Rheology of polymer systems/ Reologia dos sistemas poliméricos

1. Introduction

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Studying polymers…

- ***Rheology**:* The study of the deformation and flow of matter

- ***Elasticity**:* The ability to return to its natural shape after deformation, restoring force

- ***Viscosity**:* Resistance to shear or extensional stress

Polymer rheology

Why do materials deform?

Action of force:

Newton

- Change of movement OR
- Body deformation (change of shape)

Polymer rheology

How do bodies respond to forces (of deformation)**?**

- ☐ VISCOUS flow
- ☐ PLASTIC deformation
- ☐ ELASTIC deformation
- ☐ COMBINED (e.g. viscoelastic behaviour)

Polymer rheology

Molecular origin

Movement of macromolecule chains

- ❑"Unrestricted" – viscous def.
- ❑Restricted (by appreciable frictional forces) – plastic def.
- ❑Hindered (particularly by chemical bonds) – elastic def. (network)

Polymer rheology

A bit of theory

Force = vector

F = (F_x, F_y, F_z) or (F_1, F_2, F_3)

Deformation = change of **position** of material points

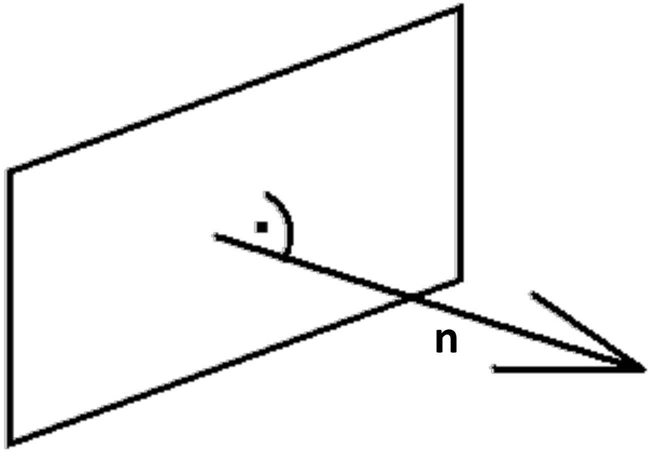
Position → positional vector

ACTION OF A VECTOR (FORCE) CHANGES ANOTHER VECTOR (POSITION)

Polymer rheology

A bit of theory

Deformation force “spreads” over an area (A) →
→ **TENSION** (**F**/A)



Position of an area – **normal vector** (**n**)
(perpendicular to tangent plane)

Tensor algebra and calculus:

$\mathbf{F}/A \equiv \mathbf{T} = \boldsymbol{\sigma}.\mathbf{n}$

$\boldsymbol{\sigma}$…stress tensor

T…T_i, $i = 1, 2, 3$
(3 components)

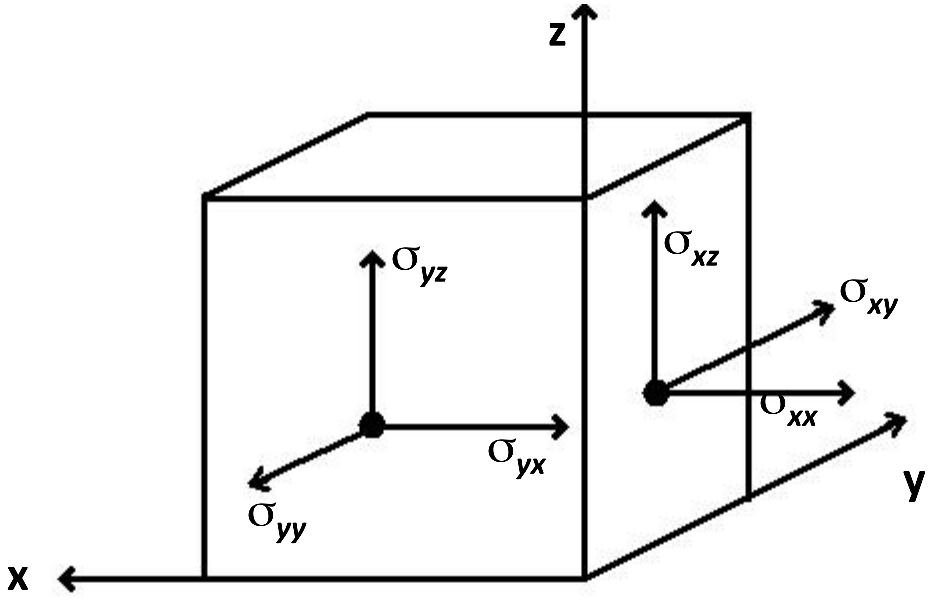
$\boldsymbol{\sigma}$… σ_{ij}; $i, j = 1, 2, 3$
(9 components)

