Rheology of polymer systems/ Reologia dos sistemas poliméricos

3. Generalized Maxwell Model

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Generalized Maxwell model

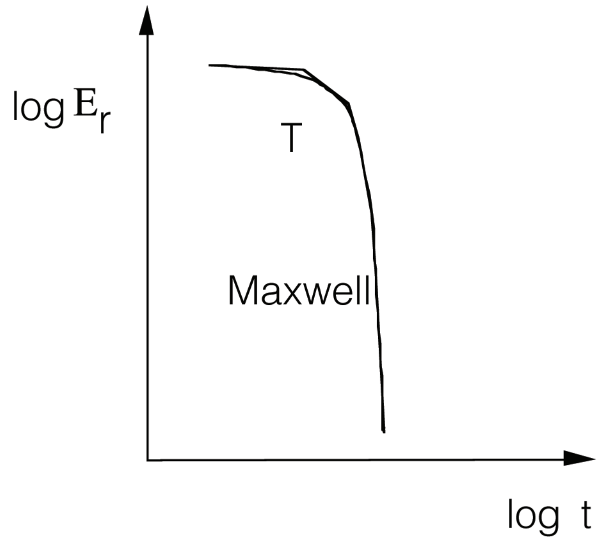
Simple Maxwell and Voigt elements do not describe polymers rheological behaviour

Stress relation for a single Maxwell element
E(t) modulus

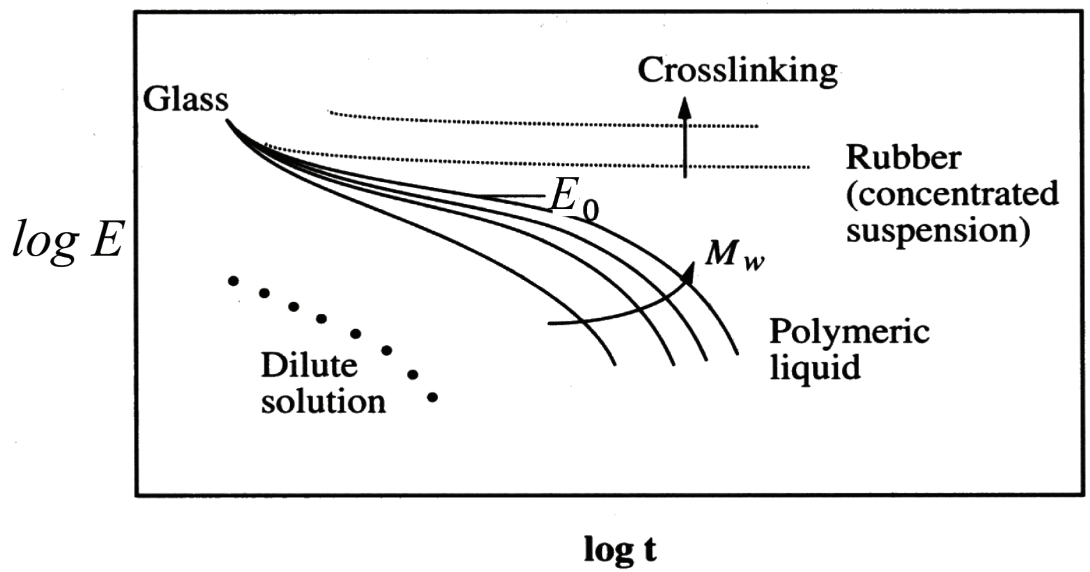
$$E(t) = \frac{\sigma(t)}{\varepsilon_0} \qquad E_r(t) = E_1\, e^{-t/\Theta}$$

Relation with the master curve ?

