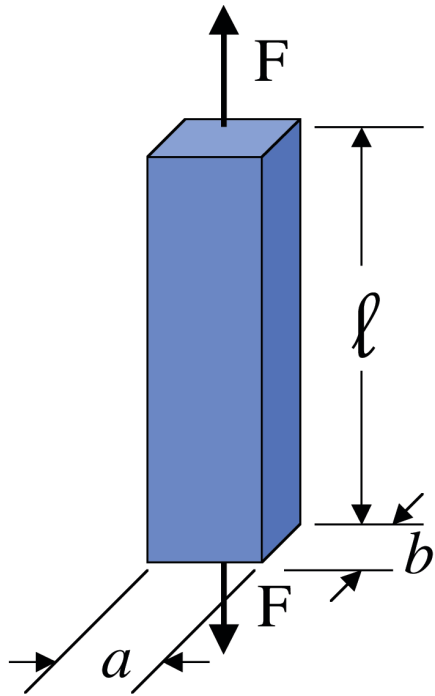


Mechanical properties

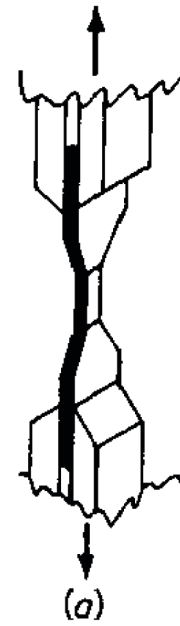
1. Young modulus
2. Stress-strain measurements
3. Resistance to impact

