Rheology of polymer systems/
Reologia dos sistemas poliméricos

2. Models

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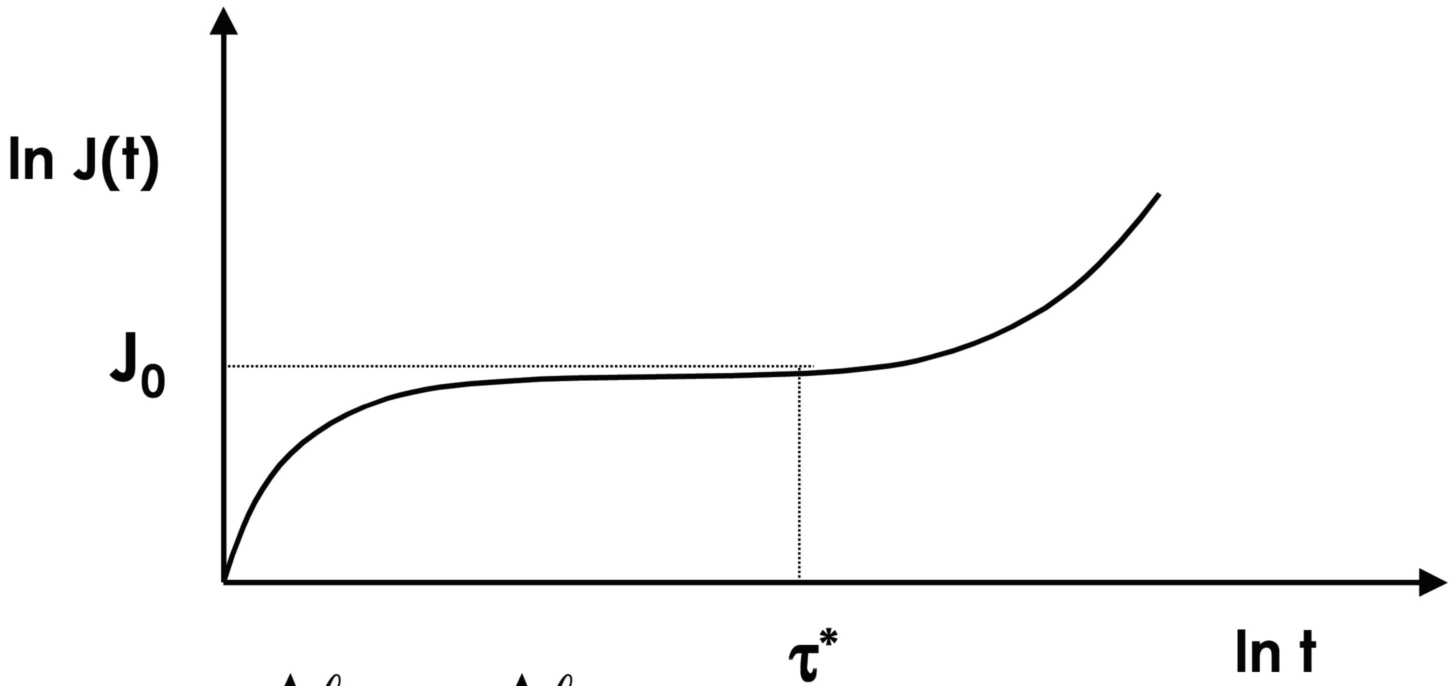
Viscoelasticity



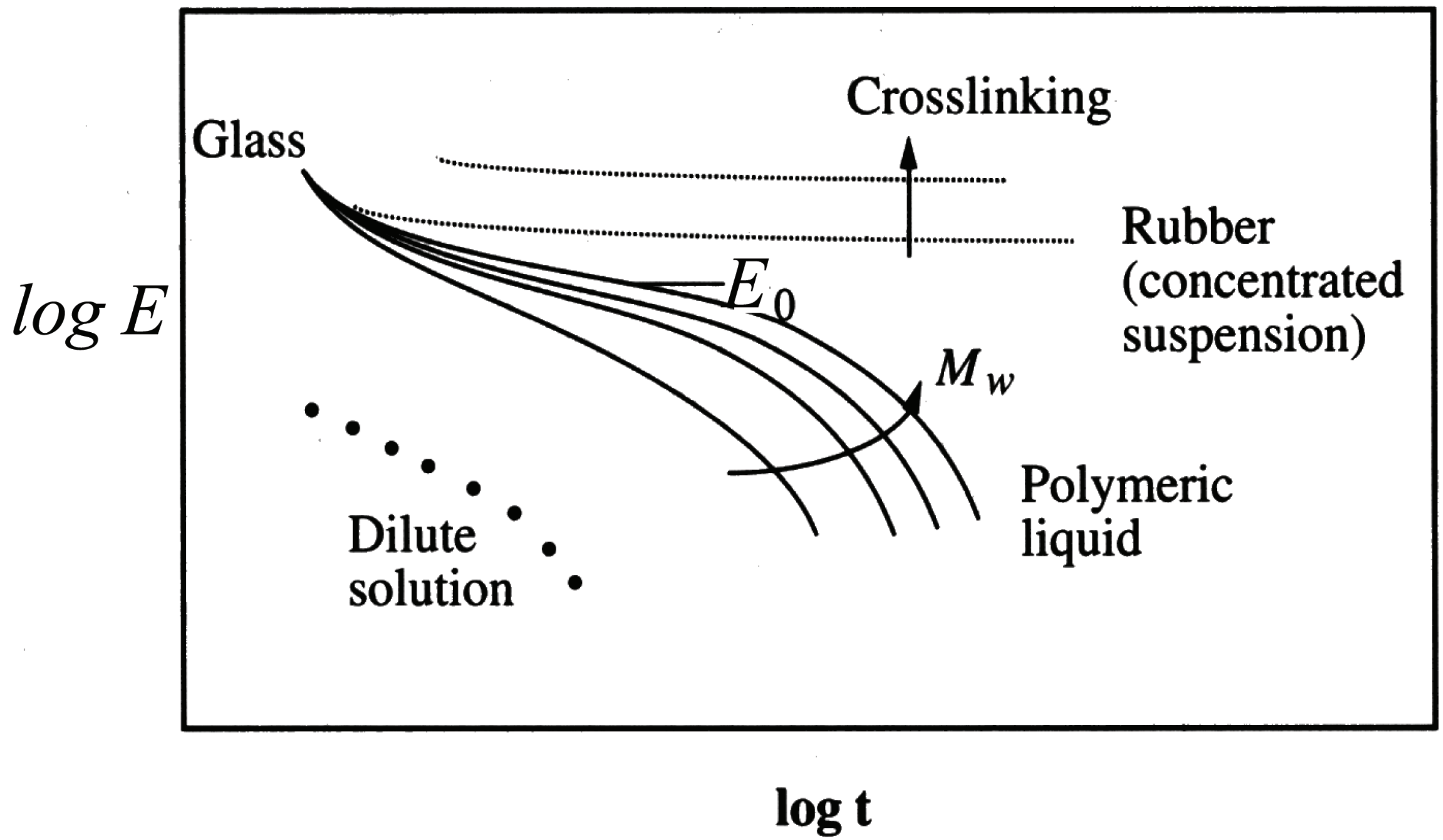
$$\sigma = J_0^{-1}\frac{\Delta\ell}{\ell} = E\frac{\Delta\ell}{\ell} = E\varepsilon$$

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

$$\sigma = J(t)^{-1}\frac{\Delta\ell}{\ell}(t) = E(t)\varepsilon(t)$$

Polymer rheology

Time-dependent modulus, E(t)

