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- **Rheology**
- **Oscillatory experiments**
- **Dynamic experiments**

Deformation of materials under non-steady conditions in the linear viscoelastic range

No relaxation and no creep experiments

Experiments under oscillatory stress or deformation to describe polymer solutions or polymer melts

Polymer – properties – function correlation

Molecular weight and Mw distribution
- poly-disperse vs. mono-disperse
- wide vs. narrow MWD

Shape of the molecule
- linear vs. branched
- type and sequence of monomers
- in the case of sugar compounds:
  - Monosaccharide, A or β conformation
  - linkage 1→2; 1→3; 1→4; 1→6

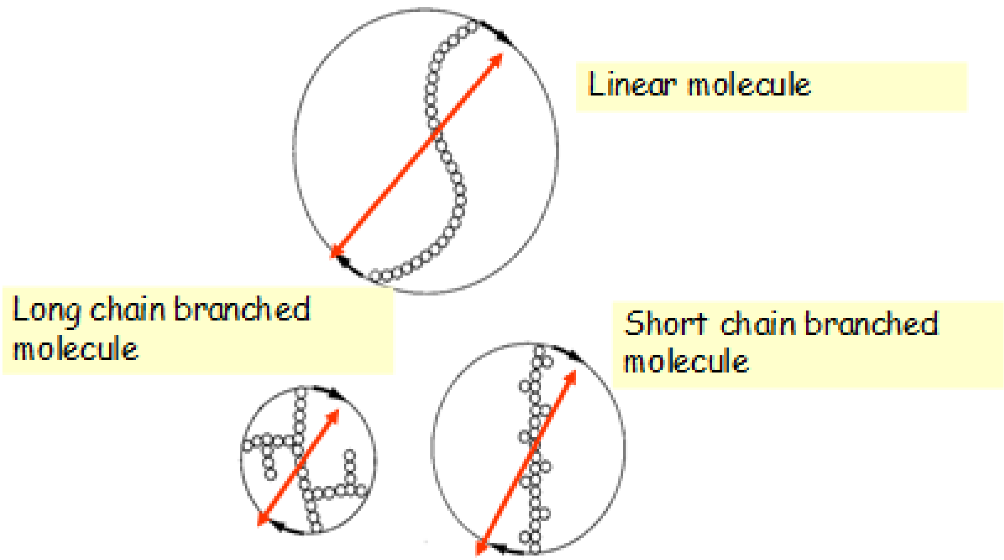
Flexibility and stability of monomer (sugar) linkages

Presence of monomer (sugar) substituents
- type
- number
- distribution

Presence of charges
- type - pH dependency?
- number
- distribution

Structure – volume relationship of molecules

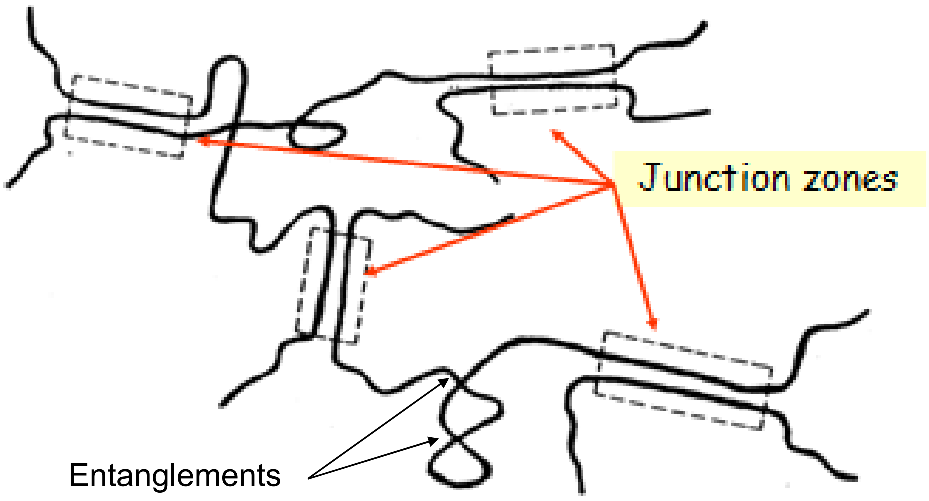
Different "effective volume" for similar molecular weight



Permission of Henc Schols

Interaction between polymers in solution/melts

Entanglement network and gel formation



Permission fron Henc Schols

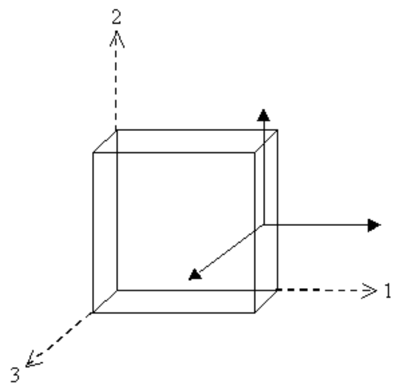
Some reminder

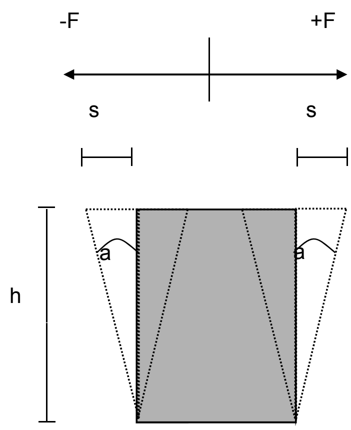
Basic behaviour of materials under stress:

Hook´s law	Newton´s law
solids	liquids
$T_{12} = G^*\gamma$	$T_{12} = \eta^* d\gamma/dt$

T_{12}	=	shear stress (tensor)	/Pa/
γ	=	deformation	/ /
$d\gamma/dt$	=	shear rate	/ s^{-1}/
η	=	viscosity	/Pa.s/
G	=	shear or elastic modulus	/Pa/

Deformation





$$\begin{matrix} \tau_{11} & \tau_{12} & \tau_{13} \\ \tau_{21} & \tau_{22} & \tau_{23} \\ \tau_{31} & \tau_{32} & \tau_{33} \end{matrix}$$

Definitions

- Deformation : (no dimension)
- Applied force F : shear stress τ_{12} tau → causes deformation (strain)
- Applied deformation: causes force, shear stress F
- Shear rate : $\dot{\gamma} = d\gamma/dt$ resp. D
  Change of deformation during deformation time

Linear viscoelastic region !! → deformation – stress proportionality

Newton - fluid:

Applied stress – cause shear rate
Viscosity

$\tau_{12} = \eta \cdot \dot{\gamma}$

Resp. $\dot{\gamma} = \tau_{12} / \eta$

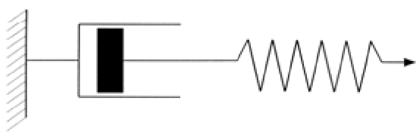
Hook – solid:

Applied stress – cause deformation
Elasticity

$$\tau(t) = G \cdot \gamma(t)$$

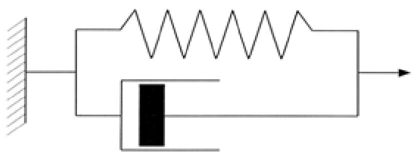
resp. $\gamma(t) = \frac{1}{G} \cdot \tau(t)$

Maxwell model



Relaxation time:

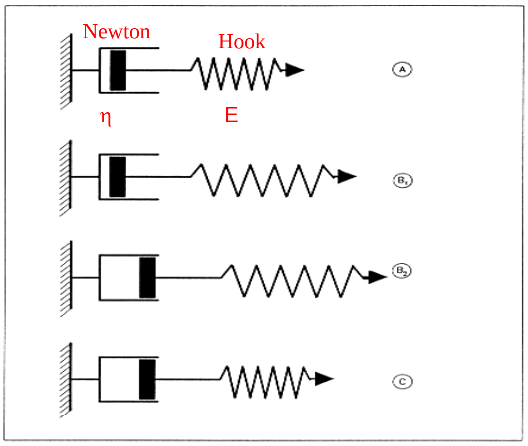
$\Lambda = \eta / G$ /s/



Voight model

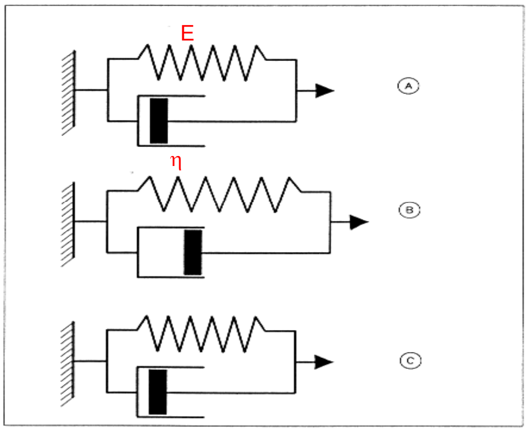
Generalized models

Maxwel



Continous relaxation time distribution

Voight



Stress applied at different frequencies

Almost no stress

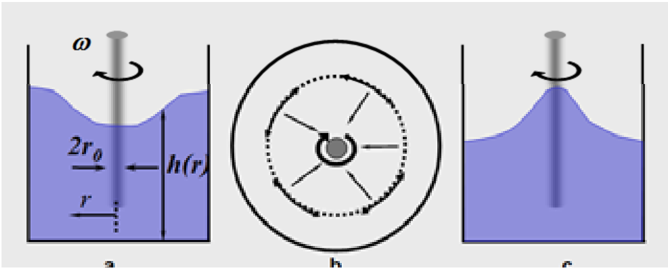
Medium stress at low frequencis

High stress at high frequencies

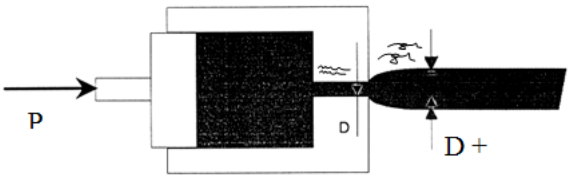
Almost no stress

Examples for elastic behaviour

- Creeping up a stirrer shaft (normal forces - Weißenberg- effect)



