Rheology of polymer systems/ Reologia dos sistemas poliméricos

2. Viscoelasticity/Viscoelasticidade

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Viscoelasticity

Depending on the frequency of the applied stress, a polymer fluid can behave as:

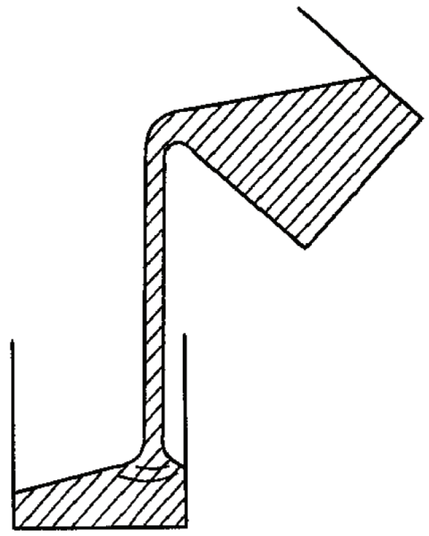
- ❑ normal, low molecular weight, liquid

or as an

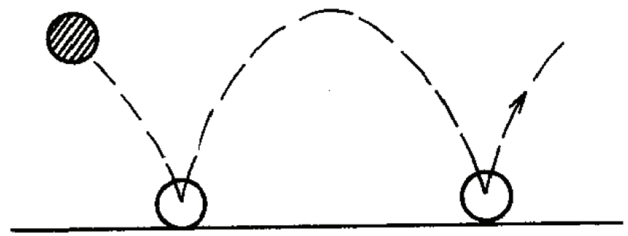
- ❑ elastic solid

Viscoelasticity

- Demonstrations



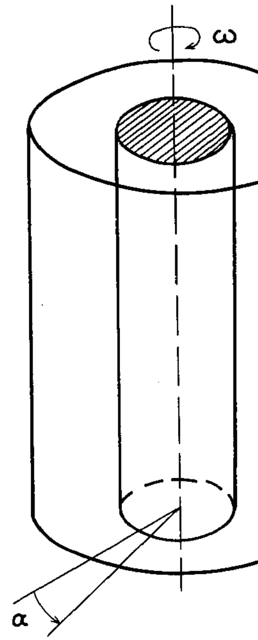
Flow

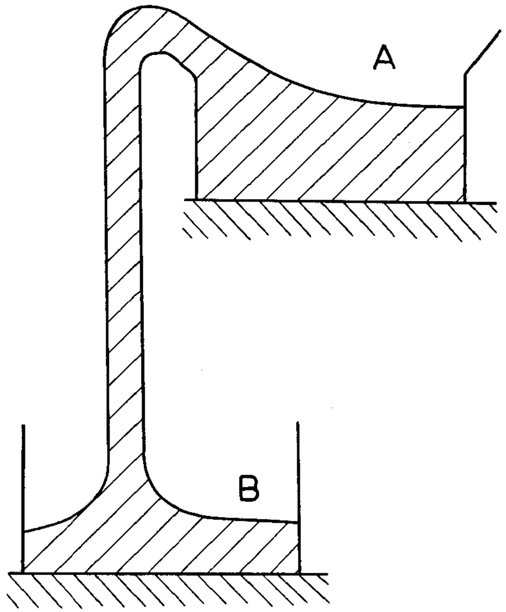


Ball bouncing on the floor

Viscoelasticity

- Demonstrations

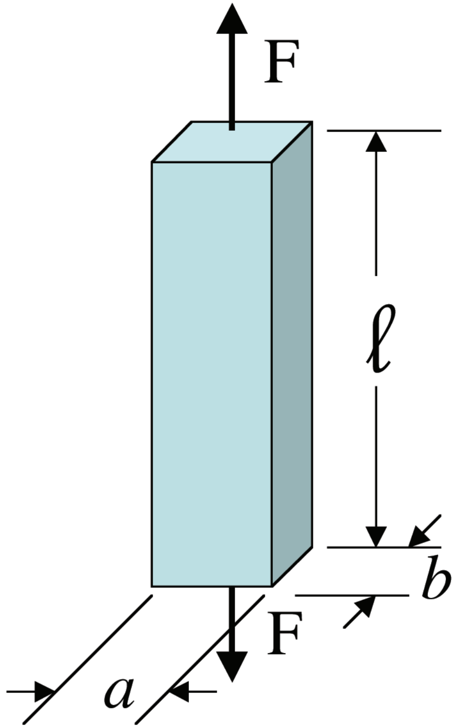




Siphon effect

Elastic modulus, E (tension)