Young modulus

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

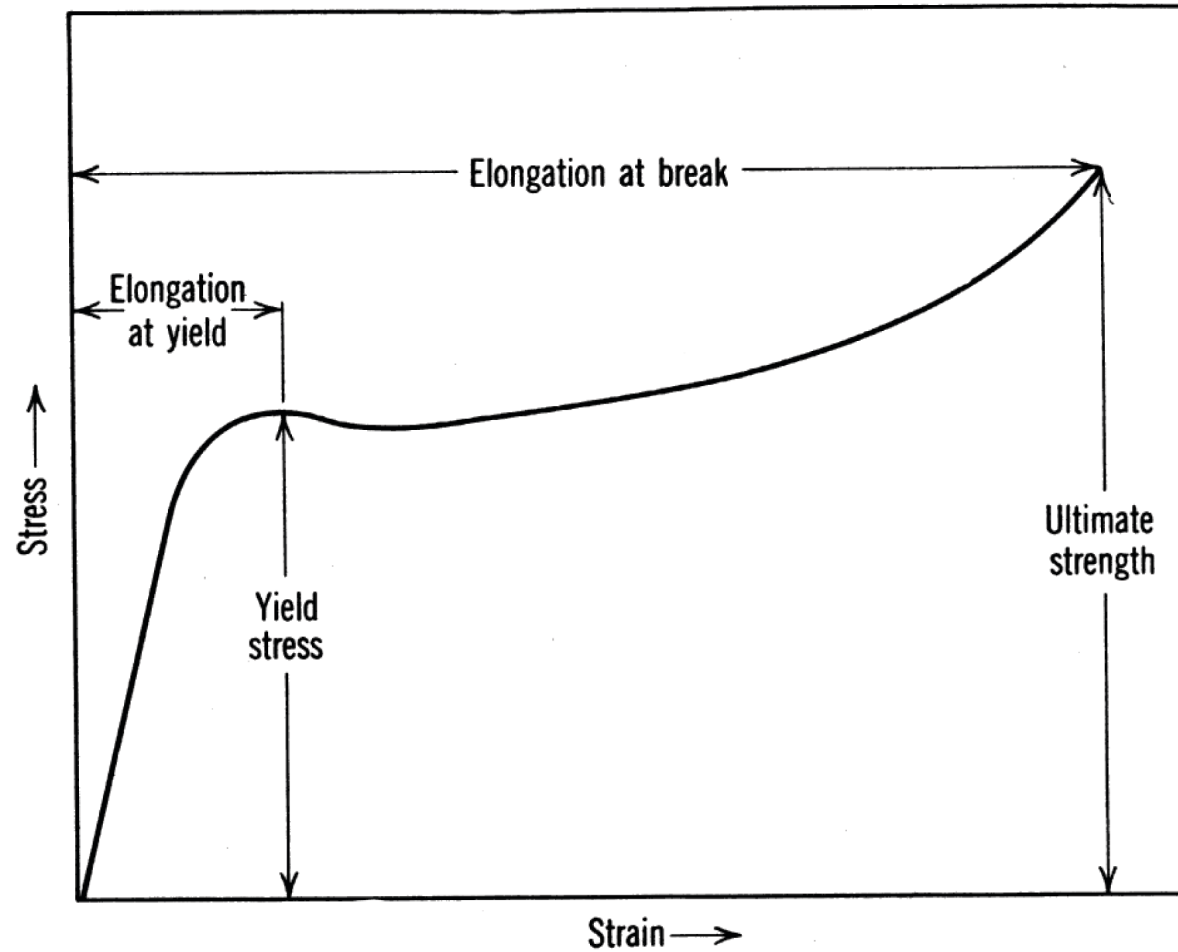


$$\sigma = \frac{F}{a_0 b_0}$$



E modulus

Experimental stress-strain curves



E modulus

Experimental stress-strain curves

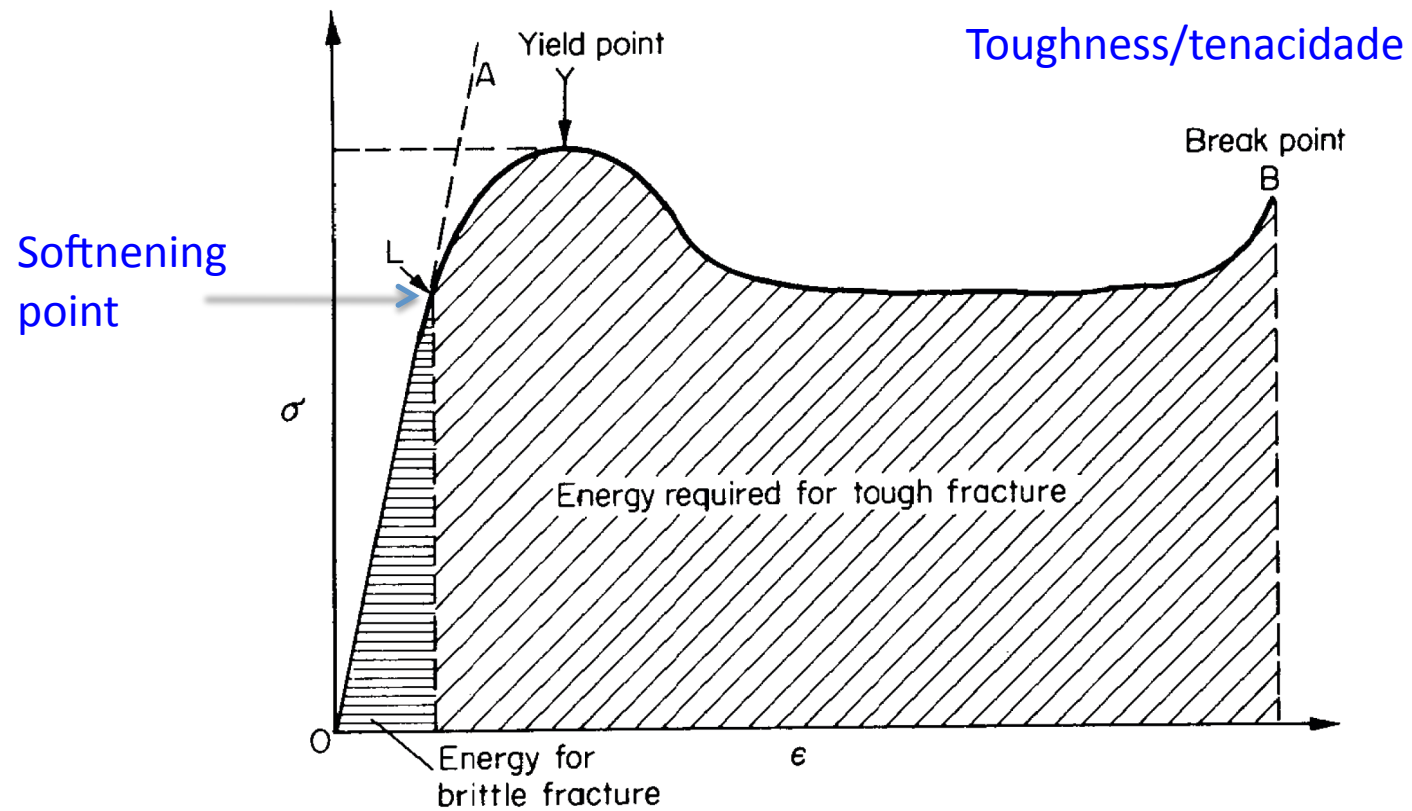
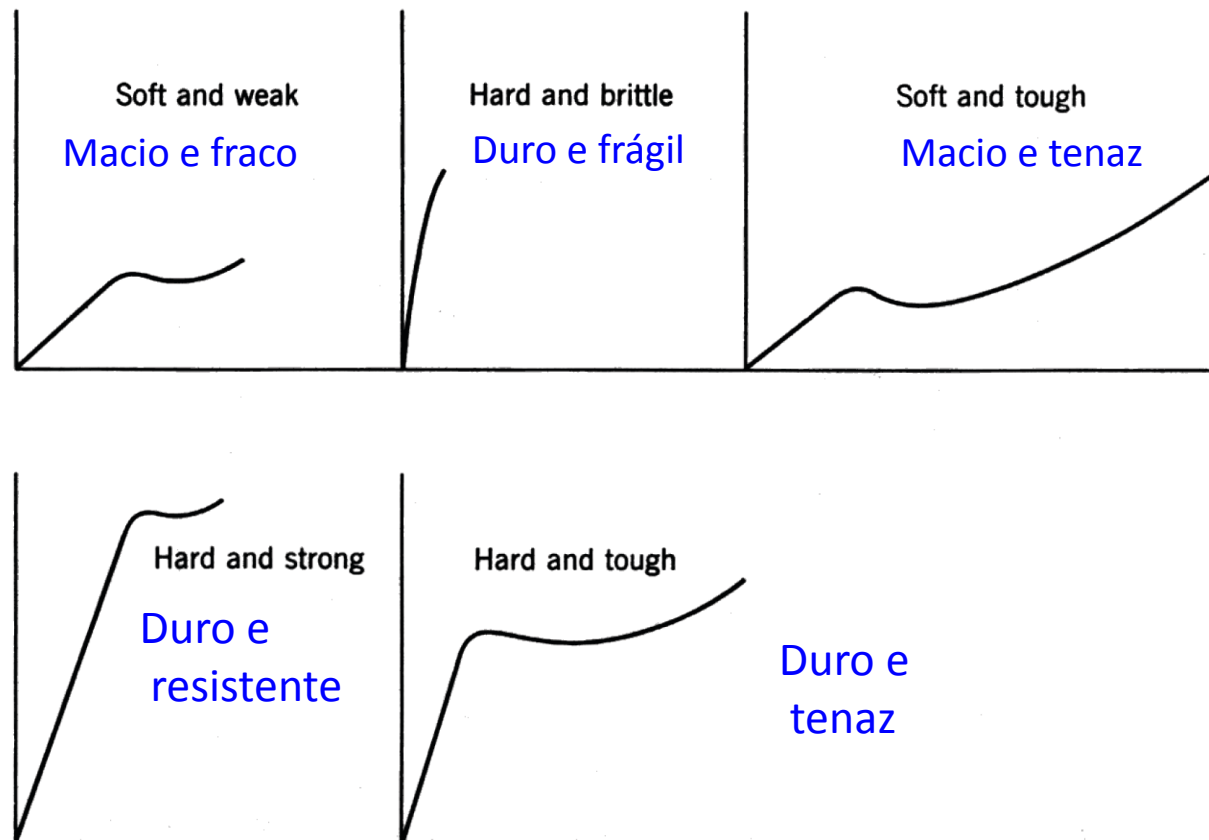