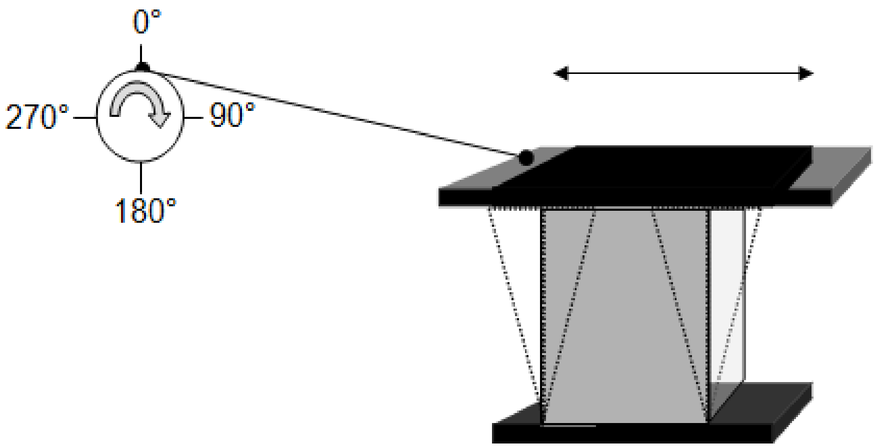
- Nozzle swell



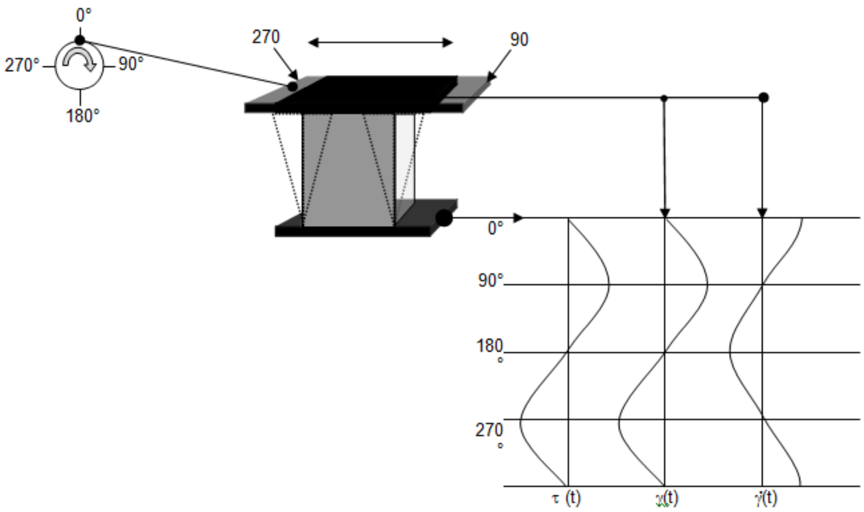
- Drawing fathoms during coating processes
- Different drop size at spray coatings or ink jet coatings
- Bad mouth feeling during chewing and swallowing
  too large elastic contribution
- High elasticity – low damping (acoustic, mechanic)
- Too low elasticity – damping element heats up (car tyre low pressure)

Oscillatory deformation

Material between two plates – sticking, no friction!!



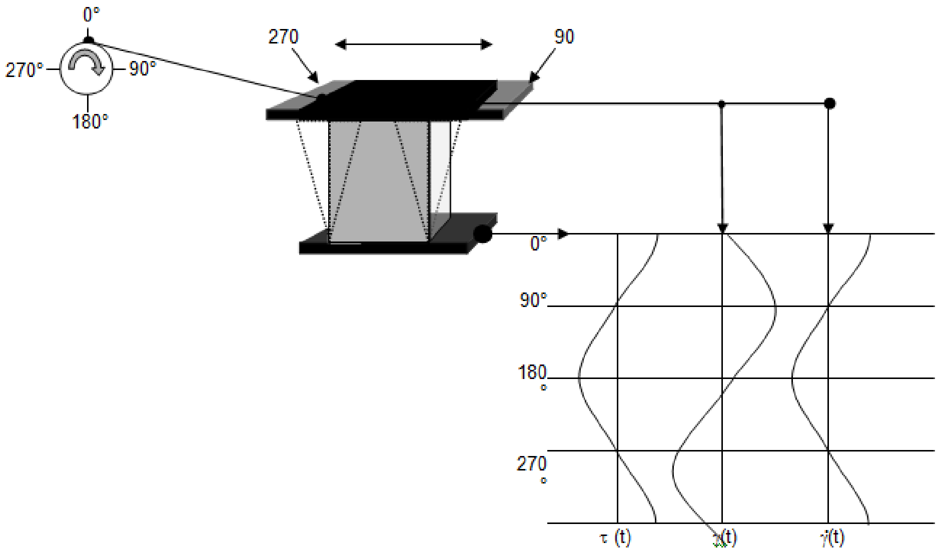
Ideal elastic substances (Hook)