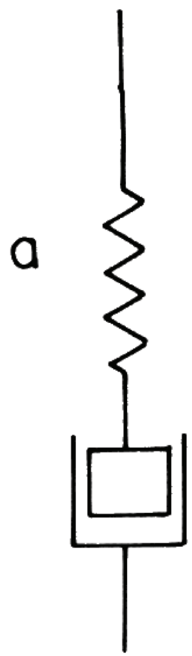


Polymer rheology

Simple models

Spring & dashpot/mola & amortecedor

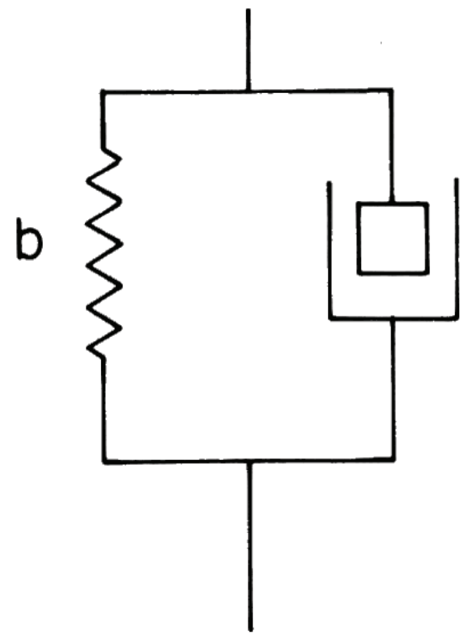
Maxwell



$$\sigma_1 = \sigma_e = E_1\,\varepsilon_1$$

$$\sigma_2 = \sigma_v = \eta \frac{d\,\varepsilon_2}{d\,t}$$

Kelvin (Voigt)



Polymer rheology

- **Steady state measurements/Ensaios em estado estacionário**
  - Stress relaxation/relaxação de tensão: $\varepsilon=\varepsilon_0=ct$, $\sigma(t)=?$
  - Creep/fluência: $\sigma=\sigma_0=ct$, $\varepsilon(t)=?$
  - (Constant rate of extension/velocidade de deformação constante: $d\varepsilon/dt=ct$)

- **Dynamic measurements/Ensaios dinâmicos**
  - Harmonic motion/deformação oscilatória sinusoidal

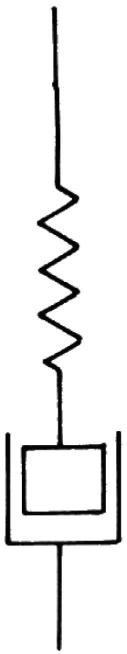
    $\sigma(t)=\sigma_0$ sen ωt ➔ $\varepsilon(t)= ?$

  or

    $\varepsilon(t)=\varepsilon_0$ sen ωt ➔ $\sigma(t)= ?$

Polymer rheology

Maxwell element



$$\sigma_1 = \sigma_e = E_1 \varepsilon_1$$

(Hookean spring)

$$\sigma_2 = \sigma_v = \eta \frac{d\varepsilon_2}{dt}$$

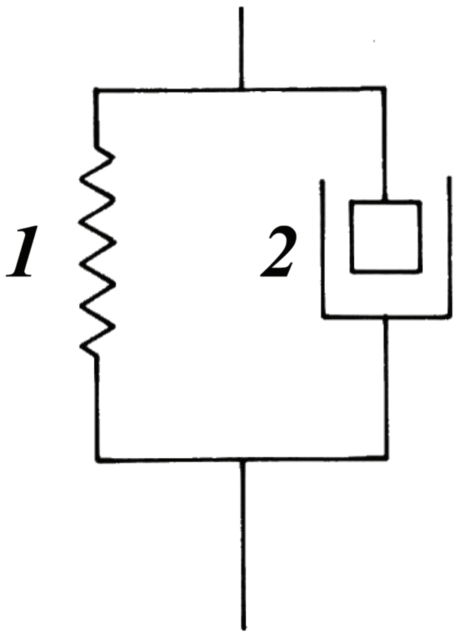
(Newtonian dashpot)

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

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt}$$

Polymer rheology

Voigt (Kelvin) element



$$\sigma_1 = \sigma_e = E_1 \varepsilon_1$$

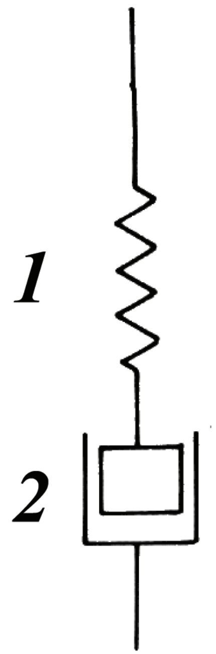
$$\sigma = \sigma_1 + \sigma_2$$

$$\sigma_2 = \sigma_v = \eta \frac{d\varepsilon_2}{dt}$$

$$\varepsilon = \varepsilon_1 = \varepsilon_2$$

Maxwell element

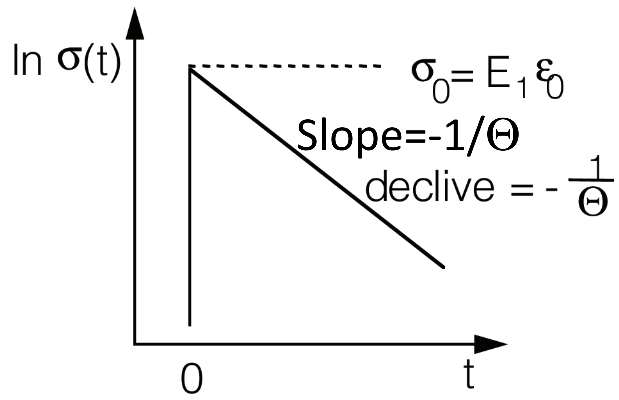
Stress relaxation/relaxação de tensão



$$\varepsilon = cte = \varepsilon_0$$

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt}$$

$$\frac{d\varepsilon}{dt} = \frac{1}{E_1}\frac{d\sigma}{dt} + \frac{\sigma}{\eta} = 0$$



$$\sigma = \sigma_0 \, e^{-\frac{t}{\theta}}$$

$\Theta = \eta / E_1$ - tempo de relaxação

Θ - relaxation time

Maxwell element

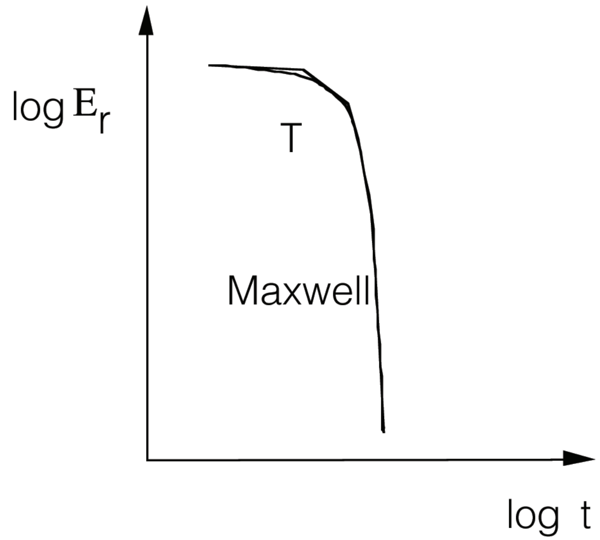
Stress relaxation/relaxação de tensão

Time-dependent modulus (of the element)