Generalized Maxwell model



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



Generalized Maxwell model

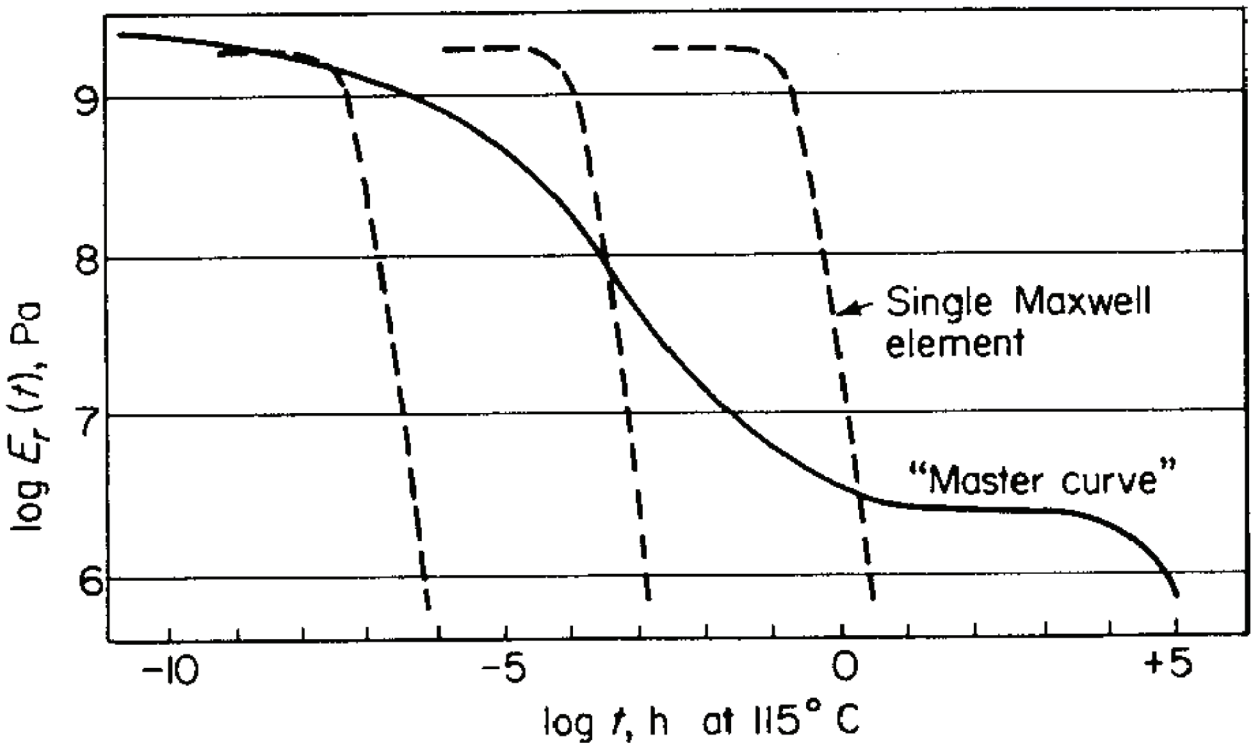


FIGURE 8-14
Master curve for poly(methyl methacrylate) compared with single Maxwell elements.

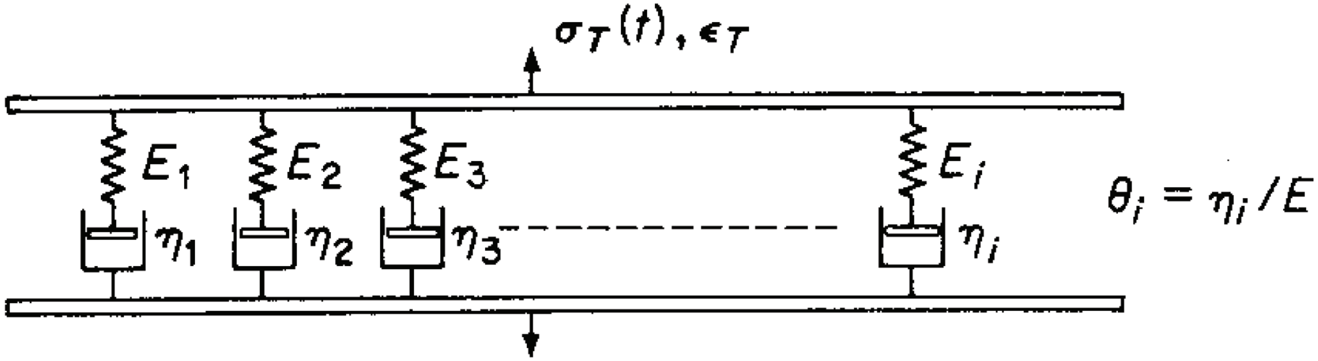
Generalized Maxwell model

Relaxation time Θ: related to the chain movements. It depends on:

- ❑Specific segment under consideration
- ❑Length of that segment

Θ_i

Generalized Maxwell model



Each element characterized by a relaxation time Θ_i

$$\sigma_i = \sigma_{0,i}\, e^{-\frac{t}{\theta_i}} \qquad E_r(t,i) = E_i\, e^{-\frac{t}{\theta_i}}$$