τ (t)-function in phase with γ (t)-function
Both sinus-functions, phase shift γ = 0°

d γ /dt -function a cosinus function

Ideal viscous substances (Newton)

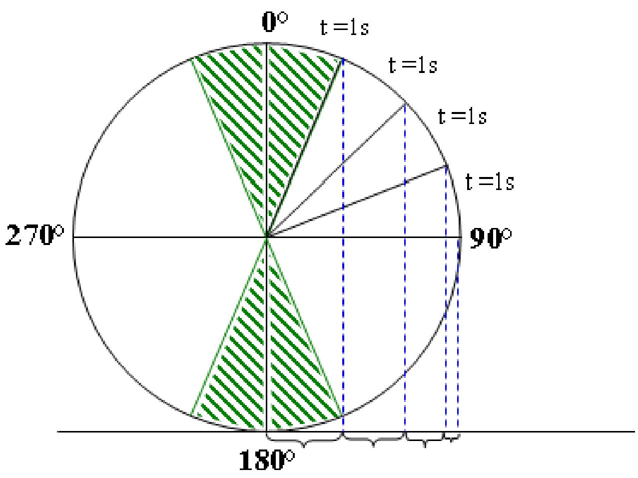


τ (t)-function in phase with $\dot{\gamma}$ (t)-function

Both cosinus – functions, phase shift $\delta = -90° = -\frac{\pi}{2}$

γ (t)-function is a sinus function

Deformation and deformation rate as a function of position



Viscoelastic substances

A superposition between viscous and elastic behaviour !!

Deformation function: $\gamma(t) = \gamma_0 * \cos \omega (t)$ preset shear stress

Shear stress function: $\tau(t) = \tau_0 \cdot \sin(\omega t + \delta)$ preset deformation

γ_0 Deformation amplitude

τ_0 Stress amplitude $|Pa|$

ω Circular frequency $|s^{-1}|$

$\omega = 2\pi \cdot f$; frequency f $|Hz|$

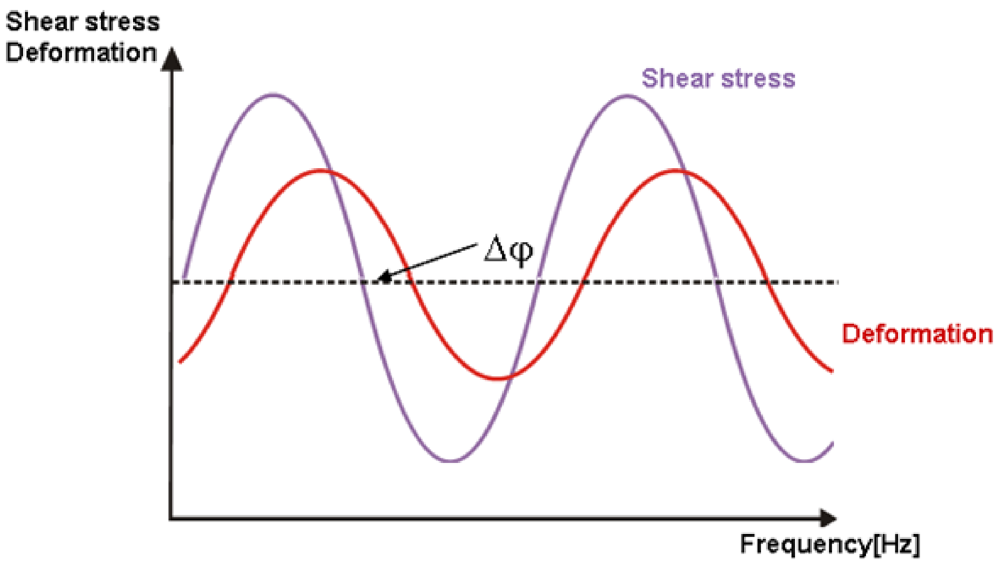
Results

Shear stress function: $\tau(t) = \tau_0 \cdot \sin(\omega t + \delta)$ deformation preset
Deformation functions: $\gamma(t) = \gamma_0 \cdot \sin(\omega t + \delta)$ shear stress preset)

A phase shift occurs between the τ (t)- function and the γ(t)-function
Phase angle 0°> δ >-90°.

- deformation $\gamma_t = \gamma_o \cdot e^{i\omega t}$
- shear rate $\dot{\gamma}_t = \gamma_o \, i\omega e^{i\omega t}$
- shear stress $\tau_t = \tau_t \, e^{i(\omega t+\varphi)}$

Phase shift between the τ (t)- function and the γ(t)-function



Evaluation of a complex equation

$\gamma_t = \gamma_o \cdot e^{i\omega t}$ → **complex equation**

real part

$\gamma_{real} = \gamma_o (\cos \omega t)$

imaginary part

$\gamma_{imag} = \gamma_o (\sin \omega t)$

$\tau_t = \tau_o e^{i(\omega t+\varphi)}$

real part

$\tau_{real} = \tau_o (\cos \omega t+\varphi)$

imaginary part

$\tau_{imag} = \tau_o (\sin \omega t+\varphi)$

Calculation of G´ and G”
storage modulus and loss modulus

Storage modulus: $G' = \frac{\tau_0}{\gamma_0} \cdot \cos \delta$

Stored energy – quantification of the elastic behaviour

Loss modulus: $G'' = \tau_0/\gamma_0 * \sin\delta$

Irreversible dissipated energy (heat) – lost. Quantification of viscous behaviour