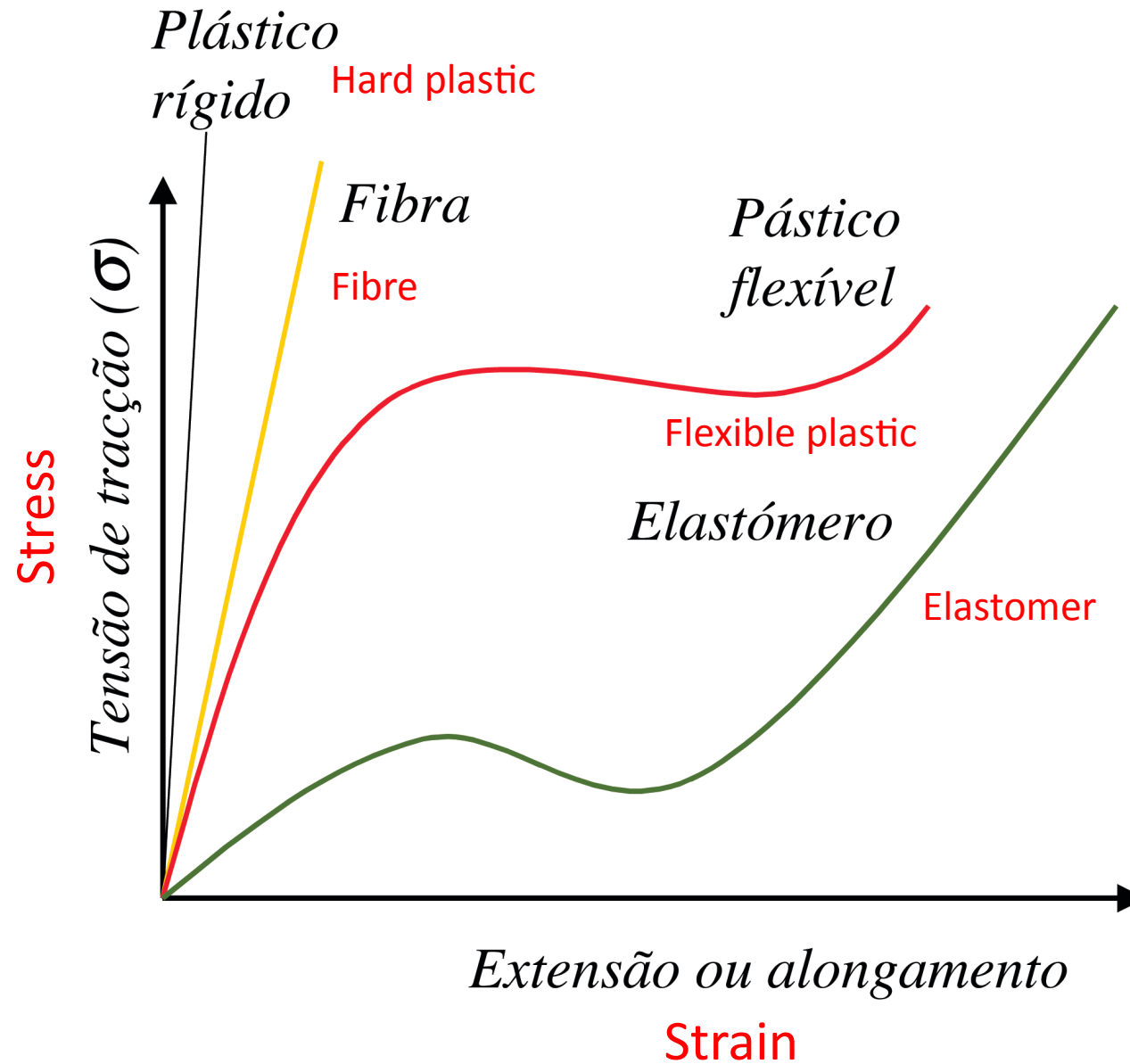
FIGURE 13.6. Idealized stress-strain curve. The slope of line OA is a measure of the modulus.

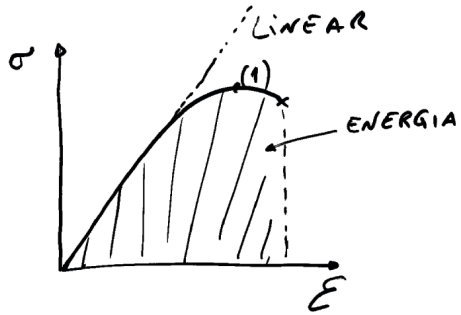
E modulus

Experimental stress-strain curves General properties of materials

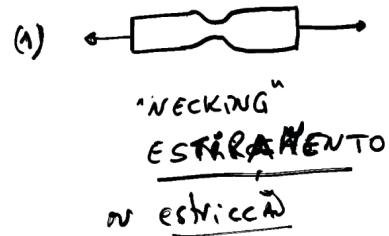


E modulus

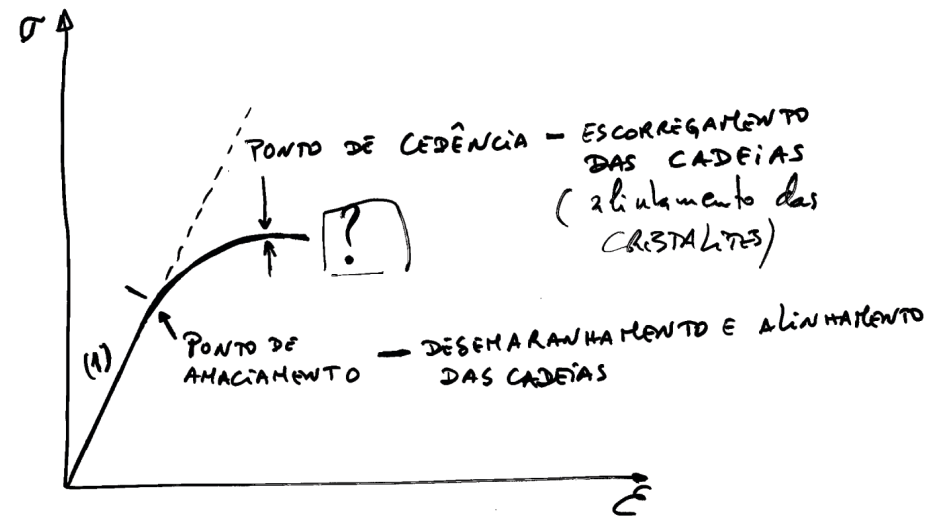




(GENÉRICO)



POLÍMEROS



- (1) COMPORTAMENTO ELÁSTICO LINEAR (AMORFOS E CRISTALINOS)
- DEFORMAÇÃO DE ÂNGULOS E EXTENSÃO DE LIGAÇÕES
 - RECUPERÁVEL INSTANTANEAMENTE

*Glasses and polymer networks with high density of cross-links – brittle (**Frágeis, quebradiços**)*

Rubbers or elastomers – high strain (or elongation) at break

Crystalline materials:

1. Oriented: Hard and strong (**Duros e resistentes**)
2. Non oriented: Show necking (**estricção**)
before breaking

Rubber elasticity

During rubber deformation:

1st law of thermodynamics

$$\Delta E = Q - W$$

2nd law of thermodynamics

$$dS = \frac{dQ_{rev}}{T}$$

When a rubber is stretched with a force f , causing an elongation dL , the work involved is:

$$dW = pdV - fdL$$

so,

$$dE = TdS - pdV + fdL$$

Rubber elasticity

During deformation, interchain distances are **approximately constant**

$$dV \approx 0$$

considering

$$dE = TdS - pdV + fdL$$

we get

$$f = \left(\frac{\partial E}{\partial L} \right)_{T,V} - T \left(\frac{\partial S}{\partial L} \right)_{T,V}$$

dE – associated to temperature, bond energies and interactions variations

dS – associated to conformational changes

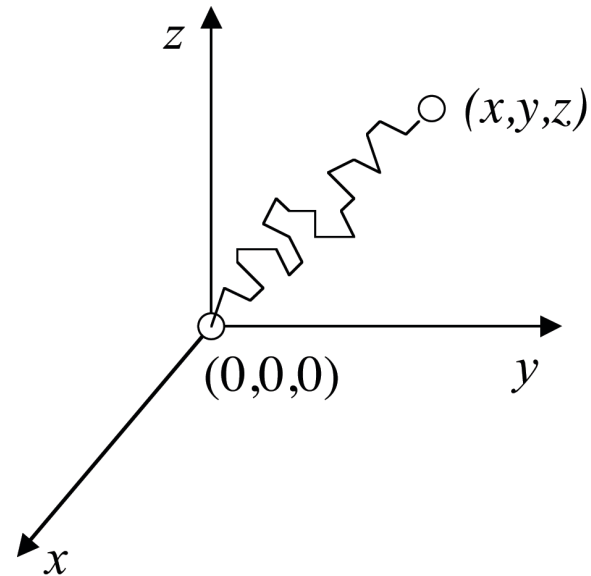
An ideal rubber should respond to an external stress *only* by uncoiling (conformational changes), without significant changes in interchain interactions. Therefore

$$f = -T \left(\frac{\partial S}{\partial L} \right)_{T,V}$$

Rubber elasticity

$$\text{Boltzmann: } \Delta S = k \ln \frac{\Omega_2}{\Omega_1}$$

If we can describe a polymer chain as a gaussian distribution of average distances between chain ends



The probability of having a chain with one end at $(0,0,0)$ and the other at (x,y,z) , is

$$\Omega(x,y,z) = \left(\frac{\beta^2}{\pi} \right)^{3/2} \exp [-\beta^2(x^2+y^2+z^2)]$$

$$\text{sendo } \beta = (3/2)^{1/2} n^{-1/2} a^{-1}$$

Rubber elasticity

Upon a change of chain dimensions

$$\Delta S = k \ln \frac{\Omega_2}{\Omega_1} = - (k/2) (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)$$

where α_x is the extension coefficient of the chain along x

$$\alpha_x = \frac{x_2}{x}$$

if there are ζ effective chains (segments with fixed ends_cross-links), the total variation of entropy is

$$\Delta S = - (k \zeta / 2) (\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)$$

Rubber elasticity

If the volume of the rubber does not change when it is stretched along x ,

$$f = \frac{kT\zeta}{L_u} \left[\alpha_x - \left(\frac{1}{\alpha_x} \right)^2 \right]$$

$$\sigma = f/A_u, \quad V_u = L_u \cdot A_u \quad (\text{original dimensions})$$

$$\sigma = kT \frac{\zeta}{V_u} \left[\alpha_x - \left(\frac{1}{\alpha_x} \right)^2 \right] = RTN \left(\alpha - \frac{1}{\alpha^2} \right)$$

N - moles of polymer chains (or segments with fixed ends) per unit volume

Rubber elasticity

The above expression for the **retractive stress** of a rubber can be “improved” by subtracting from N the chain ends that do not contribute to the elasticity ($2\rho/M_n$).

We should then consider

$$N_{\text{eff}} = N - 2\rho/M_n$$

being M_n -Number-average molecular weight before the formation of cross-links, and ρ the polymer density

Martin, Roth and Stiehler empirical relationship

$$\ln \frac{\sigma \alpha^2}{\alpha - 1} = \ln \Lambda + \lambda \frac{\alpha^2 - 1}{\alpha}$$

$$\lambda = 0.38 \pm 0.02 \text{ (constant)}$$

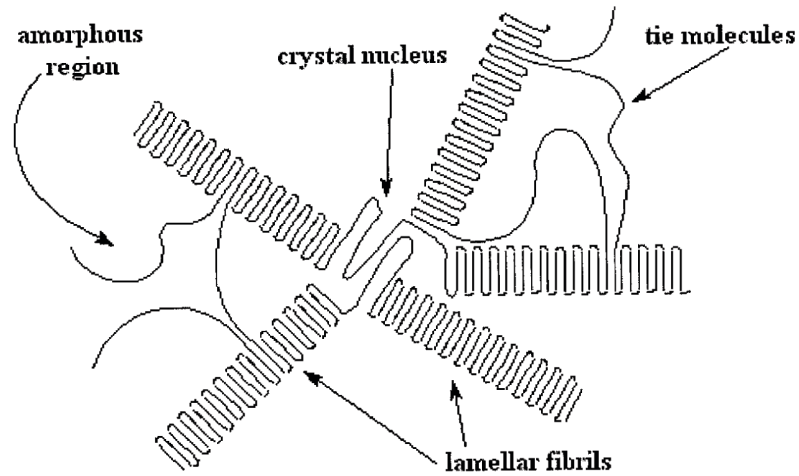
Spherulitic non-oriented polymers. Fibres.

The crystallization of a polymer from its melt leads, in general, to the orientation of the crystallites along a radial direction – **spherulites**.

