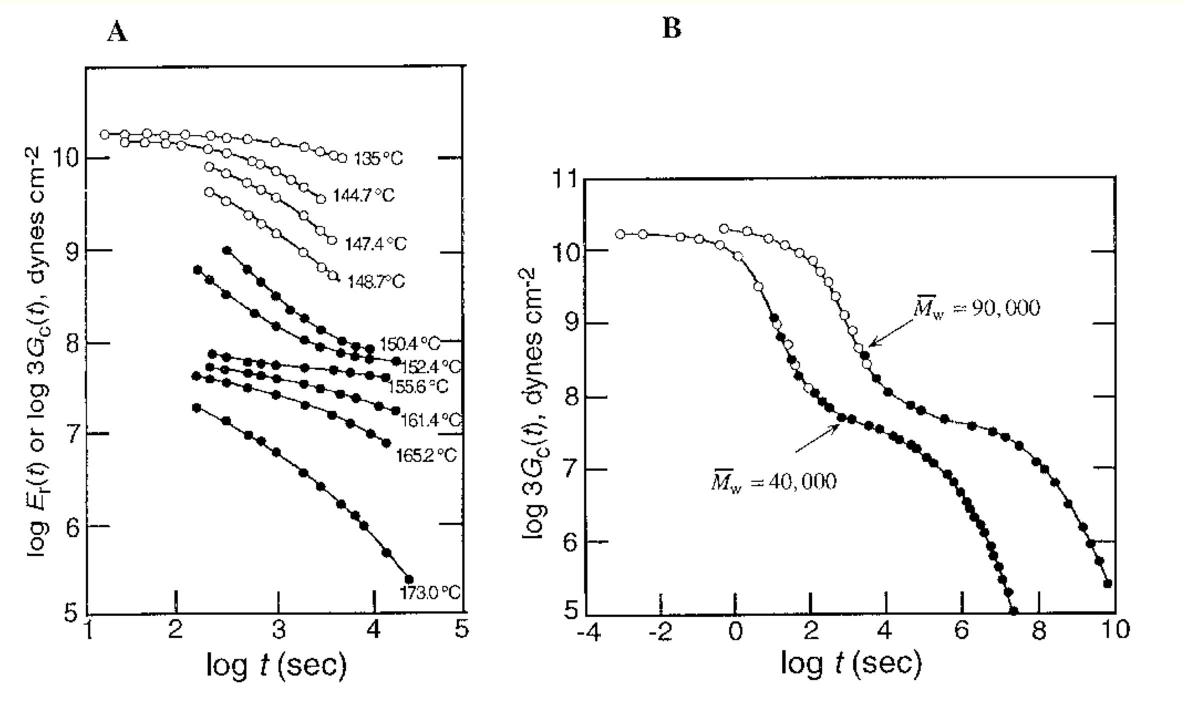
Kraus and Gruver

Effect of fillers



Chapman and Lee

Effect of temperature: time-temperature superposition



$$\text{WLF-relation:} \qquad \log a_T = \frac{-C_1\,(T-T_r)}{C_2 + T - T_r}$$

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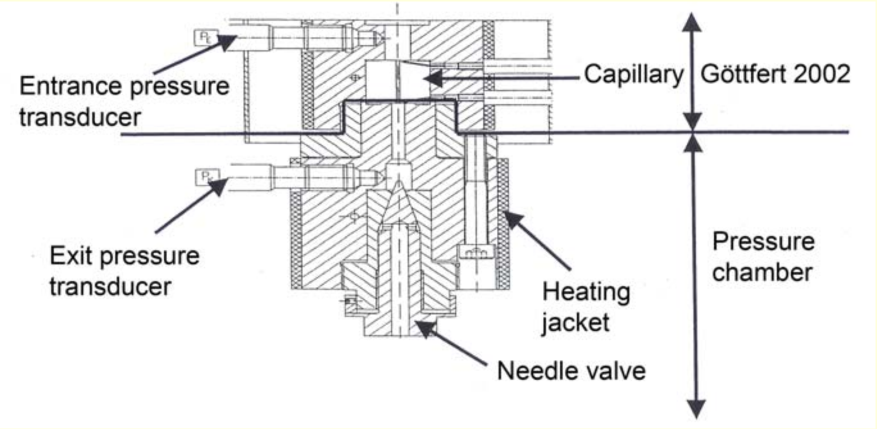
Effect of pressure on viscosity