Loss factor: $\tan \delta = \frac{G''}{G'}$

Ratio of dissipated to stored energy – viscous to elastic components

Expressed as viscosity components

Real part of complex viscosity :

(viscous component)

$$\eta' = \frac{G''}{\omega} = \frac{\tau}{\omega \cdot \gamma_0} \sin\delta$$

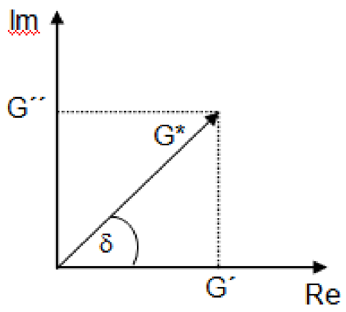
Imaginary part of the complex viscosity: $\eta'' = \frac{G'}{\omega} = \frac{\tau}{\omega \cdot \gamma_0} \cos\delta$

(elastic component)

Expression as vector diagram

The x-axis represents the real part - the y-axis represents the imaginary part

The projection of the amount of the vector G* on the x-axis represents G´,
on the y-axis G".
The vector is erected using the phase angle determined by oscillatory experiments.

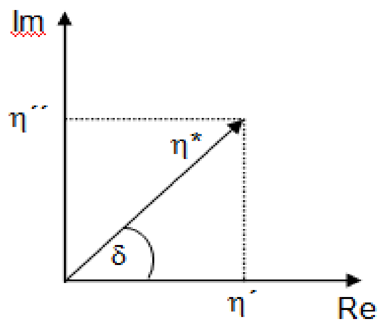


G* complex shear modulus
G' Real part of G* (Storage module)
G" Imaginary part of G* (loss module)

The amount of G*: $|G^*| = \sqrt{(G')^2 + (G'')^2}$

Expression as vector diagram

For the complex viscosity:



η^* complex viskosity
η' Real part of η^*
η'' Imaginary part of η^*

The amount of η*: $|\eta^*| = \sqrt{(\eta')^2 + (\eta'')^2}$

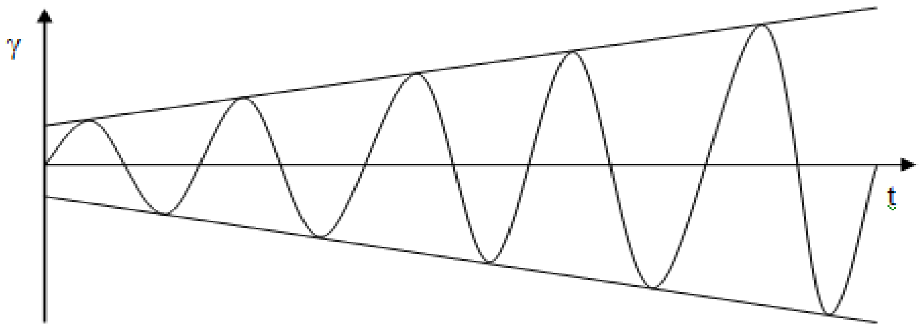
Experimental set up

Amplitude variation at constant frequency

Deformation preset (strain amplitude sweep):

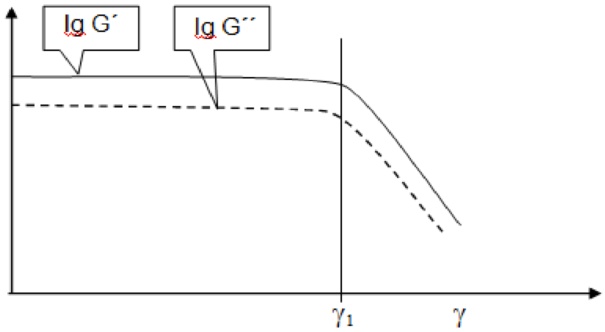
Deformation function: $\gamma(t) = \gamma_0 \cdot \sin \omega t$ at constant frequency ω