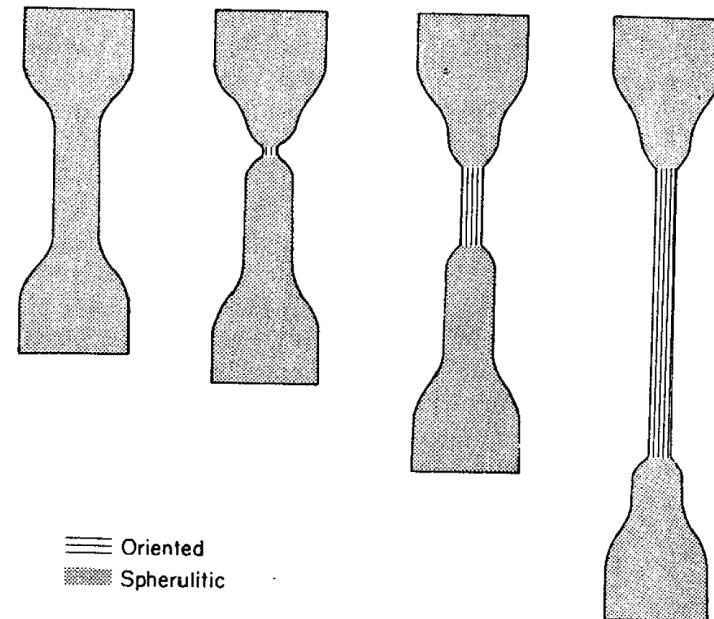
When a crystalline polymer undergoes an elongation deformation at a temperature above T_g and below T_f :

- i) **Elastic deformation**- reorientation of the polymer chains of the amorphous fraction*
- ii) Above the elastic limit, there may be a reorganization of the chains in the crystalline fraction – **crystallites orientation***

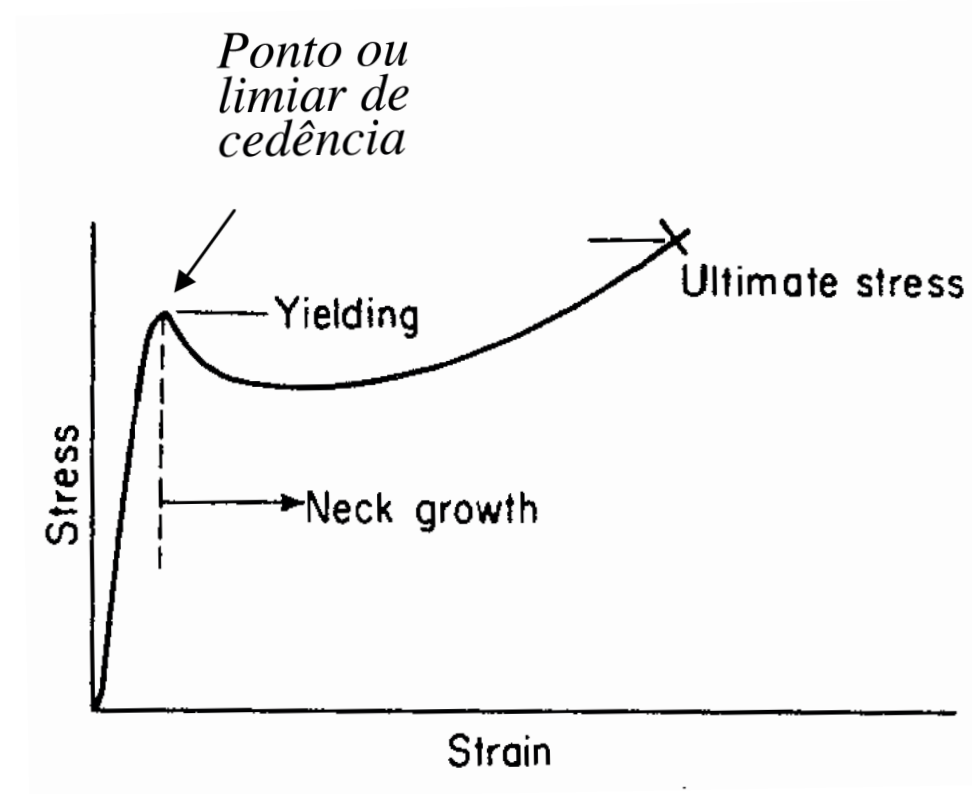
Drawing of a spherulitic polymer



a polymer crystalline spherulite



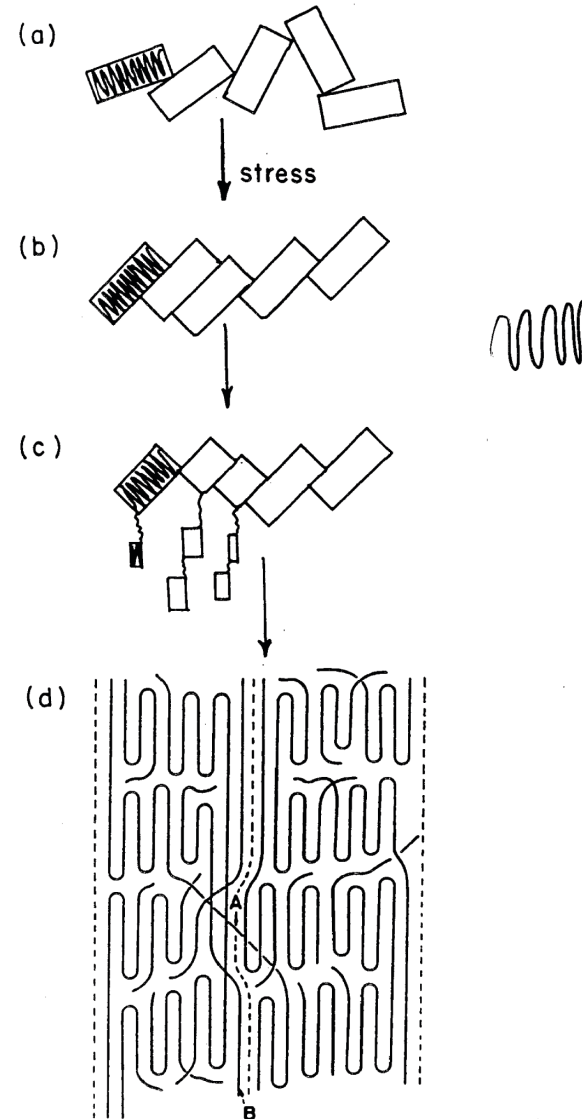
Drawing of a spherulitic polymer



Drawing occurs after the yielding point, when a necking (estricção) of the sample starts. The yielding points defines the bond deformation limit of the crystalline regions, before the spherulites become unstable.

Drawing of a spherulitic polymer

Orientation by stretching



Textile Fibres

Most synthetic fibres are highly crystalline, with the crystallites predominantly oriented along the fibre axis.