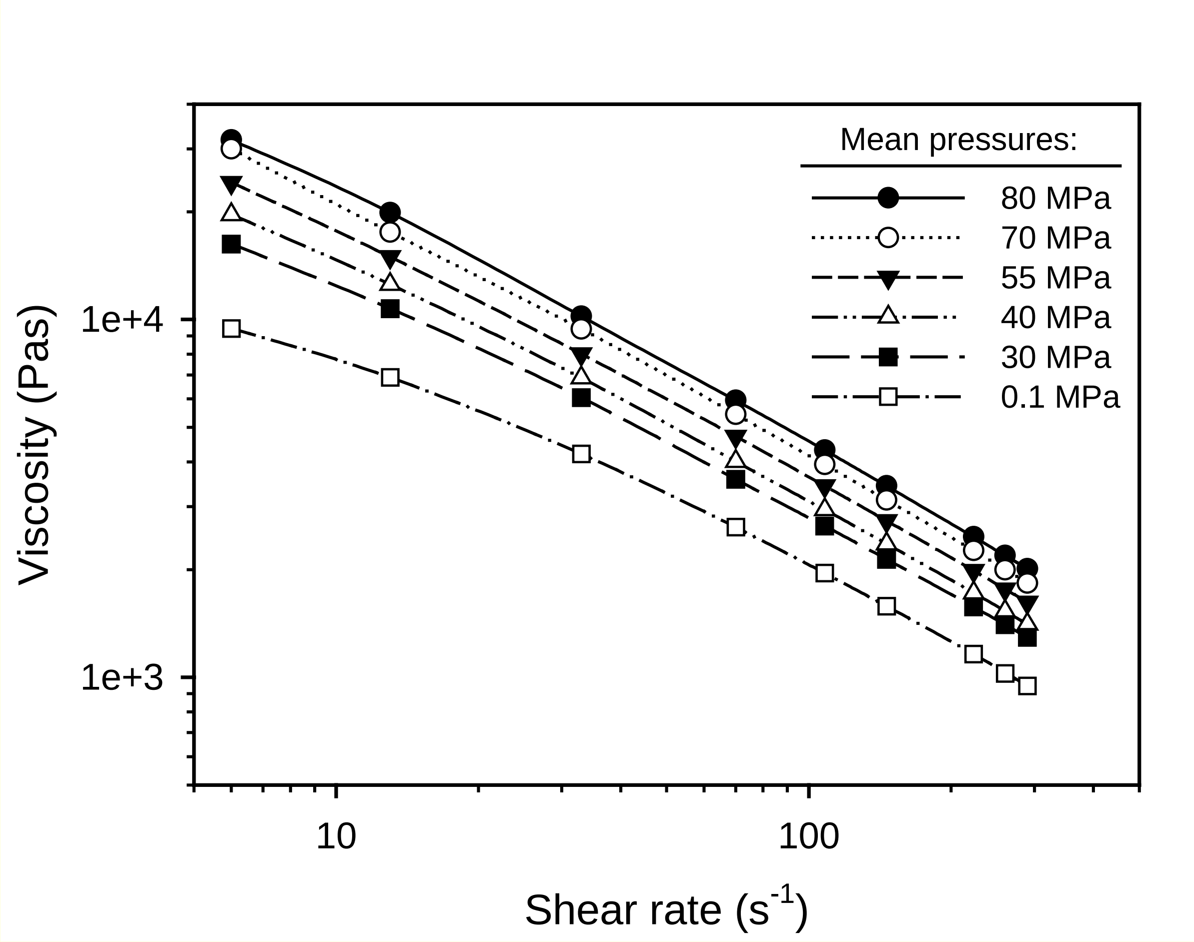


$$\beta = \left(\frac{d \ln \eta}{dP} \right)_T$$

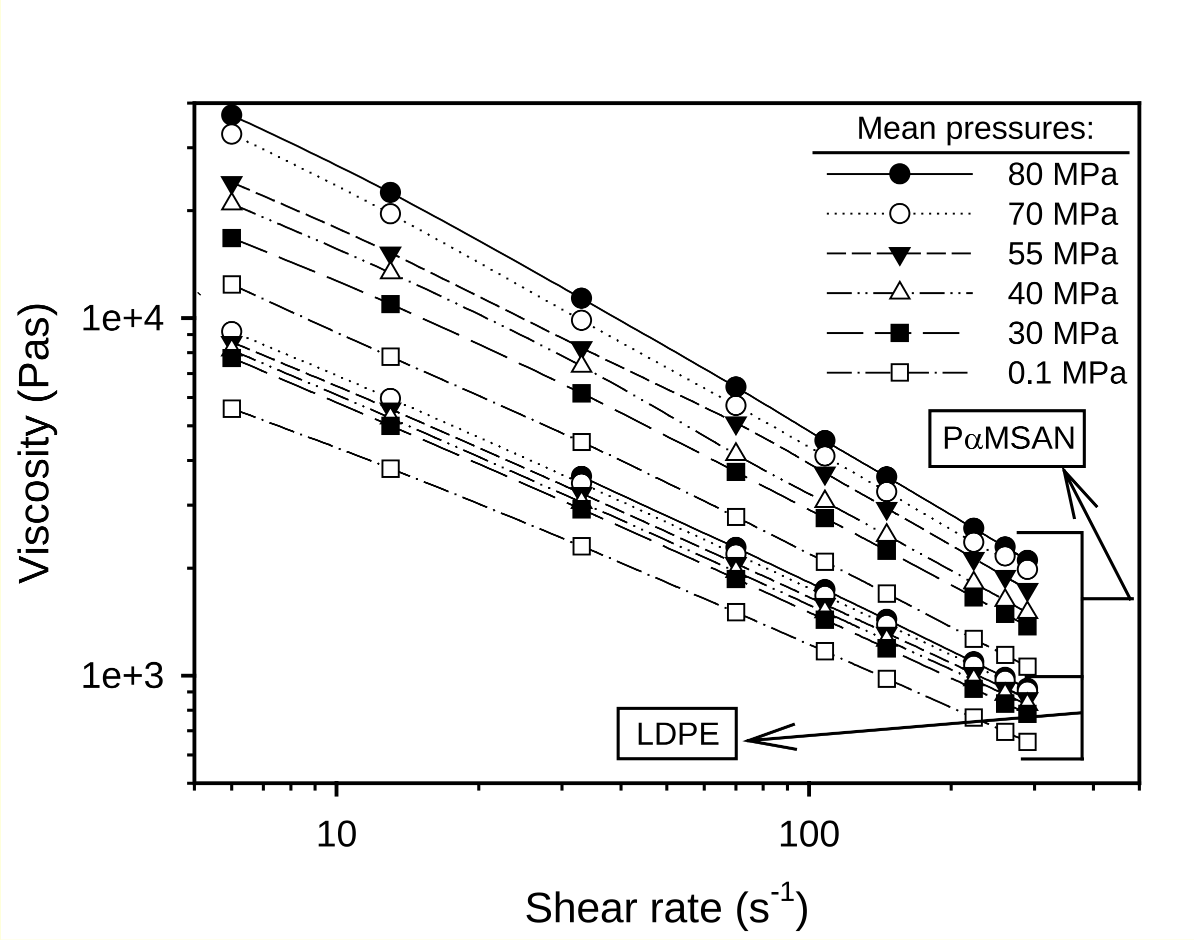
⇨Relevant for injection moulding

⇨Add-on 'pressure chamber' on Gottfert capillary rheometer

“Corrected” viscosity for PMMA (210° C)