Polymer rheology

A bit of theory

Tensors in description of deformations

Component of force in the *i*-th direction (F_i) causes deformation and **stress** not only in that direction (σ_{ii}) but also in the other two directions (σ_{ij}, $i \neq j$):



Polymer rheology

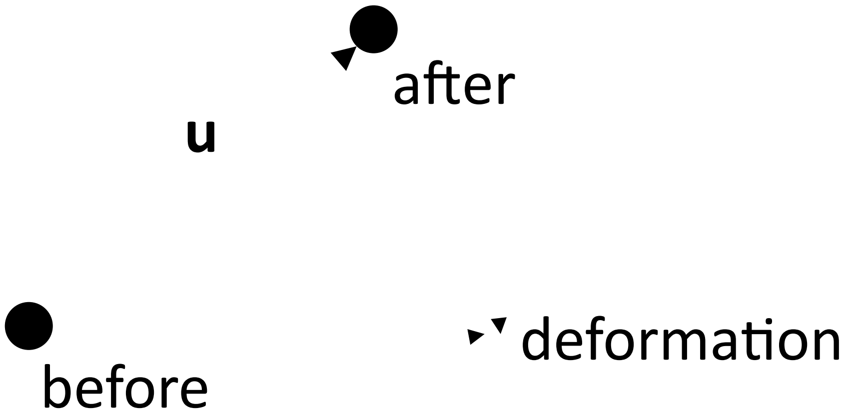
A bit of theory

Tensors in description of deformations

Deformation is described by the **strain** (or small deformation) tensor γ:

$$\gamma_{ij} = (1/2)(\partial u_i/\partial x_j + \partial u_j/\partial x_i);\ i, j = 1, 2, 3$$

$$\gamma_{ij} = \gamma_{ji}$$



after

u

before

deformation

Polymer rheology

Properties of materials are described by **constitutive equations** or (rheological) **equations of state ≡**

relation among following tensors:

- stress
- strain
- rate of strain (deformation)

  ≡ $d\gamma/dt$

Polymer rheology

Material models → material parameters

$$\textbf{Modulus =} \; \frac{\text{magnitude of acting force (stress)}}{\text{relative magnitude of resulting deformation}}$$

- Measure of material stiffness

bulk: $K = -P/(\Delta V/V_0)$

shear: $G = \sigma_{yx}/\gamma_{yx}$

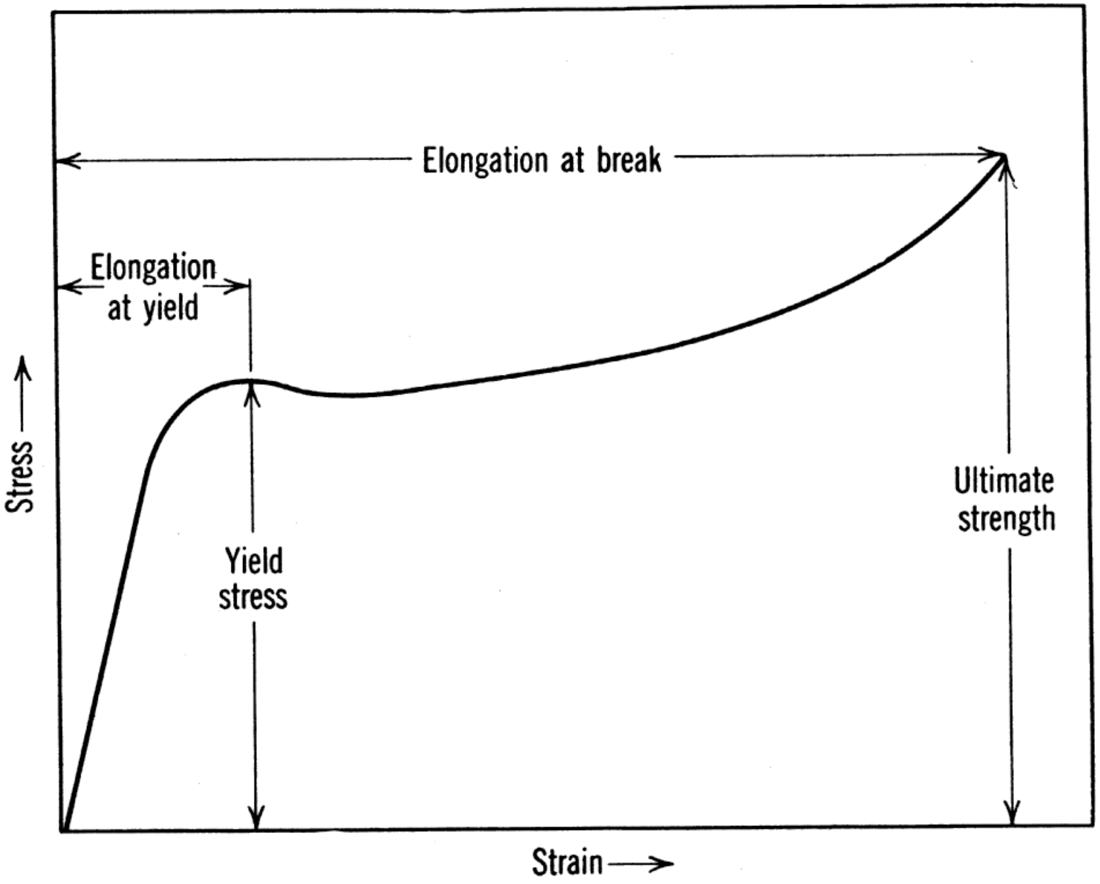
Young (elastic): $E = \sigma_{xx}/\gamma_{xx}$