Fabrication:

- 1. Extrusion of a melt (or solution) through a spinneret*
- 2. Drawing at T between T_g and T_m*

Consequences:

- 1. Higher strength*
- 2. Lower elongation at break along the fibre axis*

Factors affecting $\sigma(\epsilon)$

1. Extrinsic

- i. Strain rate*
- ii. Temperature*
- iii. Pressure*
- iv. High energy radiation*

2. Intrinsic

- i. Chemical structure (T_g , T_f)*
- ii. Crystallinity*
- iii. Water, monomer residues*
- iv. Additives (plasticizers, fibres and reinforcement particles)*

Strain rate

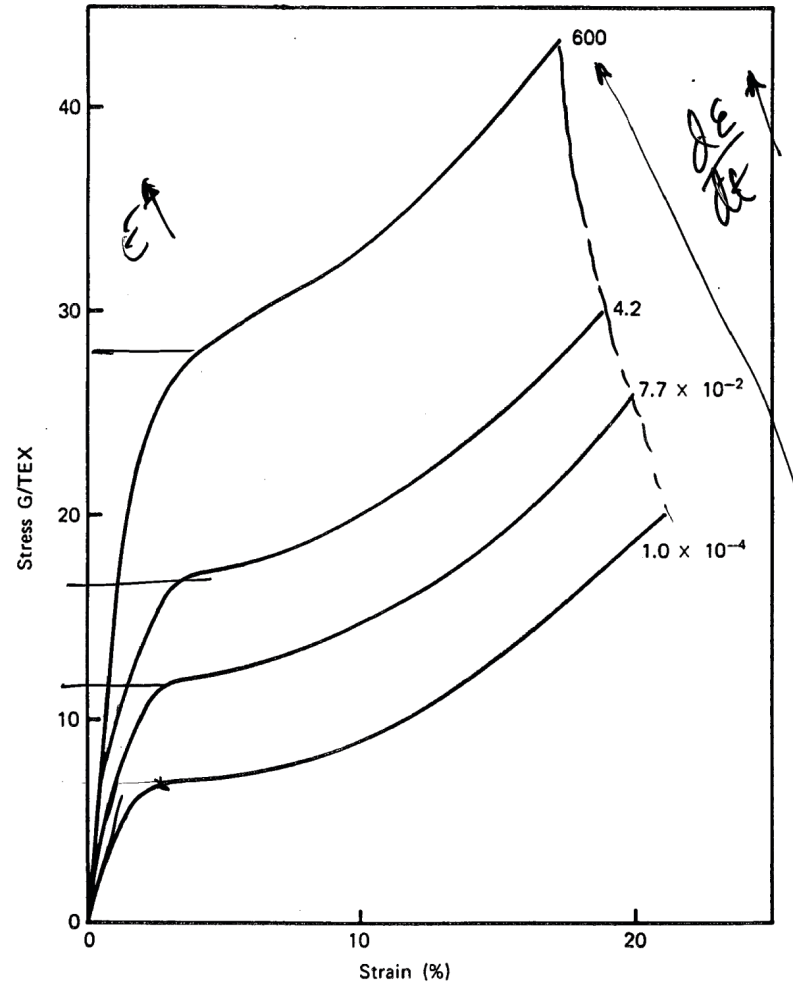


Figure 27. Effect of strain rate on tensile stress-strain curves of polyacrylonitrile fibers (77).

Temperature

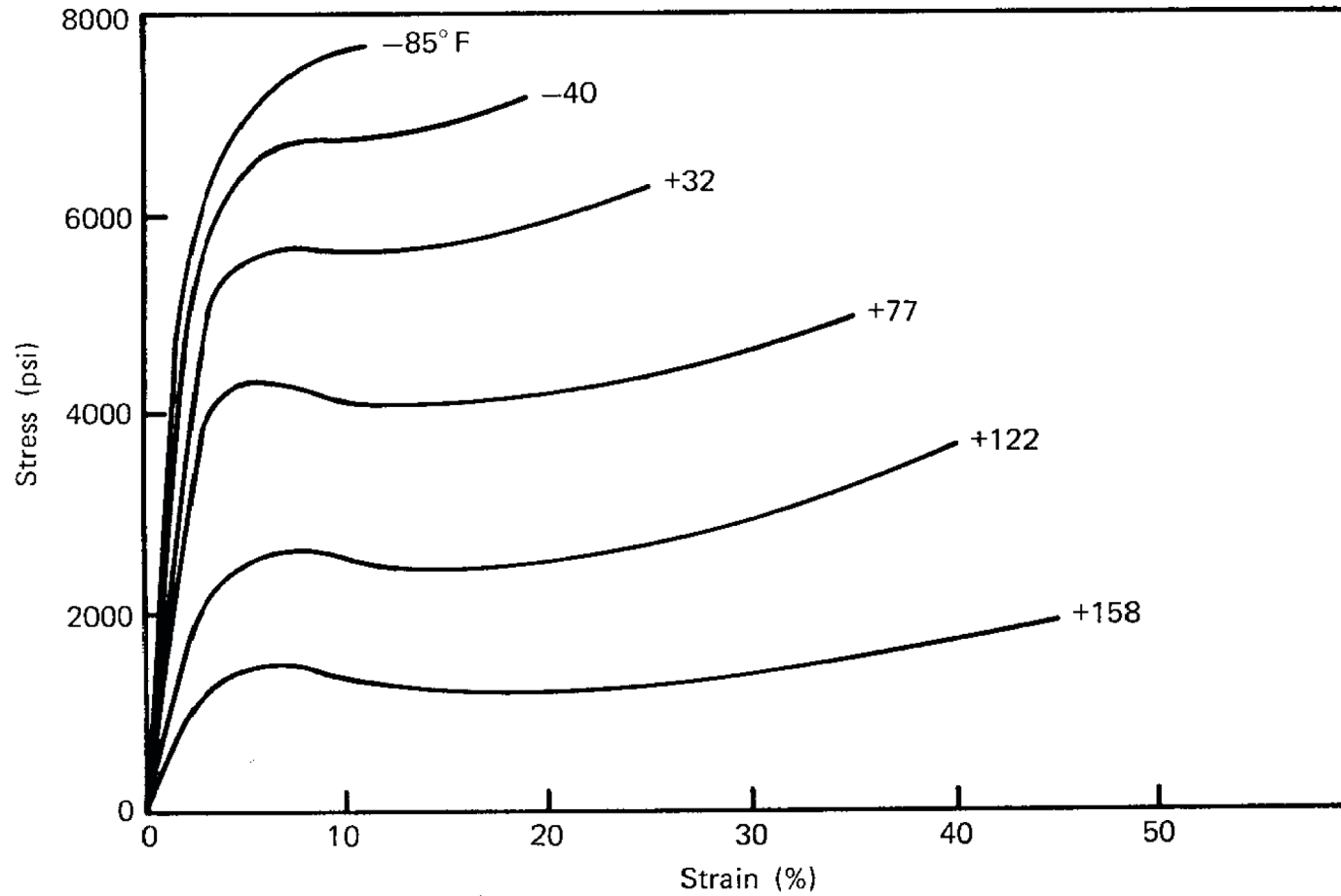


Figure 29 Effect of temperature on tensile stress-strain curves of cellulose acetate (20).