Deformation amplitude: $\gamma = \gamma_0(t)$



Amplitude variation at constant frequency

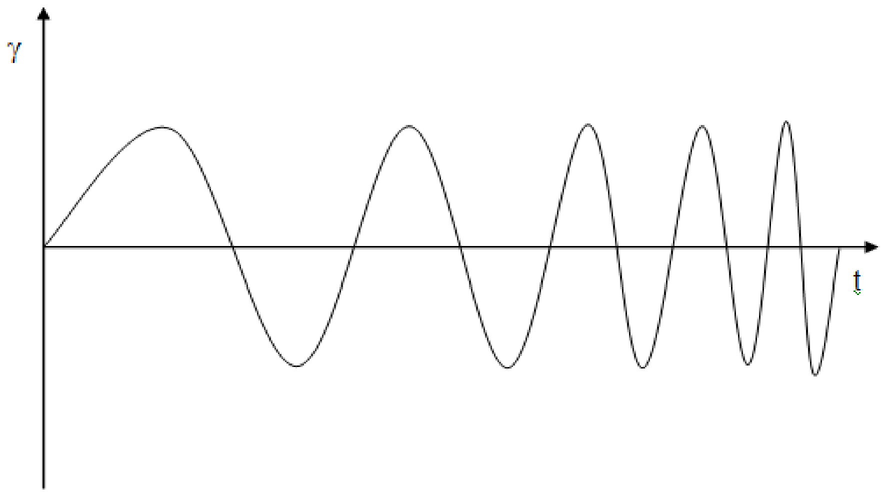
Stability of (network) structures in polymer solutions, melts and dispersions
Linear viscoelastic range



Rule of the dumb fort he limiting deformation γ_1:

- Polymer melts and solutions $\gamma_1 \leq 1$ (45 degree deformation)
  Entanglements of macromolecules
- Substances with physical super structures, dispersions, gels
  week interaction $\gamma_1 \leq 0,01$
  Only small deformations are possible

Frequency variation at constant amplitude

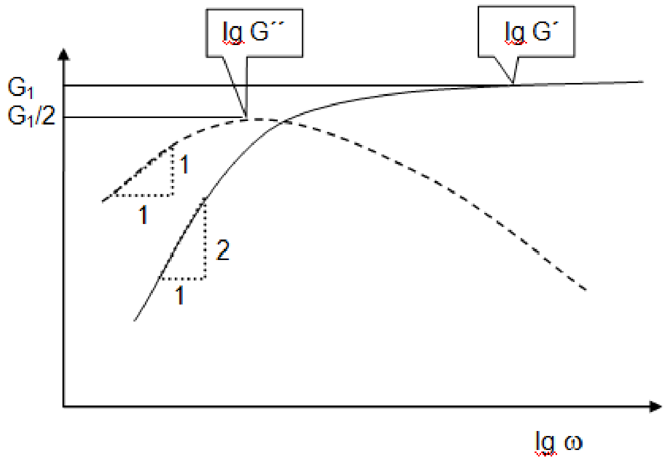


Information: frequency dependent viscosity and elasticity components
Average (representative) relaxation time
Mechanical or chemical network
Rubber elasticity

Frequency sweep

Medium molecular weight and narrow molecular weight distribution

G_1 = Plateau value t_R = Relaxation time



Parameters determined:

Zero shear viscosity: η_0 (dashpot viscosity - Maxwell):

$$\lim \frac{G''}{\omega} = \eta_0 \qquad \omega \to 0$$

Relaxation time (dominant, mean value), cross over G´G''

(position $\omega t_R = 1$; $G''(\omega)$ = maximum)

Rubber elastic plateau

Frequency sweep

Frequency function of solutions and melts:

Substances of medium molecular weight and narrow molecular weight distribution:

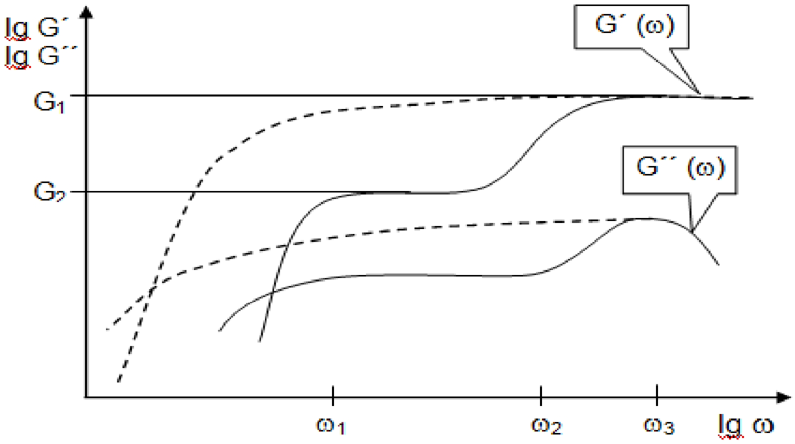
Maxwell model: (spring and dashpot serial)

$$G'(\omega) = G_1 \frac{\omega^2 t_R^2}{(1+\omega^2 t_R^2)}$$

$$G''(\omega) = G_1 \frac{\omega t_R}{(1+\omega^2 t_R^2)}$$

G_1 = Plateau value t_R = Relaxation time

High molecular weight and wide distribution



———	Substance of two narrow molecular weight fractions
---------	Substance wide molecular weight distribution

G_1, G_2 rubber elastic plateau

Different ranges:

$\leq \omega_1$	= flow zone 1
ω_1 *bis* ω_2	= rubber elastic plateau high Mw
ω_2 *bis* ω_3	= flow zone 2
$\geq \omega_3$	= rubber elastic plateau lower Mw