Poisson ratio: $\nu = \gamma_{yy}/\gamma_{xx}$

$E = 2G(1+\nu) = 3K(1-2\nu)$ (only two are independent)

Polymer rheology

General **stress-strain curve**:

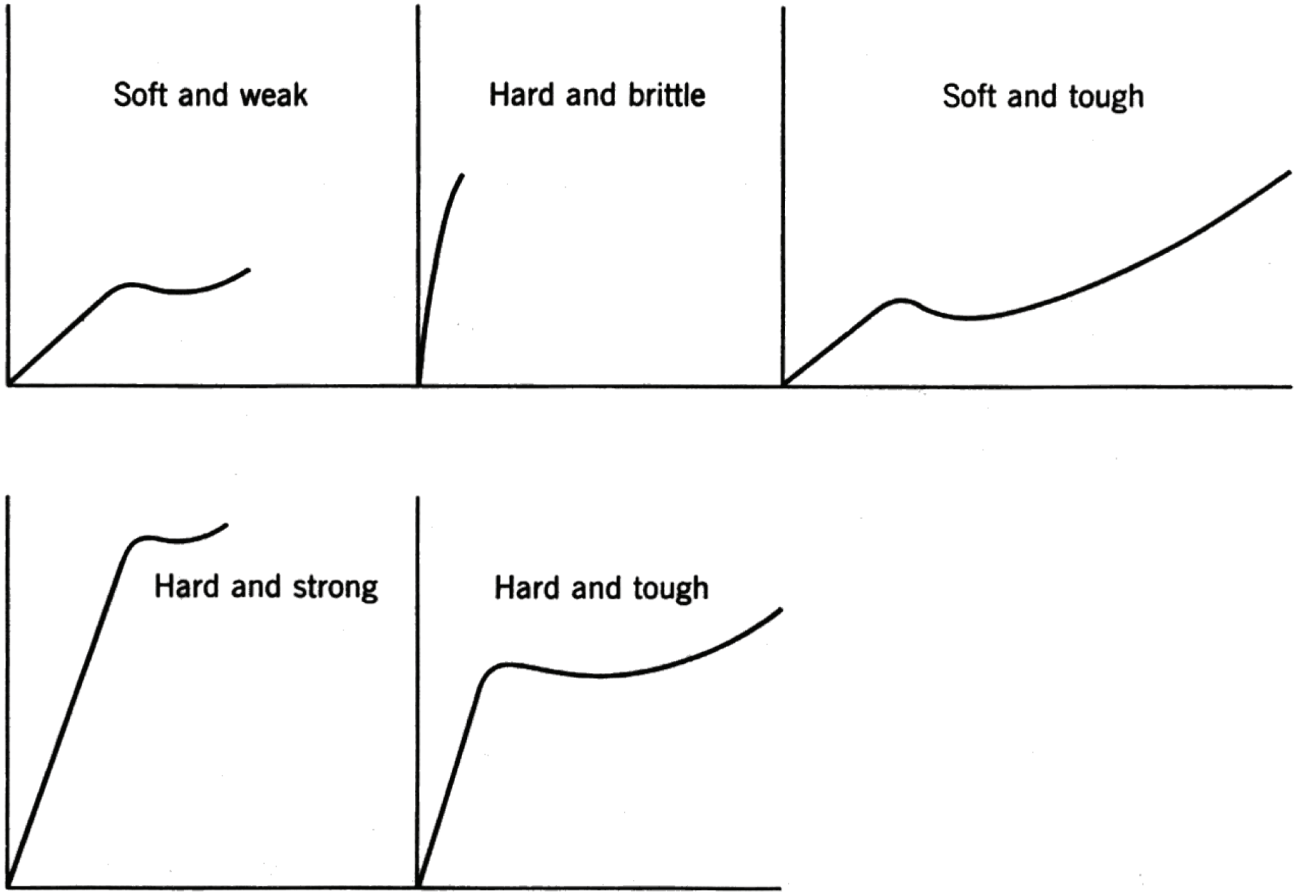


measurement of
force as the sample
is elongated at
constant rate

! rate of strain !