Pressure

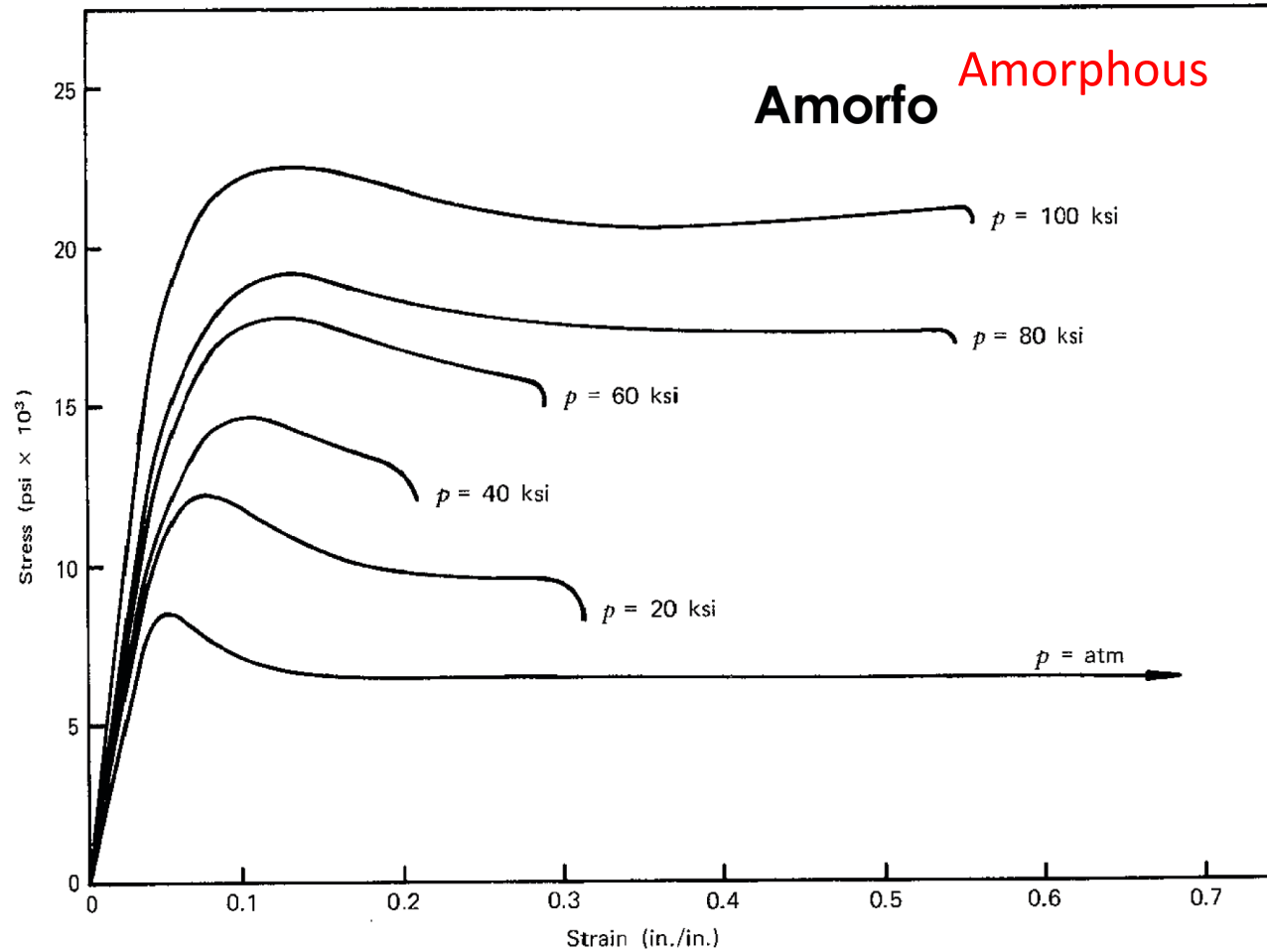


Figure 30 Effect of pressure on tensile stress–strain curves of polyvinyl chloride.

Pressure

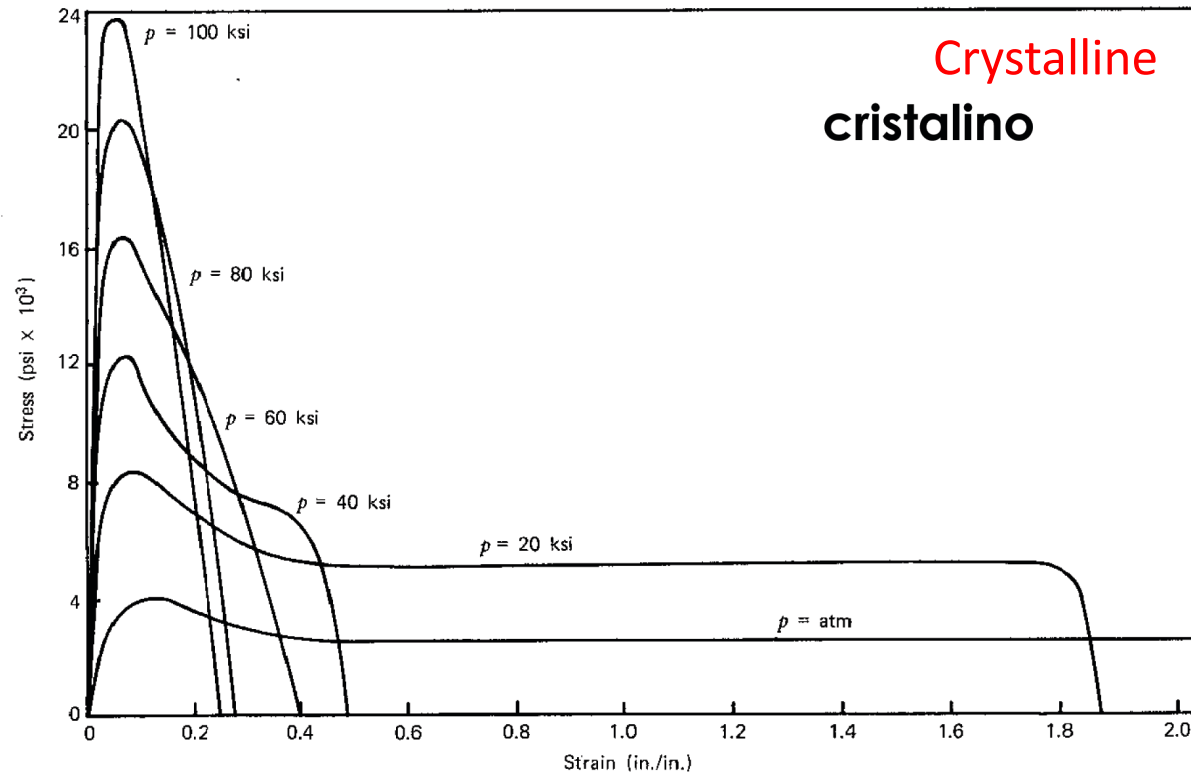


Figure 31 Effect of pressure on tensile stress–strain curves of polypropylene.