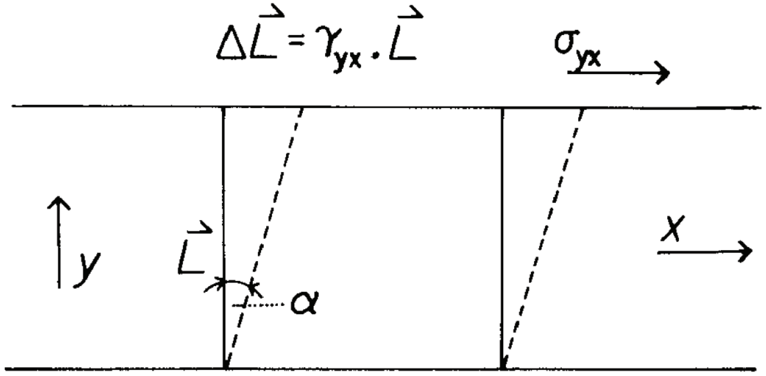
$$\sigma = E\,\varepsilon = E\,\gamma = E\,\frac{\Delta \ell}{\ell_u} = E\,(\alpha - 1)$$



$$\sigma = \frac{F}{a_0\, b_0}$$

σ- tensile stress
ε-elongation
E-Young's modulus
J-compliance (ε/σ)=1/E

Shear modulus, G

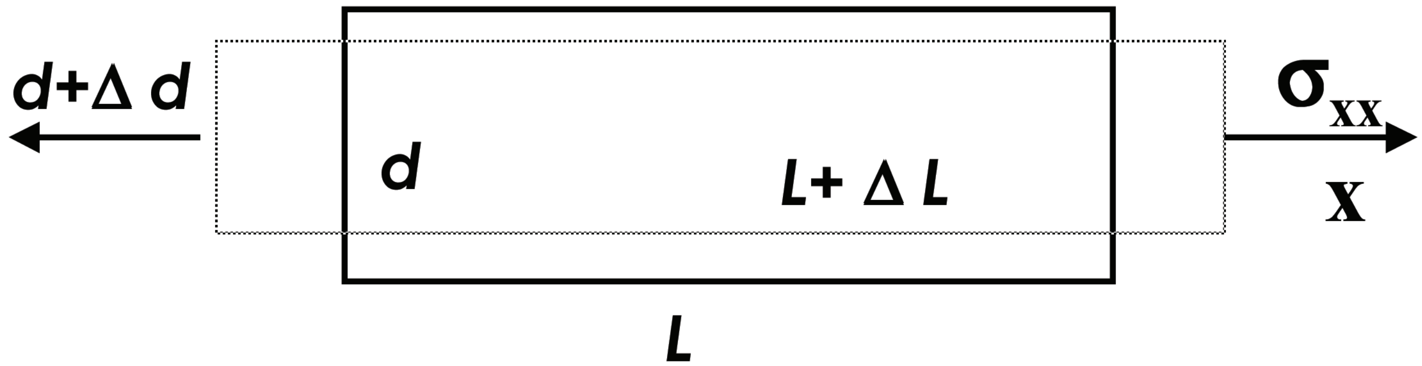


$$\sigma_{yx} = G\,\gamma_{yx}$$

σ (or τ)- shear stress
γ_{yx}-shear strain
G-shear (storage) modulus

Poisson's ratio, ν

$$\nu = -\frac{d(\ln a)}{d(\ln L)} = -\frac{d(\ln b)}{d(\ln L)} = -\frac{d(\ln d)}{d(\ln L)}$$



$$\nu = -\frac{\gamma_{yy}}{\gamma_{xx}} = -\frac{\Delta d \,/\, d}{\Delta L \,/\, L}$$

Isotropic materials: $E = 2G\,(1+\nu)$

Incompressible liquids, most rubbers, $\nu=0.5$

Compliance

J=1/E (J=1/G, in “Munk)

Bulk modulus /módulo em volume (K)