Polymer rheology

Generalized material properties from the stress-strain curve:



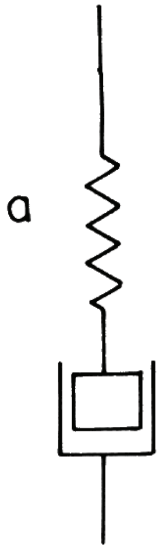
Polymer rheology

Viscoelastic materials

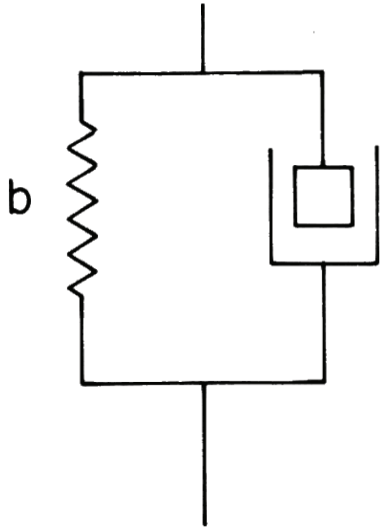
Simple models

spring & dashpot / mola & amortecedor

Maxwell

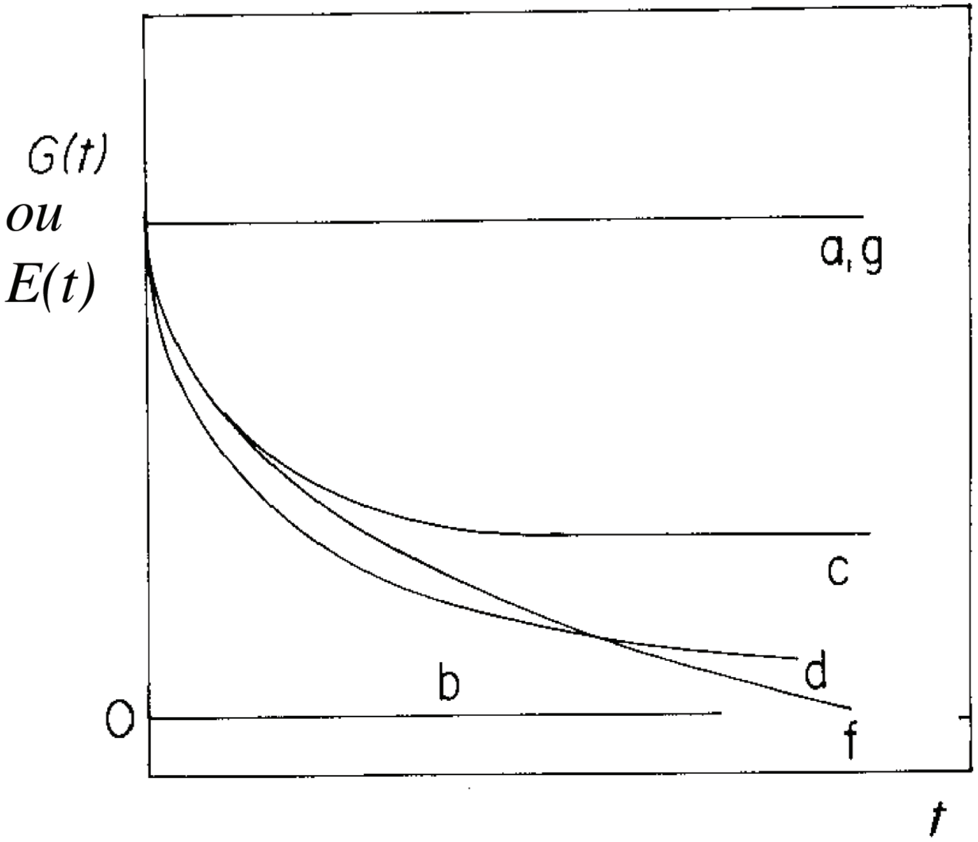


Kelvin (Voigt)



Polymer rheology

Viscoelastic materials



a-*material elástico perfeito*

b-*líquido*

c-*sólido viscoelástico*

d-*líquido viscoelástico*

f-*elemento de Maxwell*

g-*elemento de Voigt*

References

- “Principles of Polymer Systems”, 2nded., 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