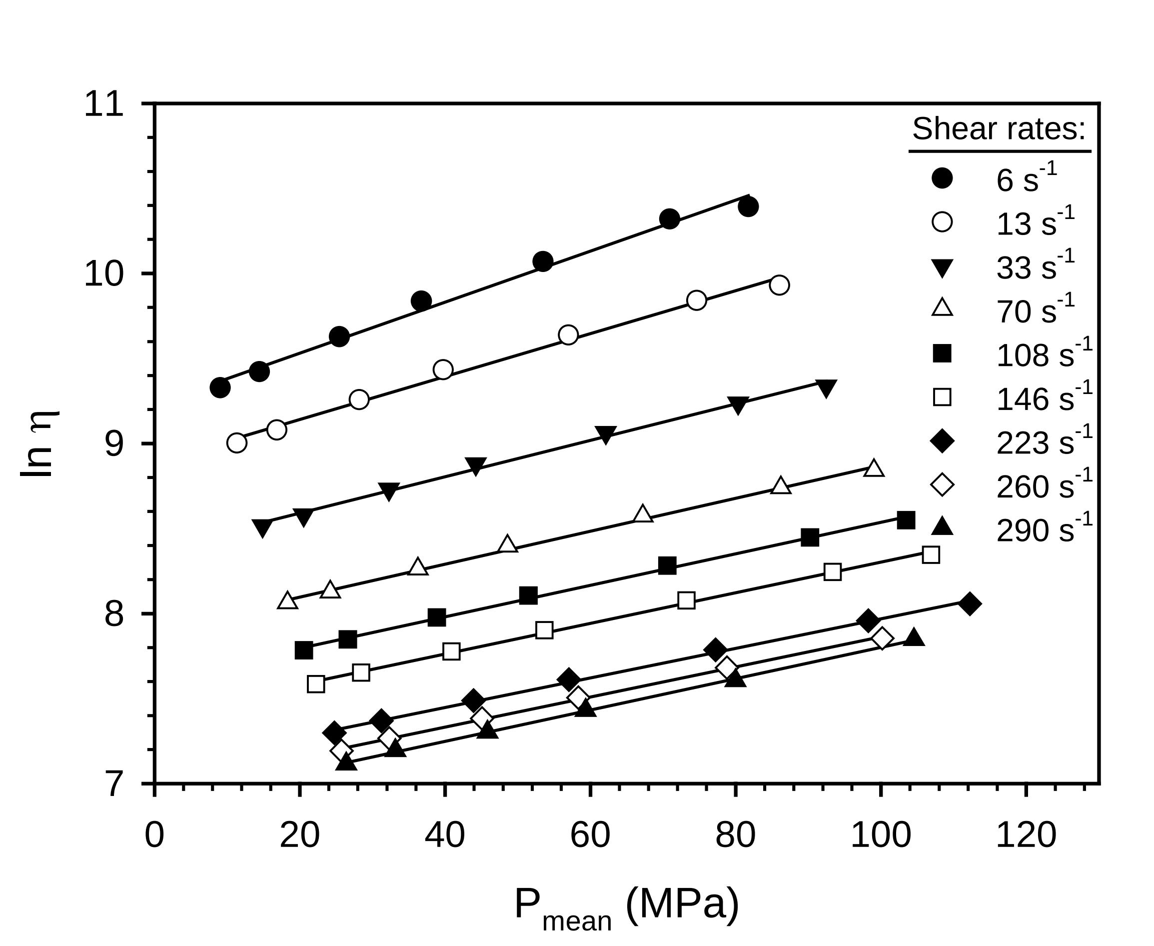


Viscoity curves for PαMSAN and LDPE

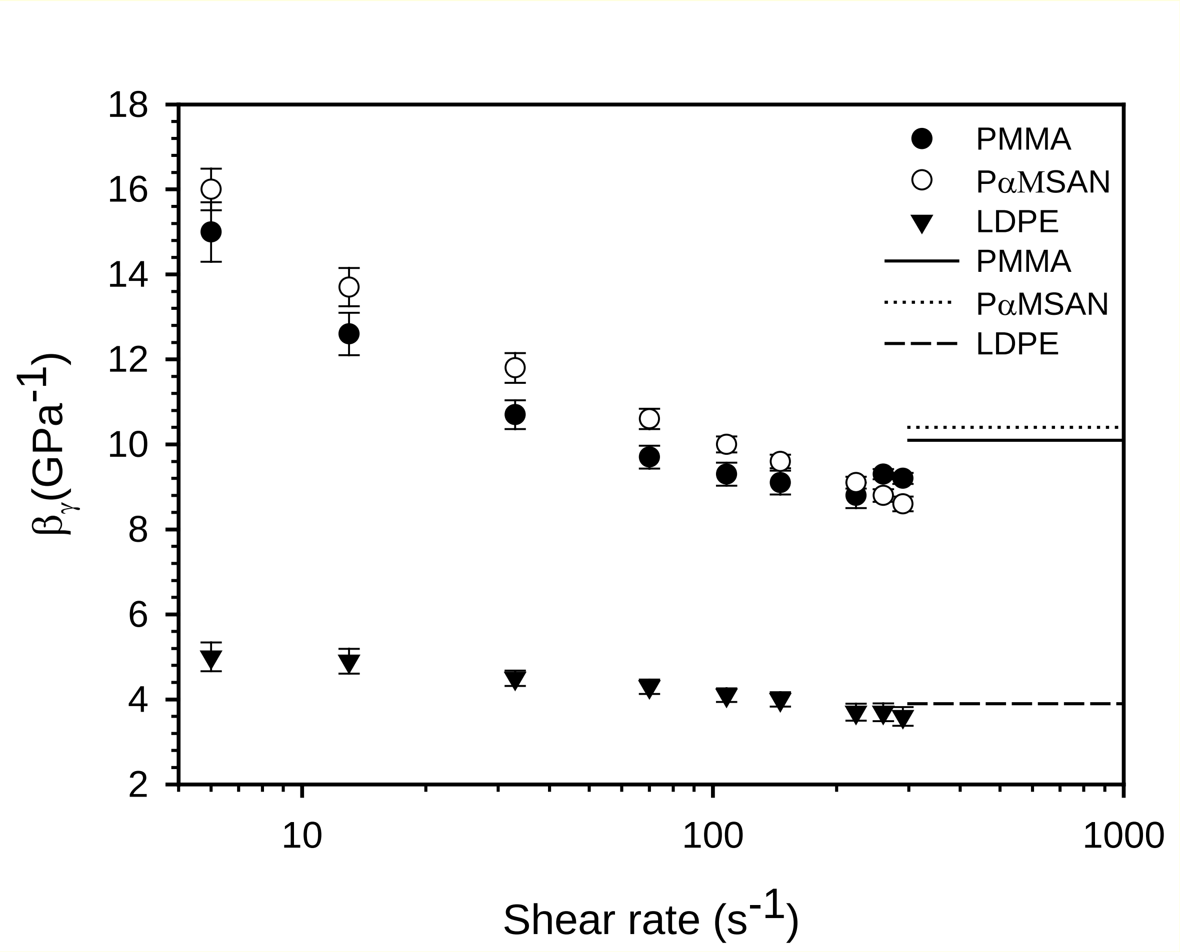


Determination of β at several shear rates