$$P = -K\frac{\Delta V}{V_0}$$

P-hydrostatic pressure
V-volume

Viscoelasticity

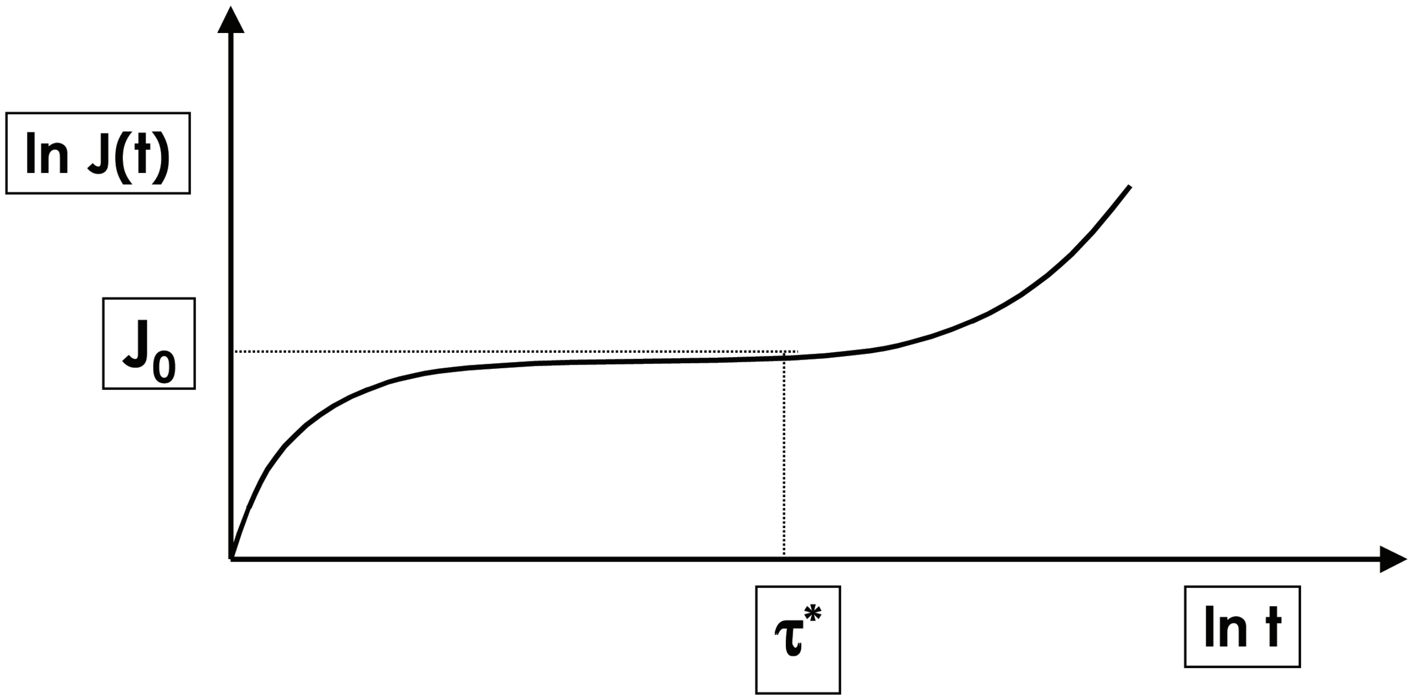
t=0: application of a constant tensile stress, σ, to a polymeric fluid (concentrated solution or melt):

The deformation is given by $\dfrac{\Delta \ell}{\ell}$

which, for small σ, is,

$$\frac{\Delta \ell}{\ell}(t) = \sigma . J(t)$$

Viscoelasticity



At the plateau, considering J_0=1/E,

$$\sigma = E\,\frac{\Delta\ell}{\ell} \quad \text{(Hooke´s law)}$$

the fluid behaves as an elastic material with modulus E

Viscoelasticity

$t > \tau^*$ - the deformation becomes irreversible (flow)