For the ensemble: $\varepsilon_i = \varepsilon$ (common)

$$\sigma_T(t) = \sum \sigma_i = \sum \varepsilon\, E_i\, e^{-\frac{t}{\theta_i}} \qquad E_{r,T}(t) = \frac{\sigma_T(t)}{\varepsilon} = \sum E_i\, e^{-\frac{t}{\theta_i}}$$

Generalized Maxwell model

For an infinite number of elements

$$E_T(t) = \int_0^{\infty} E(\Theta)\ e^{-t/\Theta}\ d\Theta$$

ou,

$$E_T(t) = \int_{-\infty}^{+\infty} \overline{H}(\log \Theta)\ e^{-t/\Theta}\ d(\log \Theta)$$

$\overline{H}(\log \Theta)$

$E(\Theta)$ funções de distribuição de tempos de relaxação com

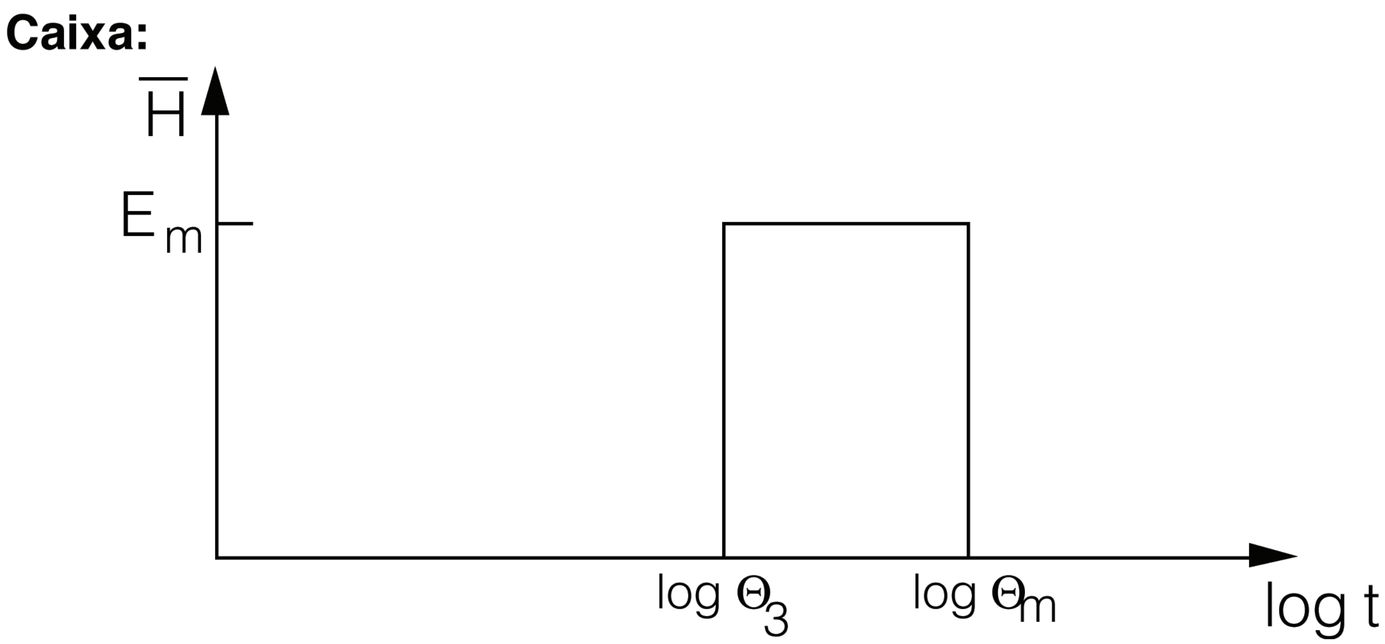
distributions of relaxation time

$$\overline{H}(\log \Theta) = 2.303\ \Theta\ E(\Theta)$$

Generalized Maxwell model

Elementary models for H(log Θ)

Box:



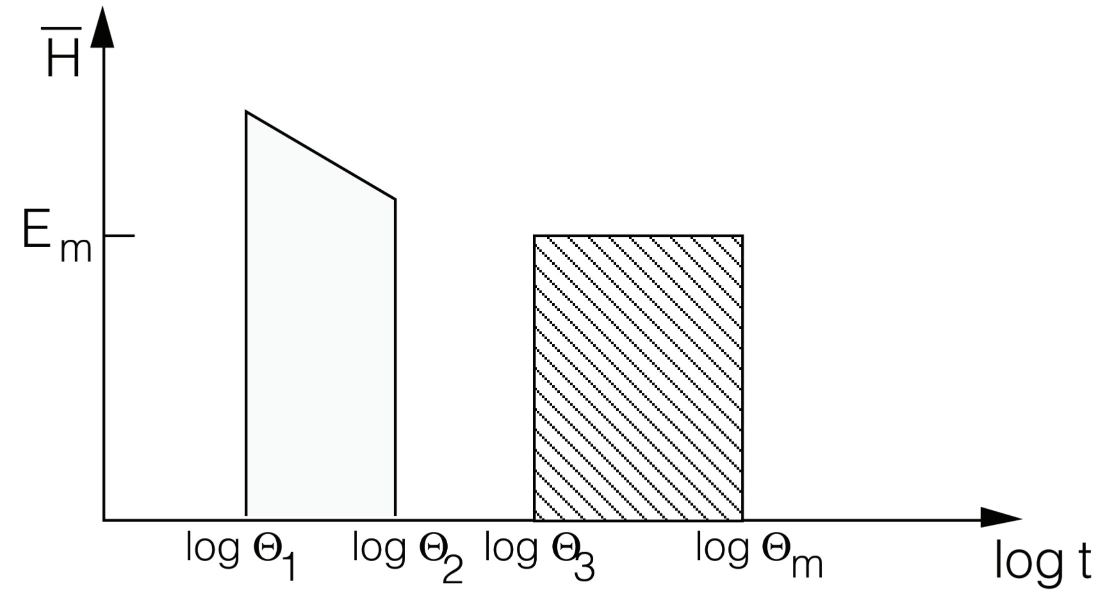
Generalized Maxwell model

Elementary models for $H(\log \Theta)$

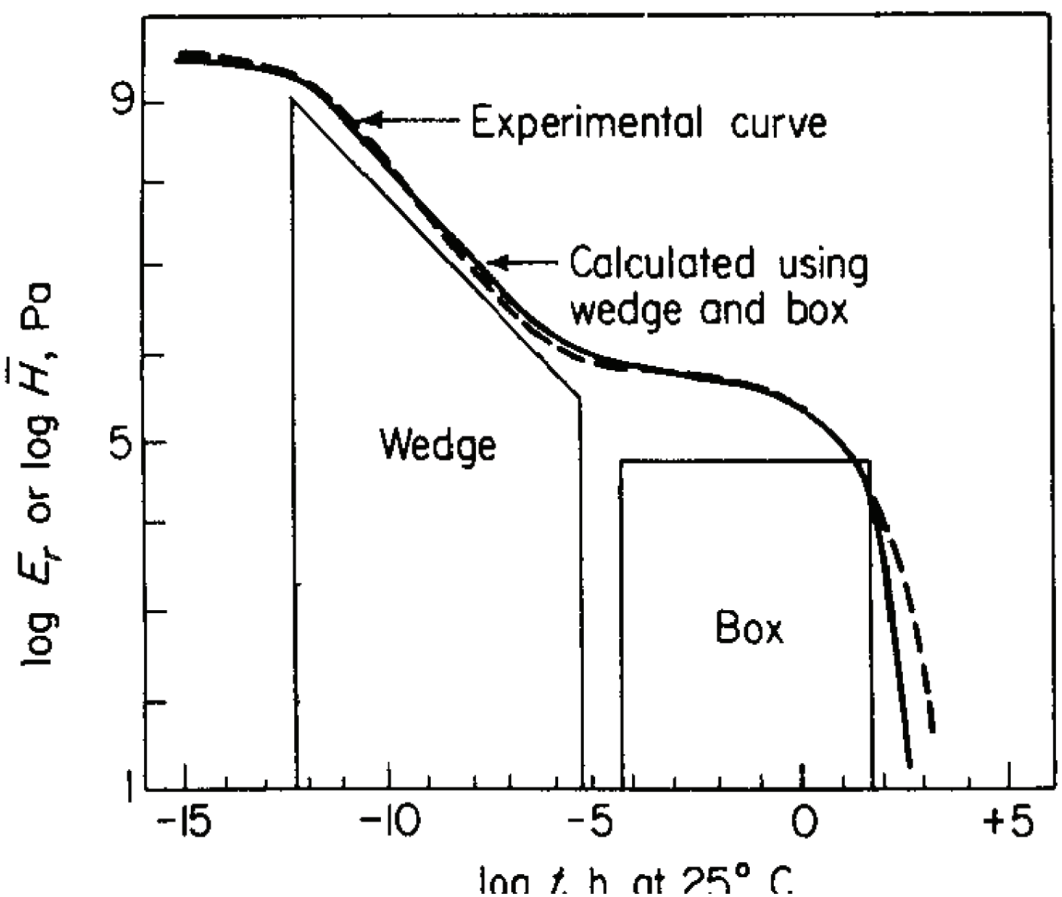
Wedge:

Cunha:

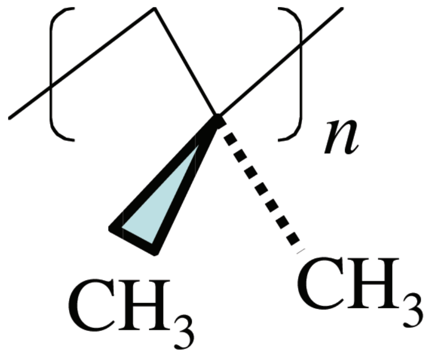
$$\overline{H} = \begin{cases} \dfrac{M_0}{\sqrt{\Theta}} & \Theta_1<\Theta<\Theta_2 \\ 0 & \Theta<\Theta_1;\ \Theta>\Theta_2 \end{cases}$$



Generalized Maxwell model



Poli(isobutileno)



Polyisobutylene

Generalized Maxwell model

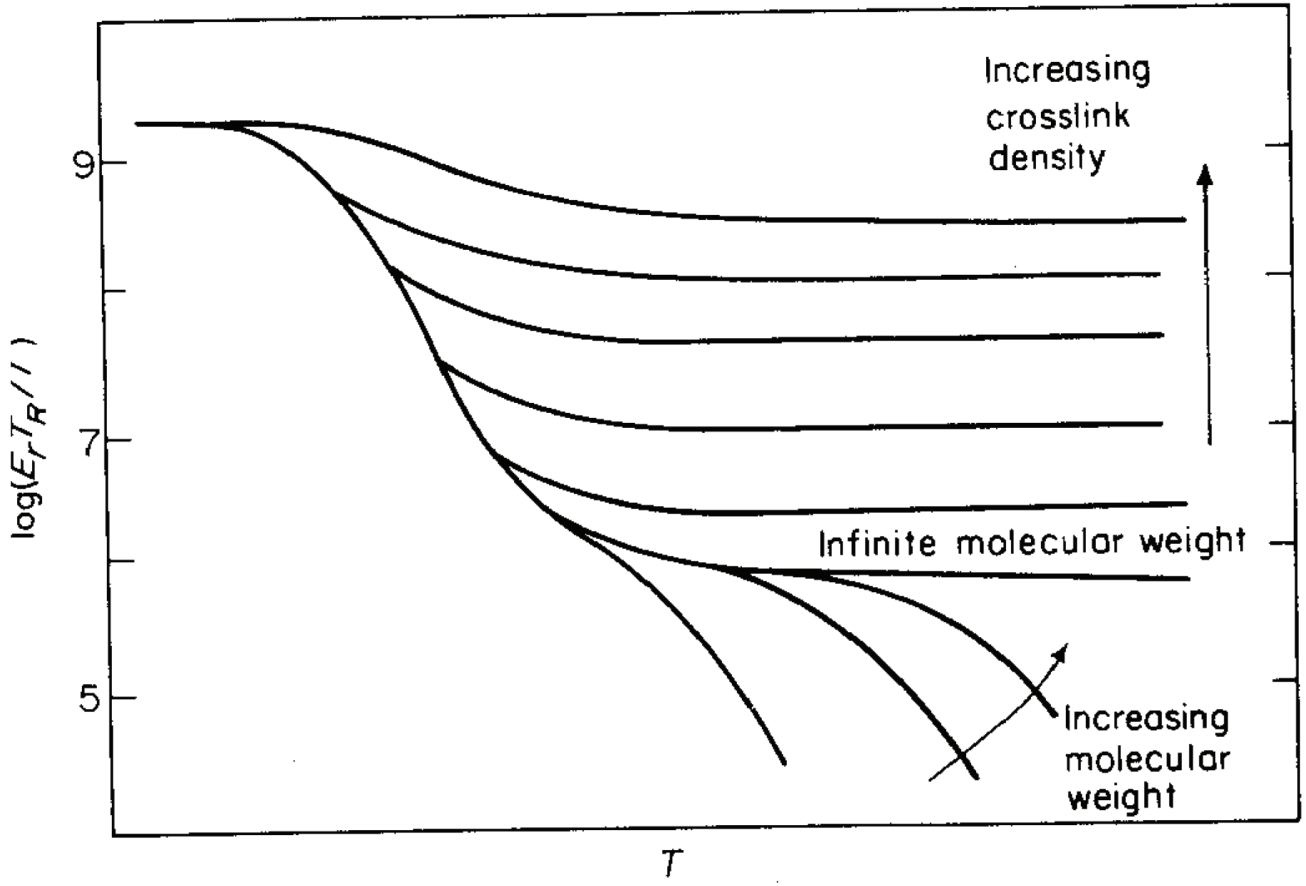
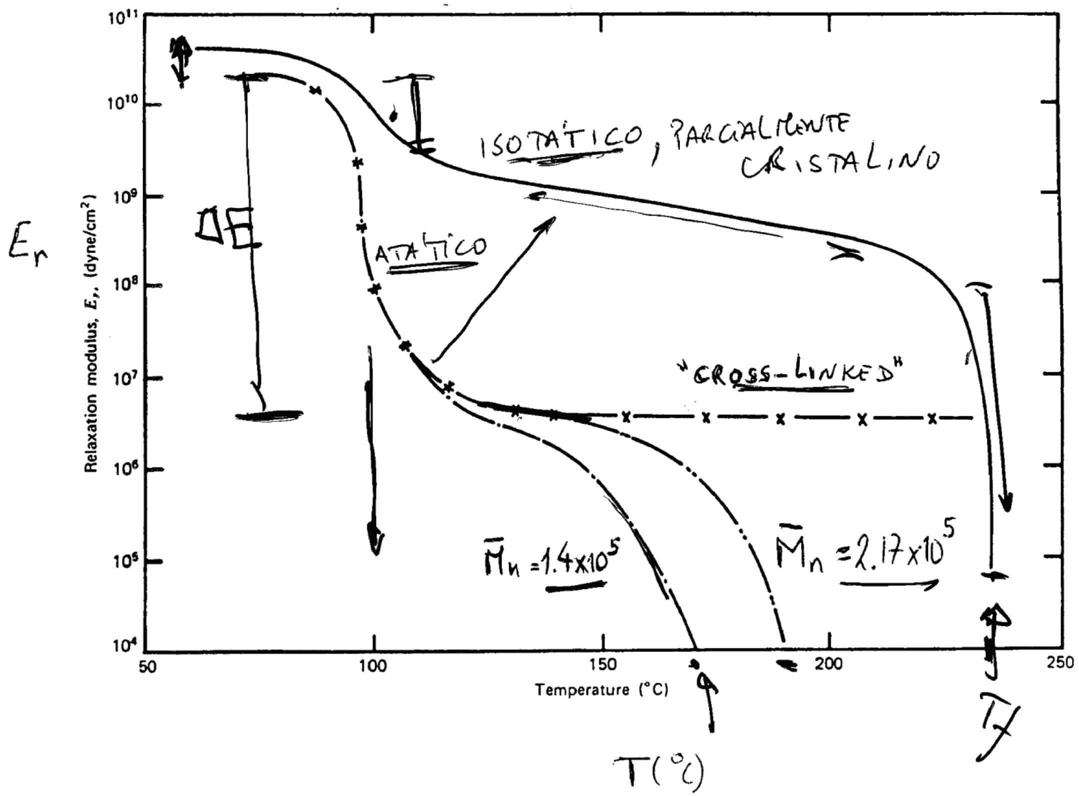


FIGURE 8-17
Qualitative effects of increasing molecular weight and cross-linking on the master curve.

Generalized Maxwell model

Polystyrene (t=10sec)



PS.: ISOTÁTICO $T_g \simeq 100°C$

$T_f \simeq 242°C$

Polymer rheology

In general

- chains packed into regular lattice
- high dimensional stability
- low swelling
- fiber-forming properties

Rheology in general

- non-isotropic → no universal behaviour
- non-uniform stress distribution
- mixture of regions with variable regularity
- no general model or equivalence

Polymer rheology

:

Temperature range	Low (5-10%)	Medium (20-60%)	High (70-90%)
	Degree of crystallinity		
Below T_g	Glassy, brittle	Hornlike, tough	Hard, brittle
Above T_g	Rubbery	Leathery, tough	Hard, brittle
Above T_m	Amorphous viscous melt		

References

Bibliografia:

•"Principles of Polymer Systems", 2ed., F. Rodriguez, McGraw-Hill-Int. Student Ed., 1983: secções 7.1 a 7.6

•"Introduction to Macromolecular Science", P. Munk, John Wiley & Sons, 1989: secção 4.1.4