$$E(t) = \frac{\sigma(t)}{\varepsilon_0}$$

$$\sigma(t) = \sigma_0 \, e^{-\frac{t}{\theta}}$$

$$E_r(t) = E_1 \, e^{-\frac{t}{\theta}}$$



Maxwell element

Creep/fluência

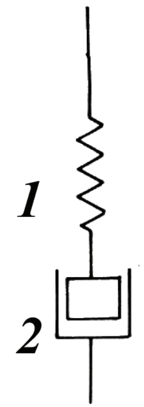
$$\sigma = cte = \sigma_0$$

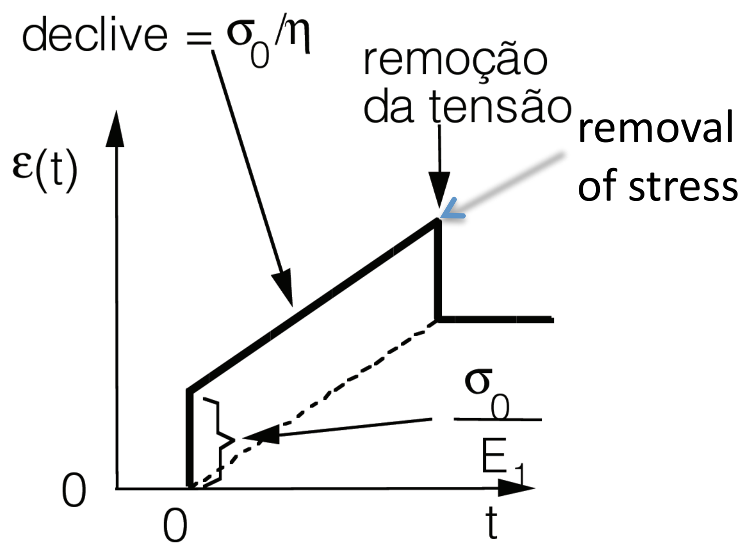
$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_1}{dt} + \frac{d\varepsilon_2}{dt}$$

$$\frac{d\varepsilon}{dt} = \frac{d\varepsilon_2}{dt} = \frac{\sigma_2}{\eta} = \frac{\sigma_0}{\eta}$$

$$\varepsilon(t) = \varepsilon_0 + \frac{\sigma_0 t}{\eta}$$

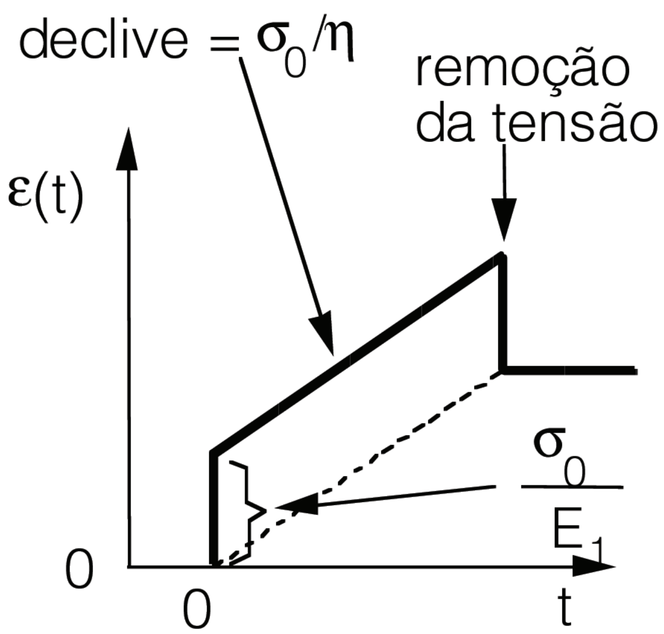
$$\varepsilon(t) = \sigma_0\left(\frac{1}{E_1} + \frac{t}{\eta}\right)$$

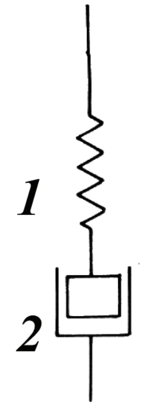




Maxwell element

Creep/fluência



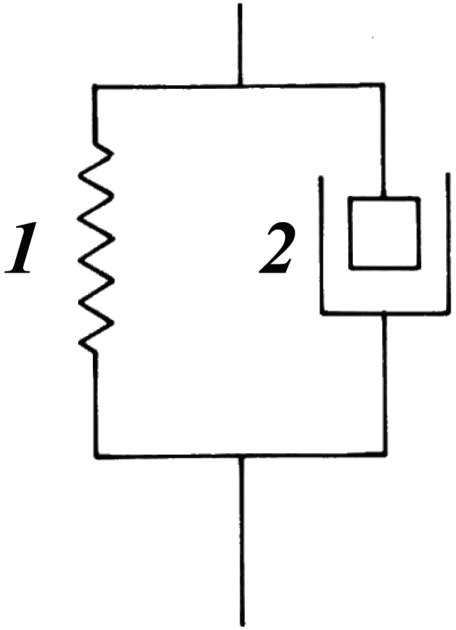


After removal of the tensile stress, the viscous component (deformation) is not recovered.

This behaviour is sometimes observed in amorphous polymers without cross links.

Voigt element

Stress relaxation/relaxação de tensão



$$\varepsilon = cte = \varepsilon_0$$

$$\sigma_1 = \sigma_e = E_1 \varepsilon_1$$

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

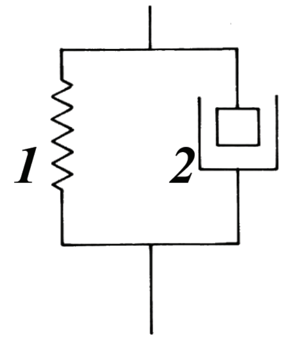
$$\sigma_2 = \sigma_v = \eta \frac{d\varepsilon_2}{dt}$$

$$\varepsilon = \varepsilon_1 = \varepsilon_2$$

$$E(t) = E_1$$

Voigt element

Creep/fluência



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

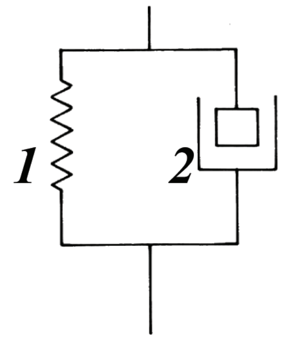
$$\sigma = \sigma_0 = cte$$

$$\sigma = \varepsilon E_1 + \eta \frac{d\varepsilon}{dt}$$

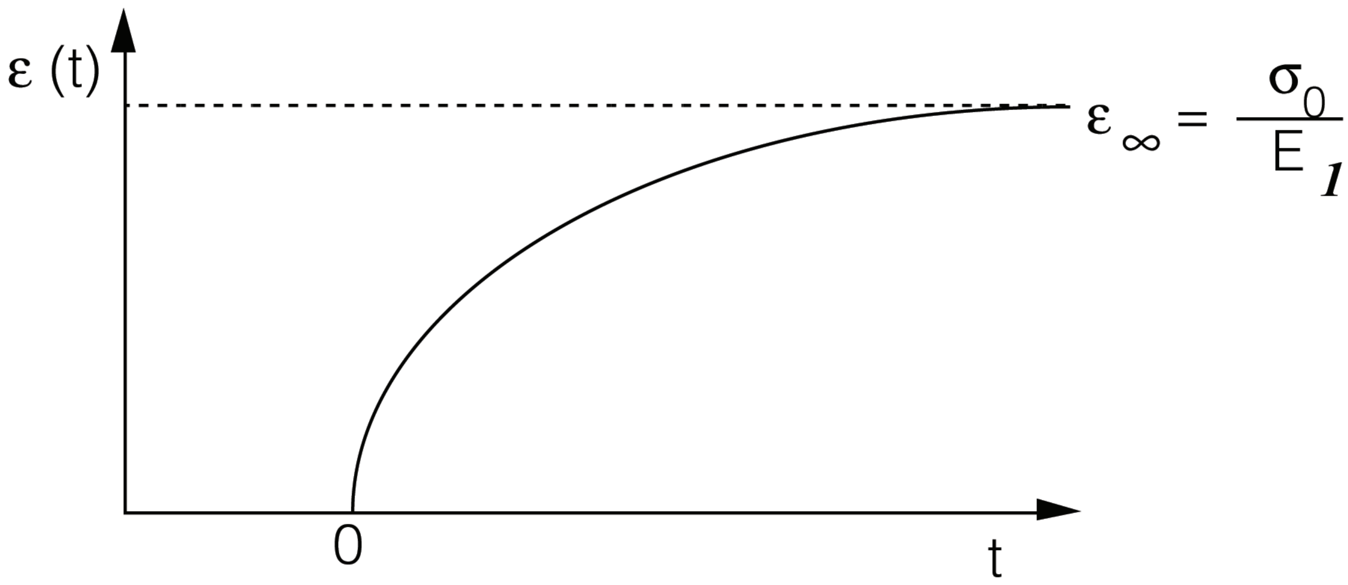
$$\frac{E_1 \varepsilon(t)}{\sigma_0} = E_1 E(t) = 1 - e^{-\frac{t}{\theta}}$$