$$\beta = \left(\frac{d \ln \eta}{dP} \right)_T$$

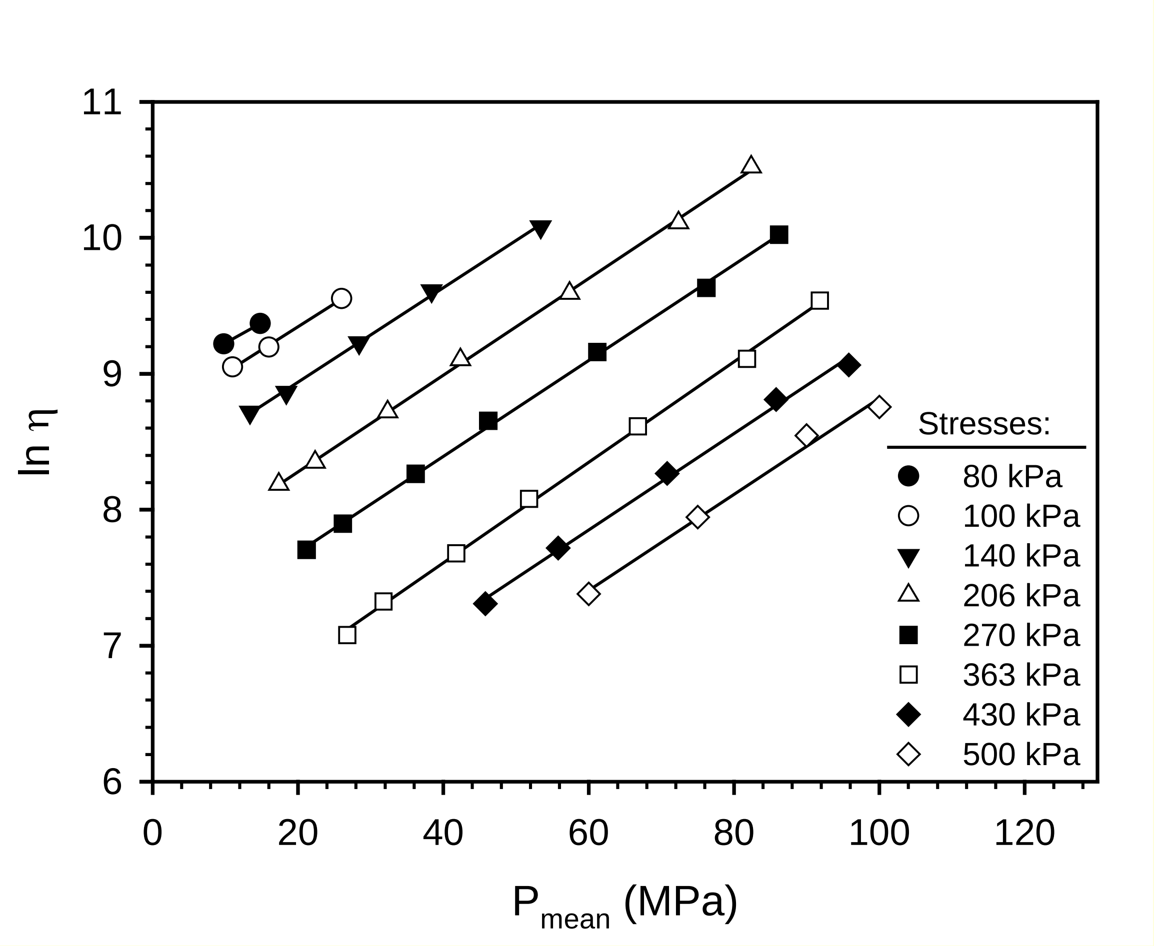


β at several shear rates

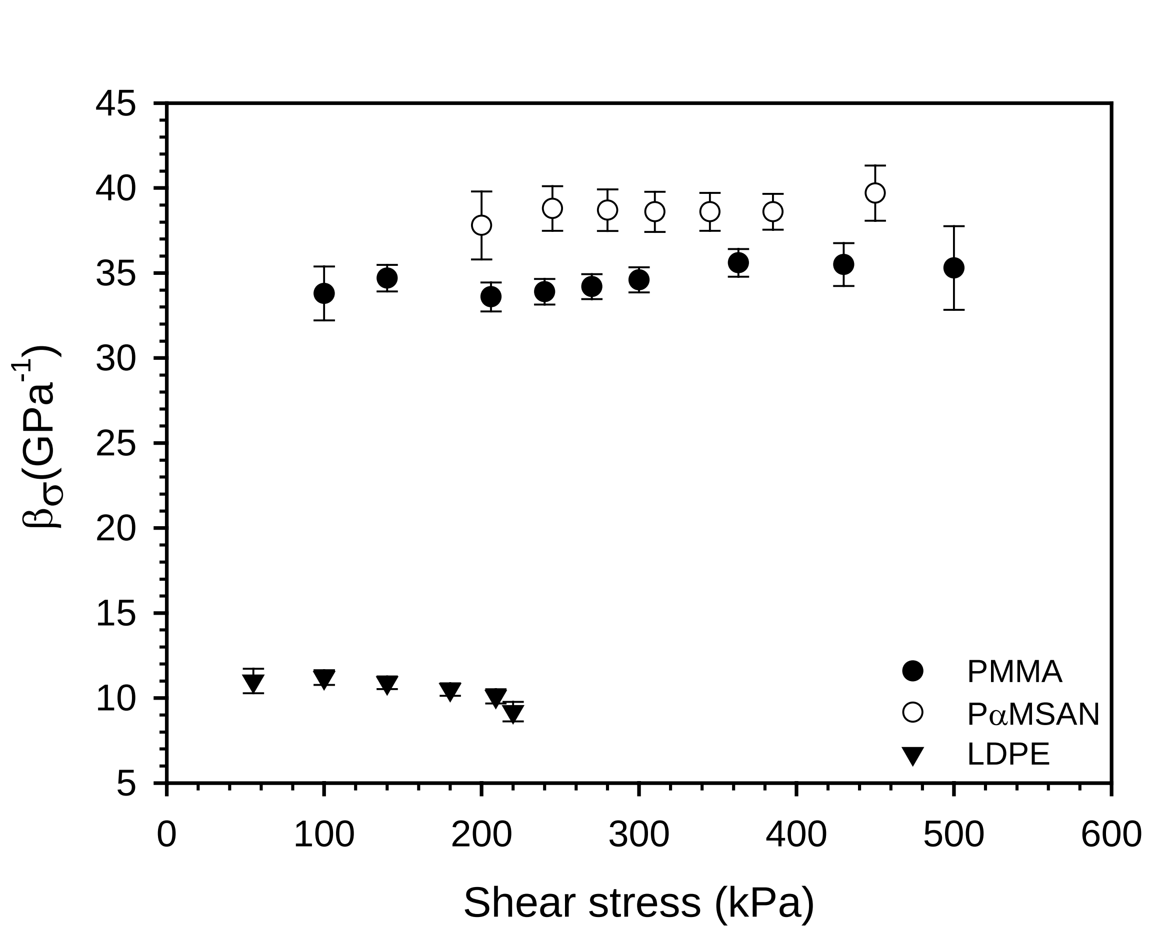


Determination of β at several shear stresses (PMMA)

$$\beta = \left(\frac{d \ln \eta}{dP}\right)_T$$



β at several shear stresses (PMMA)



Useful references concerning rheology

Rheology: Principles, Measurements and Applications

C. Macosko Ed, VCH (1994)

Understanding Rheology

F. Morrison, Oxford University Press (2001)

Structure and Rheology of Molten Polymers

J.M. Dealy and R.G. Larson, Hanser (2006)