General information

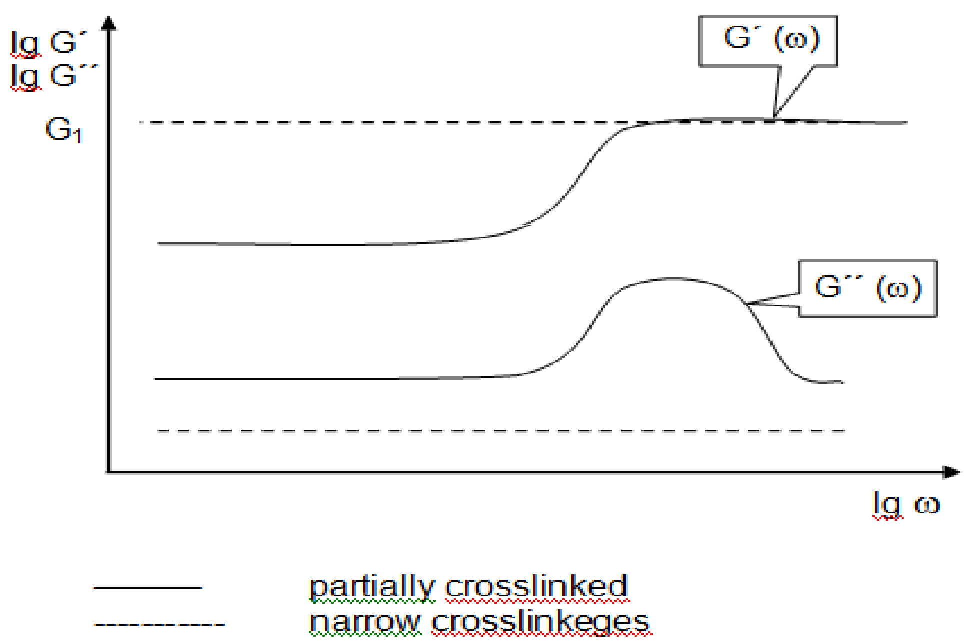
- Higher elastic plateau values indicate stronger structures – more interactions physical / chemical

- Rise at lower frequencies indicates longer relaxation times
  Large and branched molecules are only able to move at low frequencies
  Small molecules are able to move (viscous dissipation of energy) at high frequencies

- A steeper slope indicates a narrow molecular weight distribution
  – less steep slope wider narrow molecular weight distribution

- The position of the cross over point G´ and G" indicates the representative relaxation time
  - low Mw – rapid relaxation – short relaxation time - shifted to higher
  - high Mw – slow relaxation – long relaxation time - shifted to lower frequency

Frequency dependent deformation of chemically cross linked substances



Mechanically (temporary entanglements) and chemically (permanent entanglements) cross linked substances

mechanically cross linked:

$$\lim G'(\omega) = 0\ Pa \qquad \text{G'- function} = 0 \qquad \omega \rightarrow 0$$

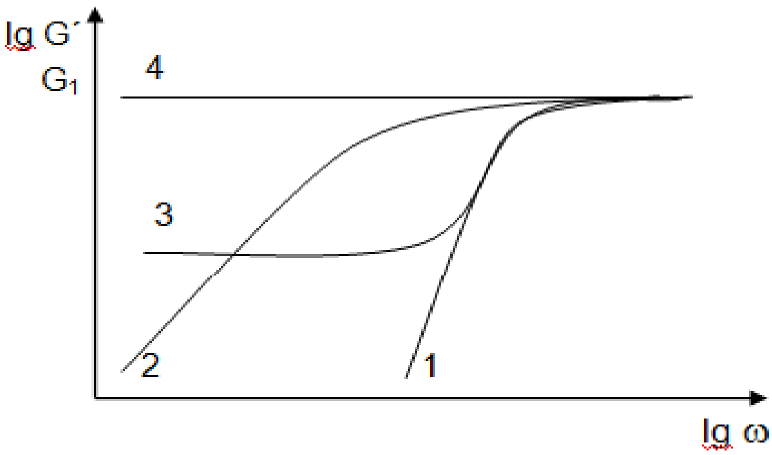
chemically cross linked:

$$\lim G'(\omega) \neq 0\ Pa \qquad \text{G'- function} > 0 \qquad \omega \rightarrow 0$$