Voigt element

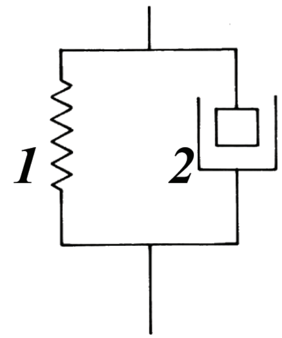
Creep/fluência



$$\frac{E_1 \varepsilon(t)}{\sigma_0} = E_1 E(t) = 1 - e^{-\frac{t}{\theta}}$$



Voigt element
Creep/fluência



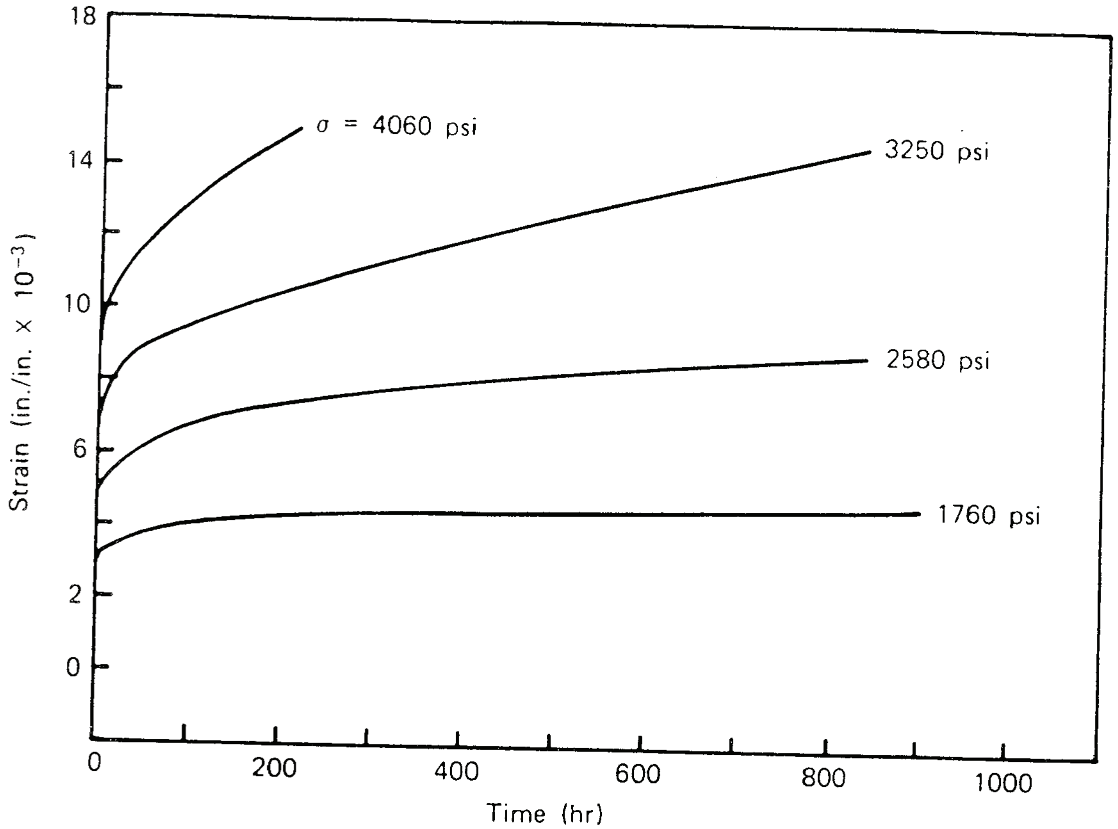


Figure 23 Creep curves for polystyrene at various tensile stresses (62).

Polymer rheology

Simple models

Maxwell		Kelvin (Voigt)
	Stress relaxation Relaxação de tensão (ε = const)	
$E(t) = E_1 \exp(-t/\theta)$		$E(t) = E_1$
	Creep Fluência (σ = const)	
$J(t) = J_1 + t/\eta$		$J(t) = J_1 \, [1 - \exp(-t/\theta)]$

$$\theta = \eta/E_1$$

$$J = 1/E$$

Good model for liquids	Good model for solids

Polymer rheology

Dynamic measurements/Ensaios dinâmicos

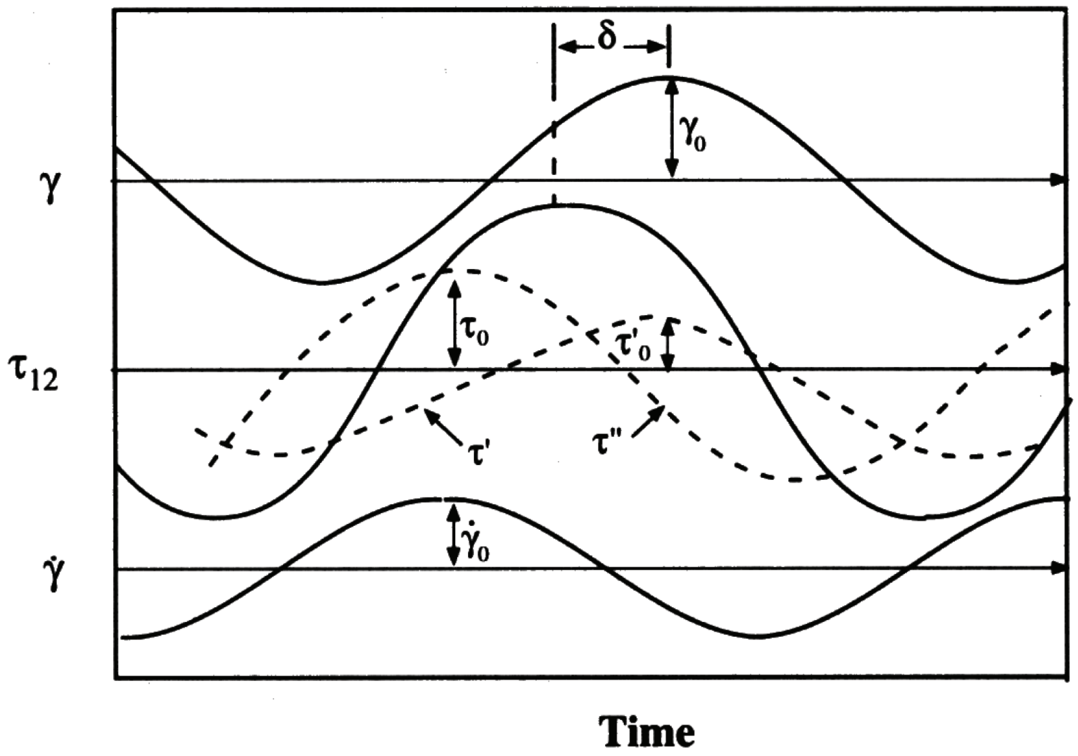
Harmonic (sinusoidal) motion

$$\varepsilon = \gamma = \gamma_0 sen(\omega t)$$

Tensão
desfasada de δ:

$$\sigma = \sigma_0 sen(\omega t + \delta)$$

Stress (σ or τ):
phase shifted by δ



Polymer rheology

Dynamic measurements/Ensaios dinâmicos

Expressing σ as a “in phase” (σ’) plus an “out of phase” (σ“) components

$$\sigma = \sigma' + \sigma'' = \sigma'_0 sen(\omega t) + \sigma''_0 cos(\omega t)$$

$$tan\,\delta = \sigma''_0 / \sigma'_0$$

$$E' = \sigma'_0 / \gamma_0; \quad E'' = \sigma''_0 / \gamma_0$$

E’(ω) módulo de armazenamento (em fase), módulo elástico

storage modulus (in phase), elastic modulus

E’’(ω) módulo de perda (desafasado), módulo viscoso

loss modulus (out of phase), viscous modulus

$$tan\,\delta = \frac{E''}{E'}$$

Polymer rheology

Dynamic measurements/Ensaios dinâmicos

$$\sigma = \sigma'_0 sen(\omega t) + \sigma''_0 cos(\omega t) \quad \& \quad exp(i\theta) = cos\theta + isen\theta$$

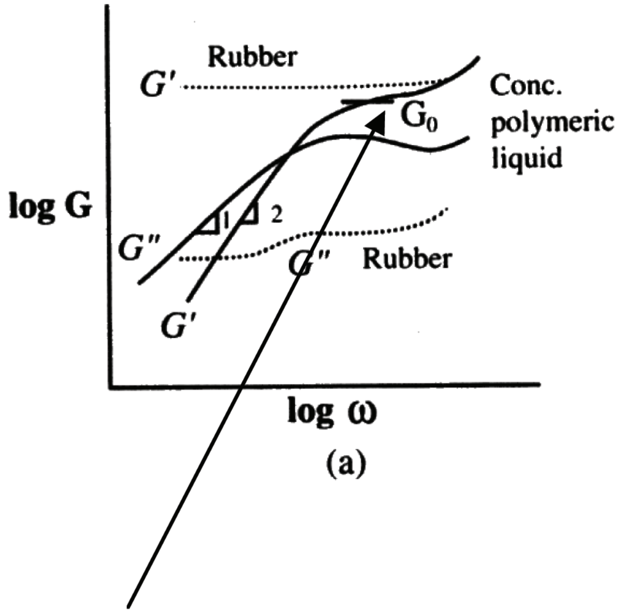
$$\sigma' = Im[\sigma'_0 exp(i\omega t)] \quad \sigma'' = Re[\sigma''_0 exp(i\omega t)]$$

$$\gamma = Im[\gamma_0 exp(i\omega t)]$$

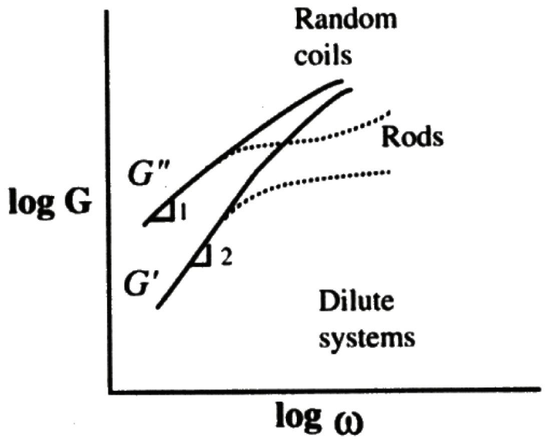
$$E^* = E' + iE''; \quad \left|E^*\right| = \frac{\sigma_0}{\gamma_0}$$

$$\sigma = E'\gamma_0 sen(\omega t) + E''\gamma_0 cos(\omega t)$$

Polymer rheology



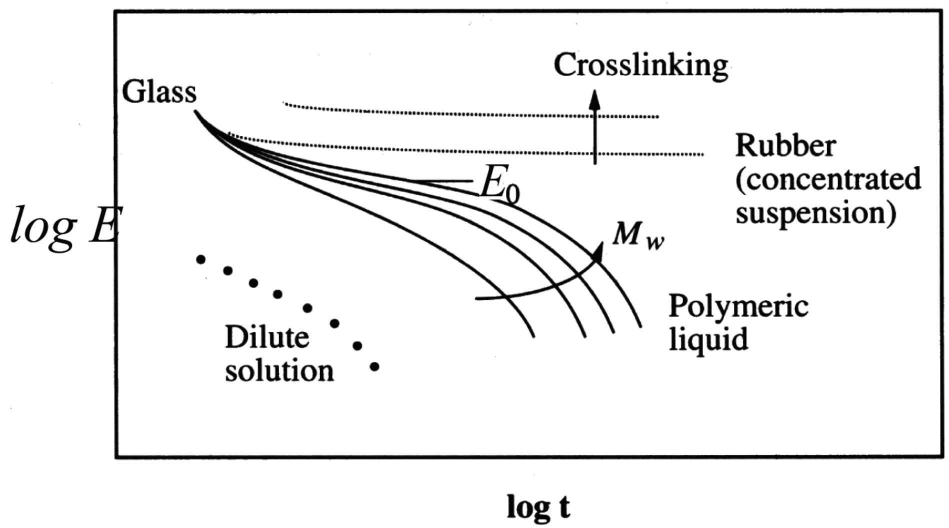
(a)



(b)

Dynamic moduli
(depend on ω)

Patamar elástico
(G´ ou E')



Dependence on frequency (ω) is equivalent to the dependence on 1/t

Effect of temperature

$$\theta = \theta(T) = \frac{\eta(T)}{E_1(T)}$$

$$\theta(T) \approx \frac{\eta(T)}{E_1}$$

Doolittle: $$log\,\eta = A + \frac{BV_0}{V_f}$$

$$\eta \propto e^{\frac{1}{f}} \quad \Rightarrow \quad \theta \propto e^{\frac{1}{f}}$$