$$J(t) = J_1 t + J_2$$

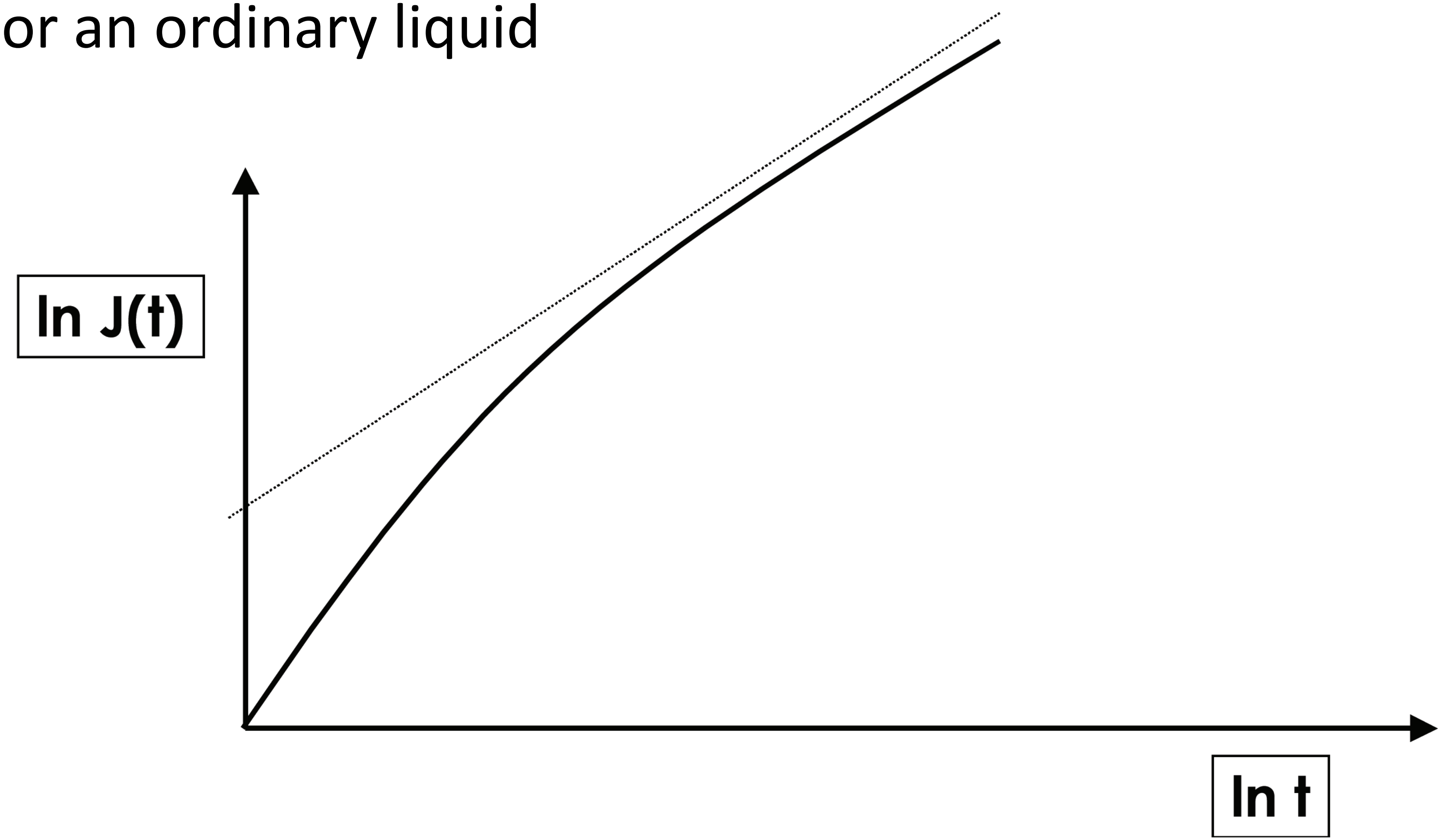
$$\sigma = J_1^{-1} \frac{d(\Delta\ell / \ell)}{dt}$$ (typical of fluids)

which is equivalent to (viscous flow)

$$\sigma = \eta \frac{d(\Delta\ell / \ell)}{dt}$$

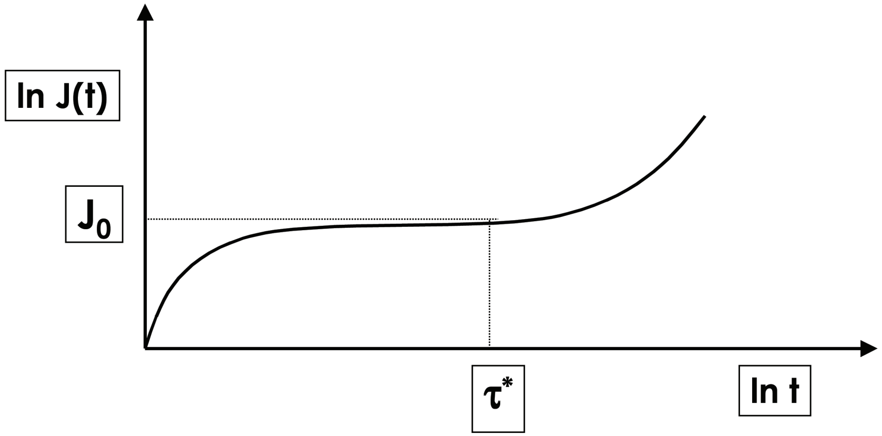
Viscoelasticity

For an ordinary liquid



There is no elastic plateau

Viscoelasticity



Melt behaves as an elastic body

Polymer behaves as an ordinary liquid

τ^*-maximum relaxation time
(at which there is a change in response of the melt)

Viscoelasticity

Meaning of τ* within the reptation model ?

A polymer chain interacts with its neighbours through effective cross links, which have an average lifetime on the order of τ***.**

It corresponds to the time required for a given chain to diffuse from the initial to the next tube *(so the cross links have to break).*

- $t < \tau^*$- the cross links hold the sample together-"elastic body"
- $t > \tau^*$- the cross links start decaying so the sampe flows

References

- “Principles of Polymer Systems”, 2nd ed., F. Rodriguez, McGraw-Hill-Int. Student Ed., 1983: § 7.1 - 7.6
- “Introduction to Macromolecular Science”, P. Munk, John Wiley & Sons, 1989: § 4.1.4
- “Giant Molecules-Here, There and Everywhere …”, A. Yu. Grosberg, A.R. Khokhlov, Academic Press, 1997.