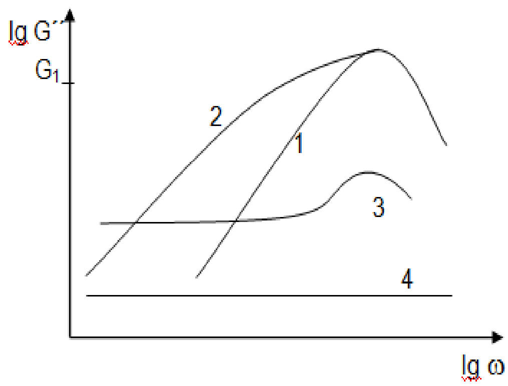
Comparison Storage modulus

$$\left[G'(\omega)\right]$$

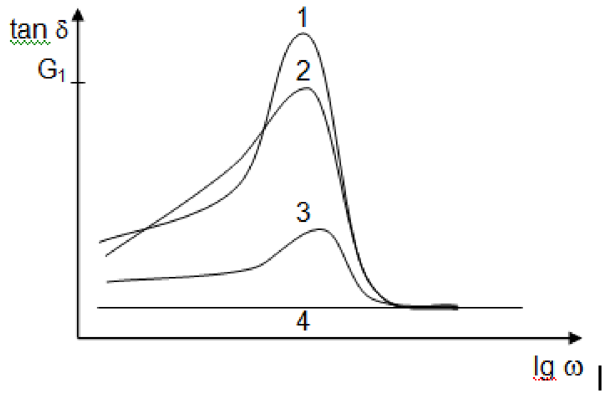
1	not cross linked, medium Mw
2	not cross linked, wide Mw distribution
3	partially cross linked
4	totally cross linked



Loss modulus and loss factor



Loss modulus $[G''(\omega)]$



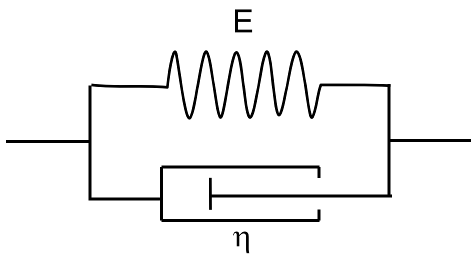
Loss factor [tan δ(ω)]

Modelling viscoelasticity

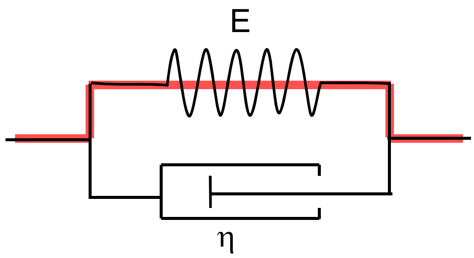
- Modeling using a combined HOOKE and NEWTON elements
- Simplest constitutive equations describing the behavior are linear differential equations with constant coefficients

The 2-element solid

KELVIN-VOIGT-body

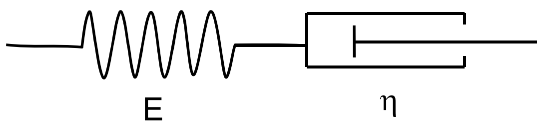


Characteristics ?



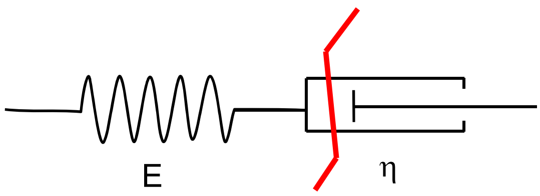
There exists a connection between the end points exclusively over HOOKE elements

The 2-element-fluid



MAXWELL-Body

Characteristics ?



There exists a separation line exclusively over NEWTON elements

Simple constituitive equation

The storage and loss modulus (G´, G´´) of many polymer systems generally follow a single-relaxation Maxwell model. A Maxwell model comprises an elastic component connected in series with a viscous component.
In this model G´ and G" are described by the following equation:

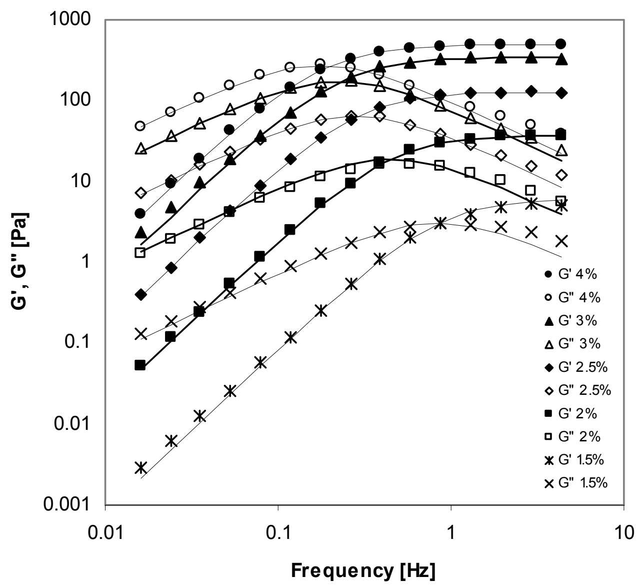
$$G' = \frac{G_{\infty}\omega^2\lambda^2}{1+\omega^2\lambda^2}$$

$$G'' = \frac{G_{\infty}\omega\lambda}{1+\omega^2\lambda^2}$$

where G_{∞} reperesent the plateau value of G´ at the highest frequencies

ω is the angular frequency and λ is the relaxation time

The 2-element-fluid



The storage modulus (close symbol) and loss modulus (open symbol) of HEUR models as function of frequency for different concentration. The curves are the best fit of single-relaxation Maxwell model.

Experiments under oscillatory loads stress or deformation

Mechanical spectroscopy - similar to optical spectroscopy

Select proper frequency to obtain meaningful answers from the materials

No destruction of structures – material characterisation
no process characterisation !!