Effect of temperature

In a stress relaxation experiment of a Maxwell element

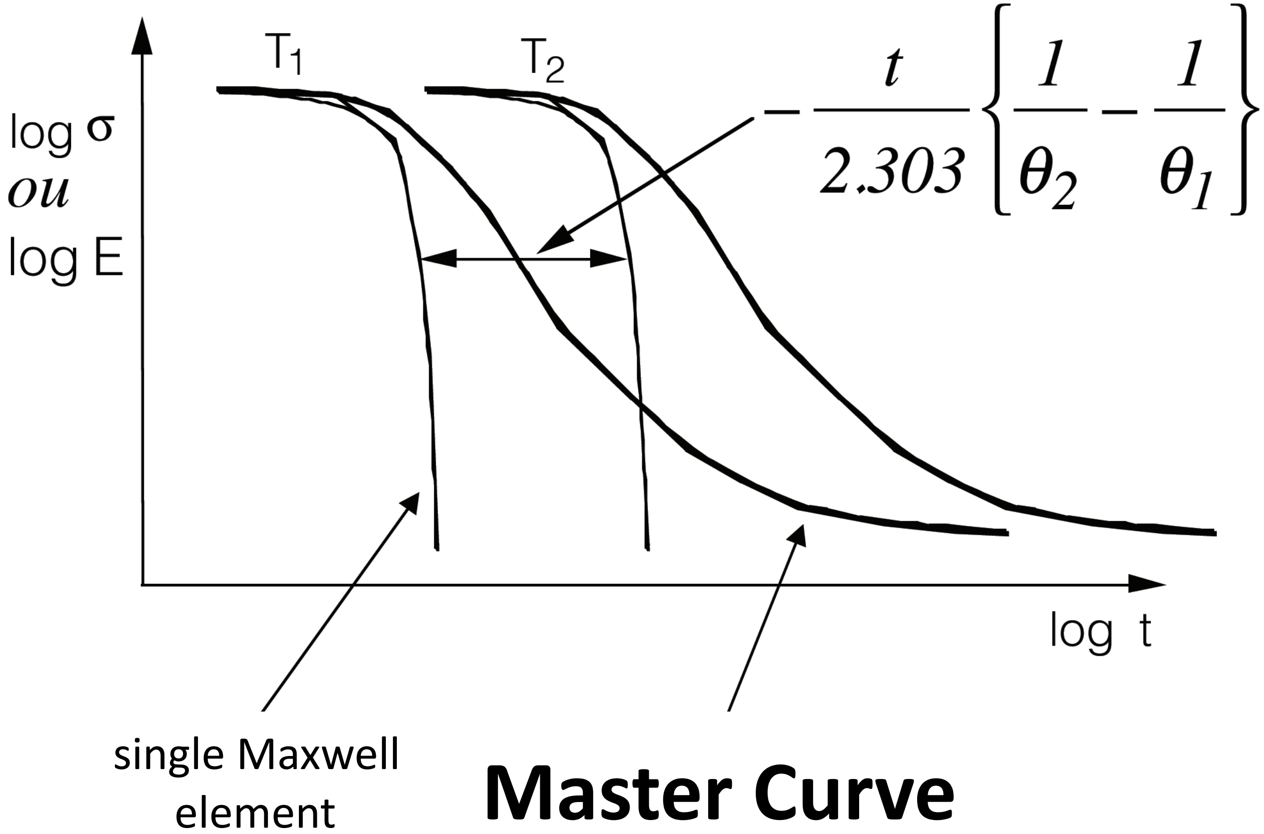
$$\sigma(T_1,t)=\sigma_0\, e^{-\frac{t}{\theta_1}}$$

$$\sigma(T_2,t)=\sigma_0\, e^{-\frac{t}{\theta_2}}$$

$$\frac{\sigma(T_2,t)}{\sigma(T_1,t)}=e^{-t\left\{\frac{1}{\theta_2}-\frac{1}{\theta_1}\right\}}$$

Effect of temperature

$T_1 > T_2 \Rightarrow \theta_1 < \theta_2$



Effect of temperature

$$a_T = \frac{\eta(T)}{\eta(T_0)}$$

WLF:

$$\log a_T = \log \frac{\eta(T)}{\eta(T_g)} = \frac{-17.44(T - T_g)}{51.6 + (T - T_g)}$$

Stress relaxation/relaxação de tensão, $E_r(t)$

Polímeros amorfos reais

PMMA

Amorphous polymer

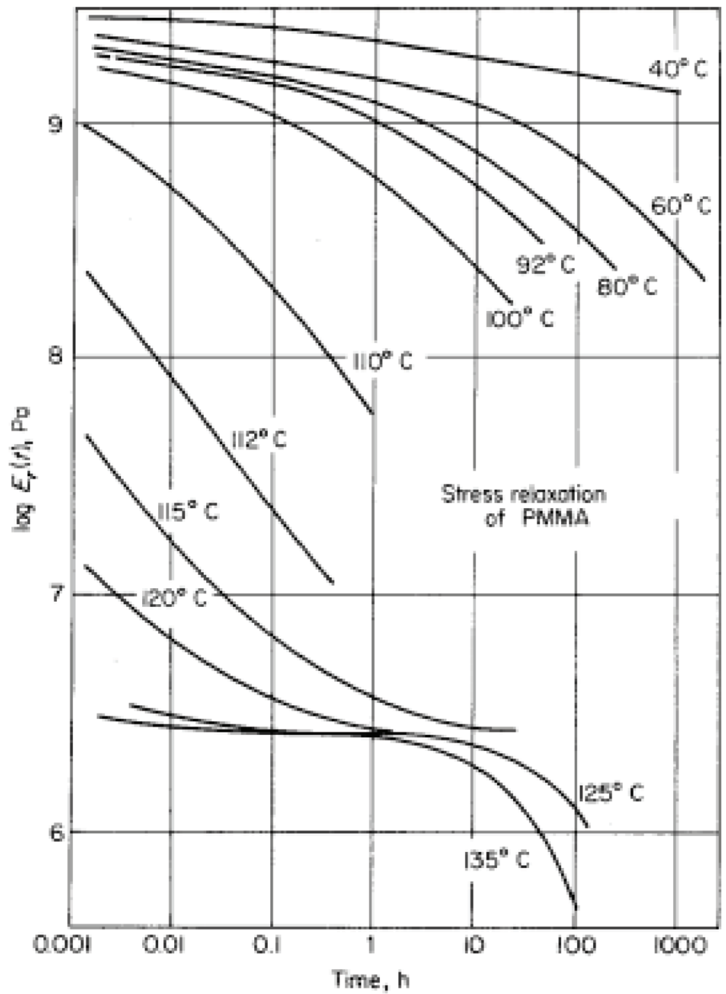
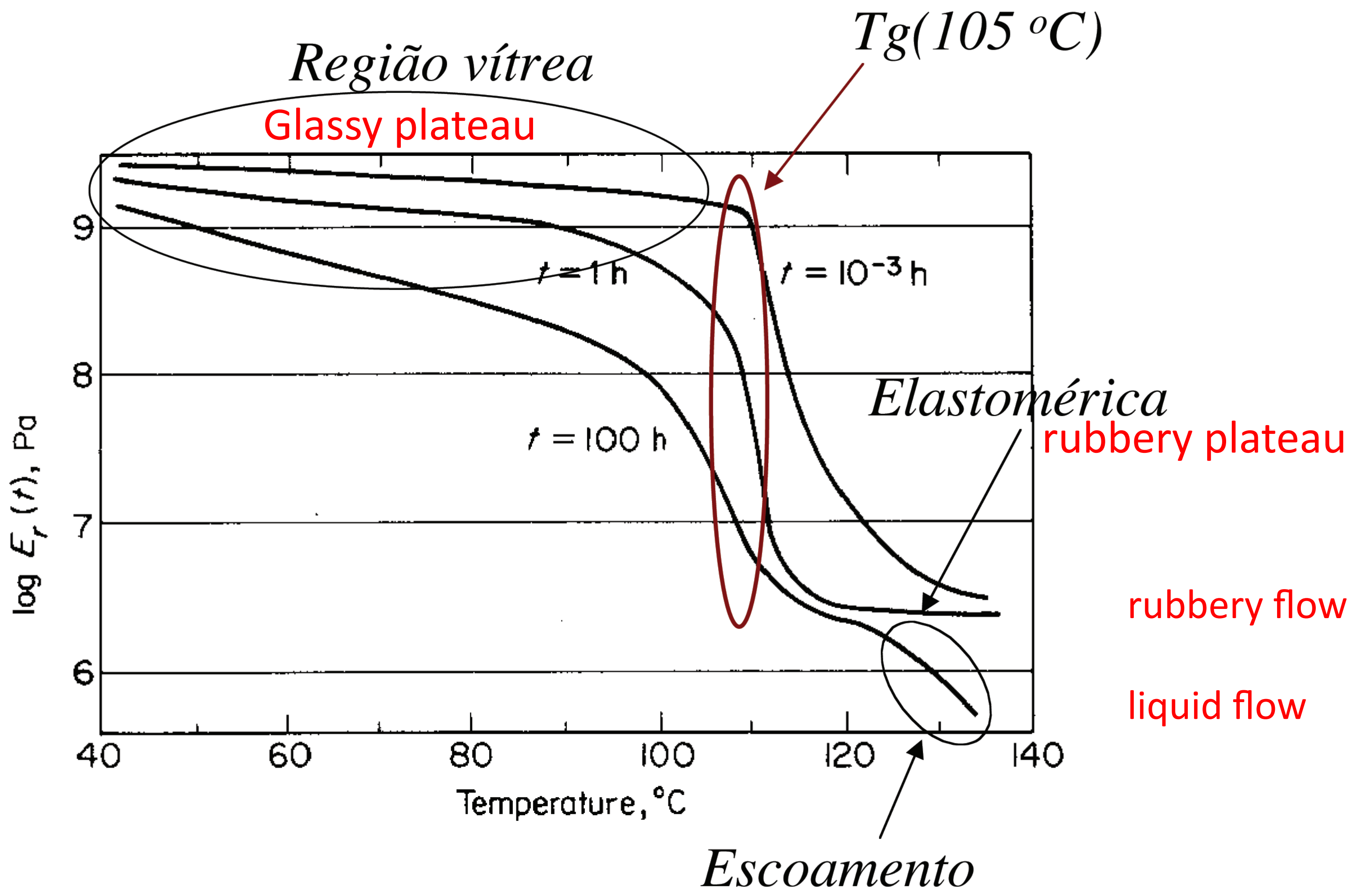


FIGURE 8-11
Log $E_r(t)$ vs. log t for unfractionated poly(methyl methacrylate) of $\bar{M}_v = 3.6 \times 10^6$ [14].

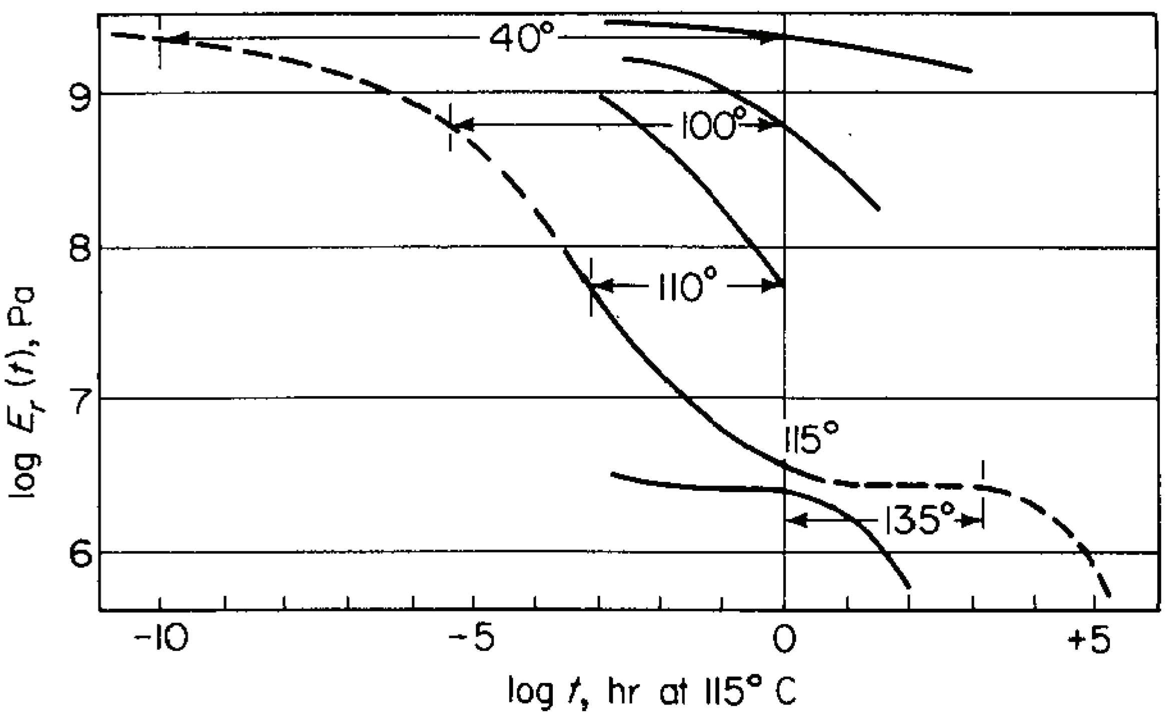
Stress relaxation/relaxação de tensão, $E_r(t)$

Amorphous polymers
Modulus-temperature master curve



Stress relaxation/relaxação de tensão, $E_r(t)$

Amorphous polymers
Modulus-time master curve



Stress relaxation/relaxação de tensão, $E_r(t)$

Amorphous polymers
Modulus-time master curve

Deslocamento horizontal: $\log t(T) - \log t(T_R)$

$$\log a_T = \log \frac{t(T)}{t(T_R)} = \frac{a_1(T - T_R)}{a_2 + (T - T_R)}$$

Se $T_R = Tg$,

$$\log a_T = \log \frac{t(T)}{t(Tg)} = \frac{-17.44(T - Tg)}{51.6 + (T - Tg)}$$

Polymer rheology

Time-temperature equivalence

low temperature
high frequency (short time)

- no segments movements

higher temperature
low frequency (long time)

- segments movements

TIME AND TEMPERATURE DEPENDENCES ARE RELATED

Polymer rheology

Time-temperature equivalence
Dynamic measurements

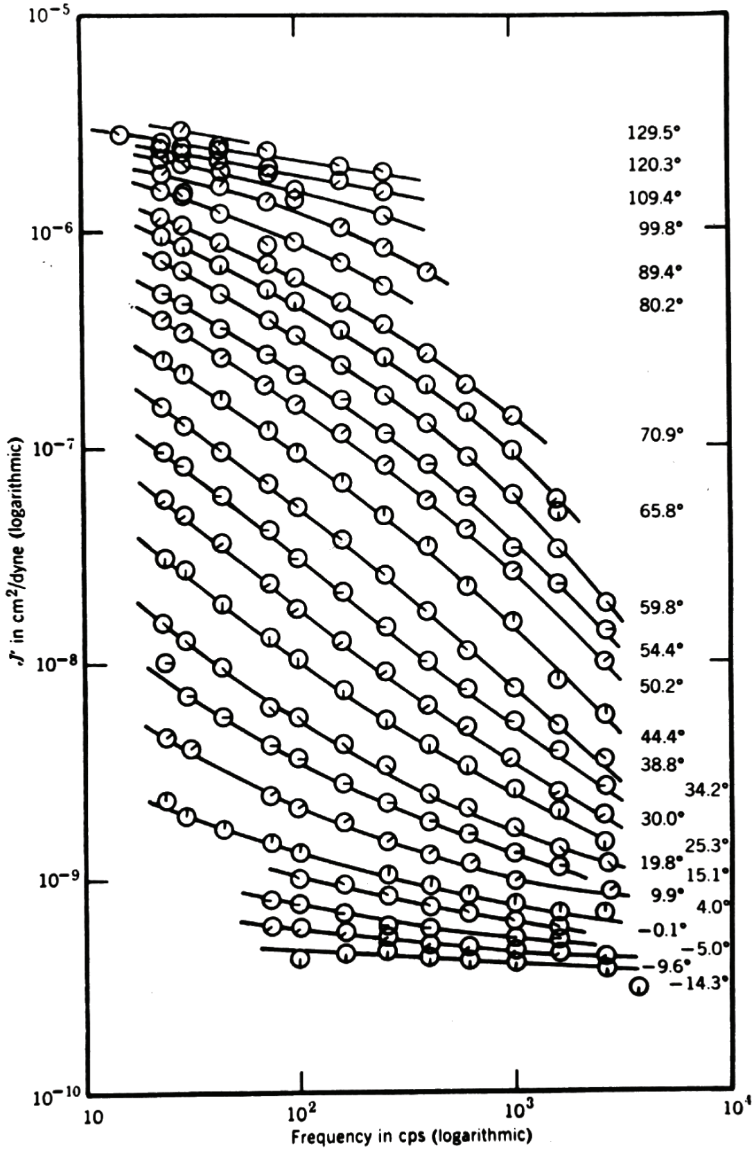
$$E^{*} = E' + iE''; \quad \left|E^{*}\right| = \frac{\sigma_0}{\gamma_0}$$

$$J^{*}(\omega) \equiv \frac{1}{E^{*}(\omega)} = J'(\omega) + iJ''(\omega)$$

Polymer rheology

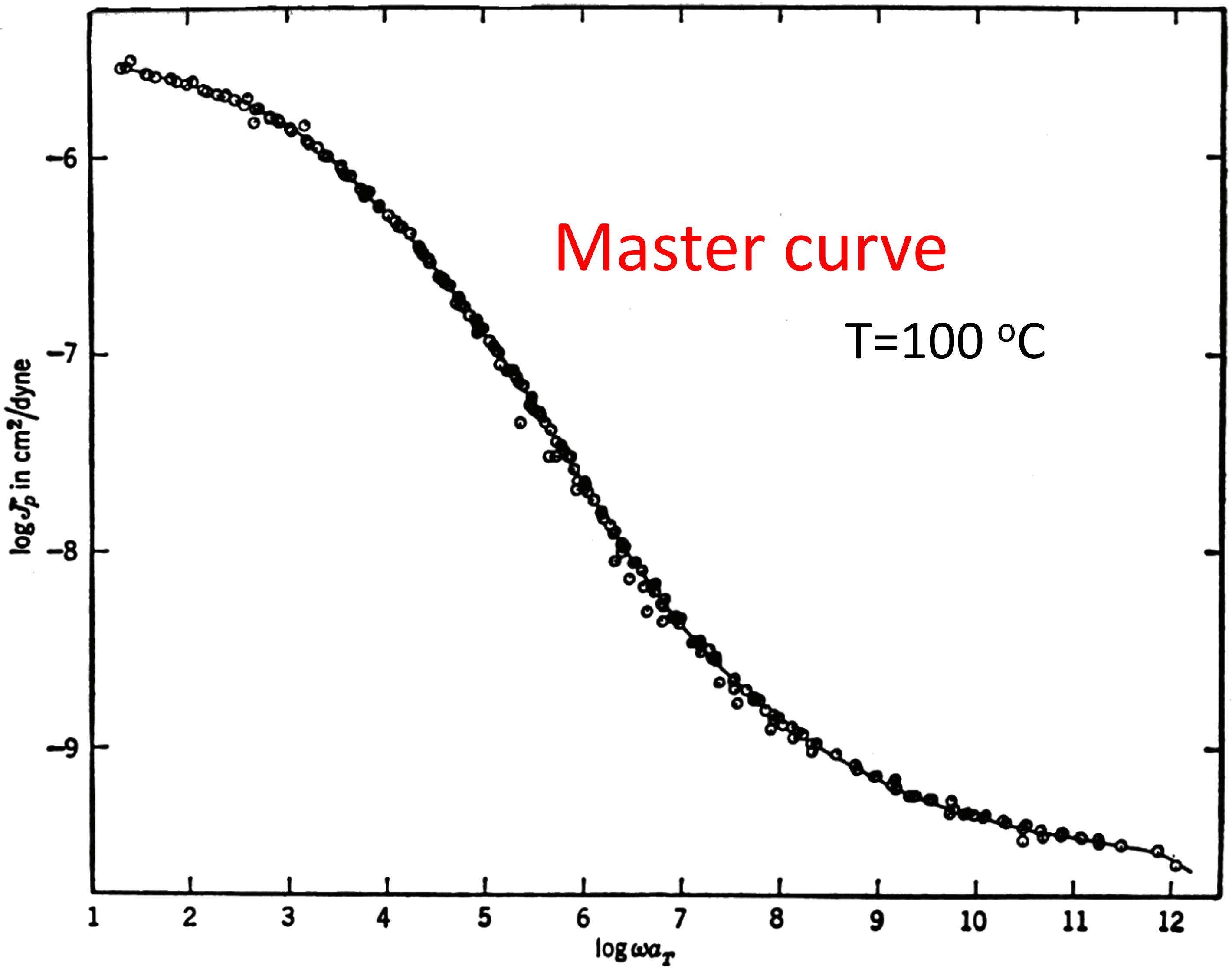
Time-temperature equivalence

Storage compliance (J')
for PMMA



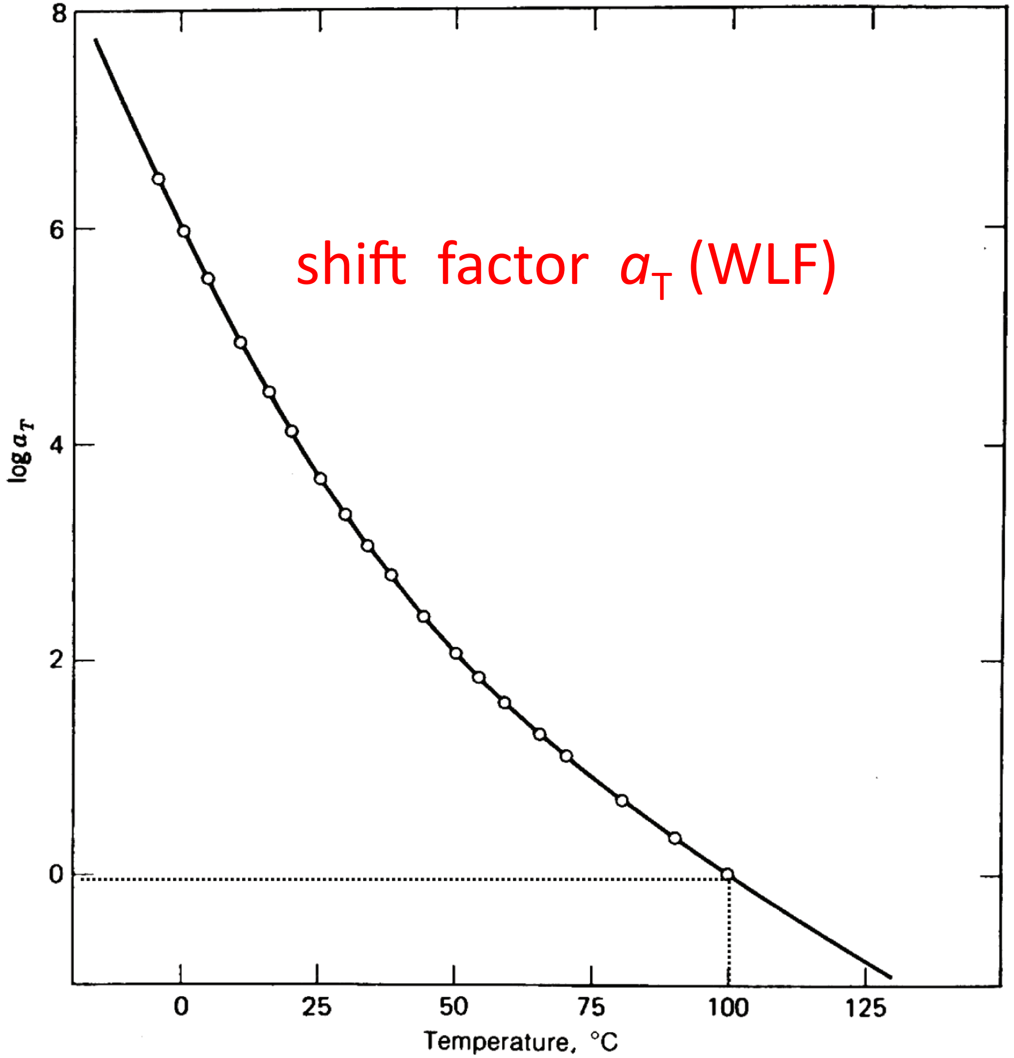
Polymer rheology

Time-temperature equivalence



Polymer rheology

Time-temperature equivalence



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