Radiation

Initial effects: excitation and ionization

Subsequent effects: polymer dependent

- i) C-C bond scission (M decreases)*
- ii) Formation of cross-links (from radicals in neighbouring chains) (M increases)*
- iii) Change of crystallinity (creation of defects)*

Crystallinity

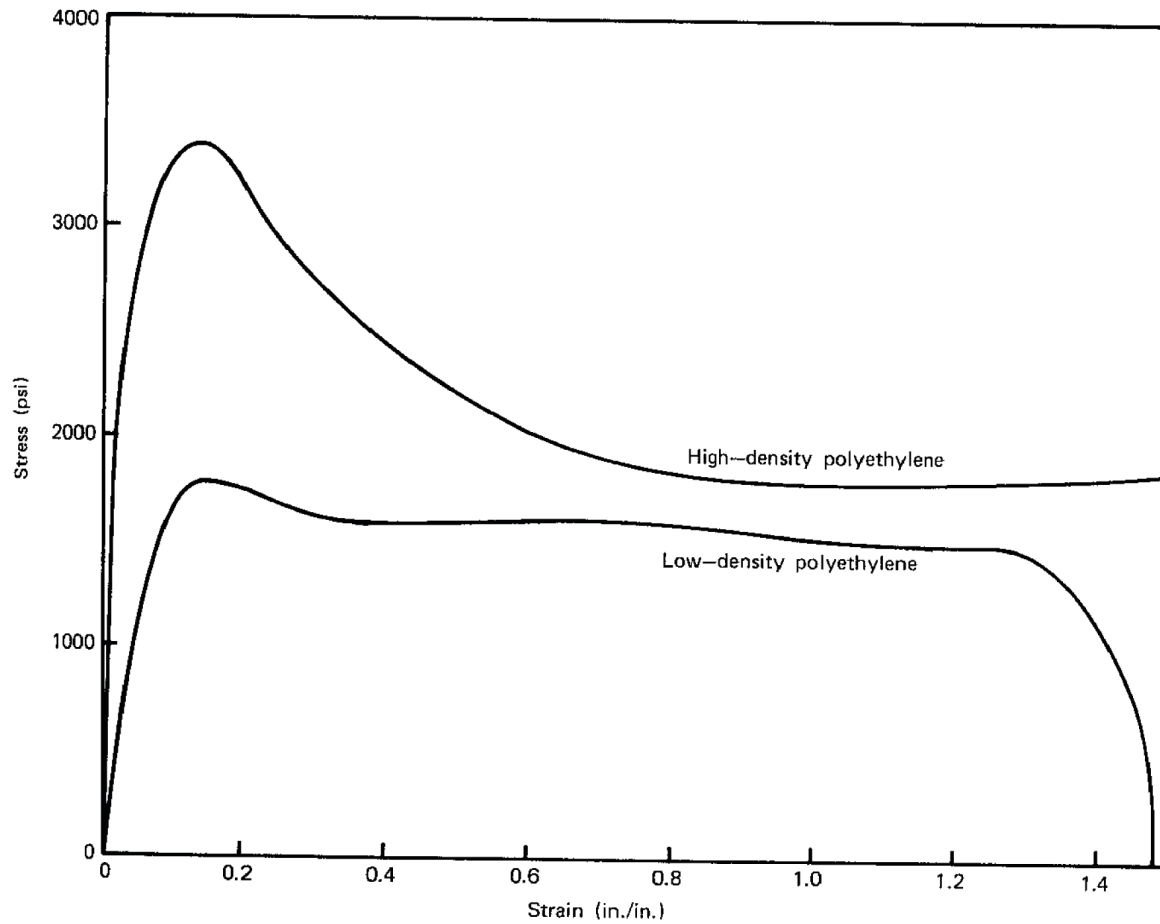


Figure 34 Tensile stress-strain curves of low-density and high-density polyethylene.

Ultimate properties: Resistance to impact

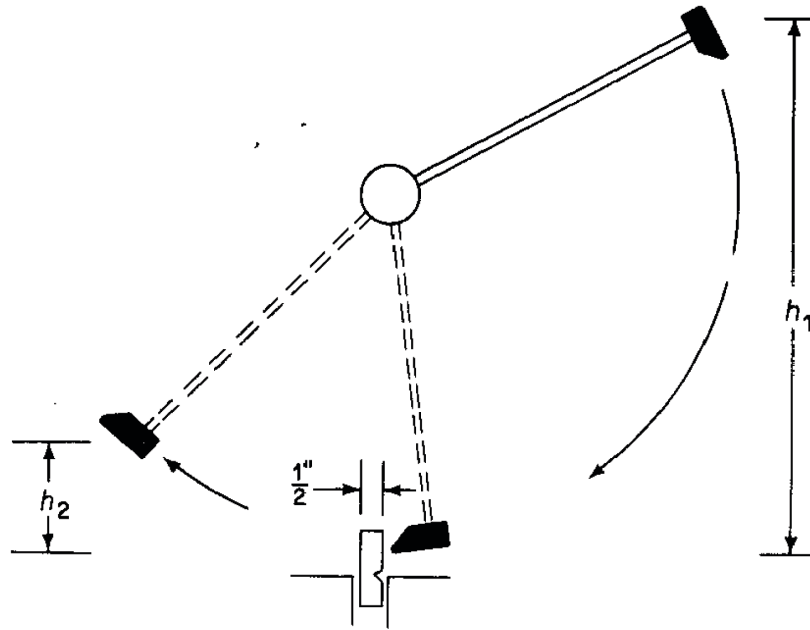


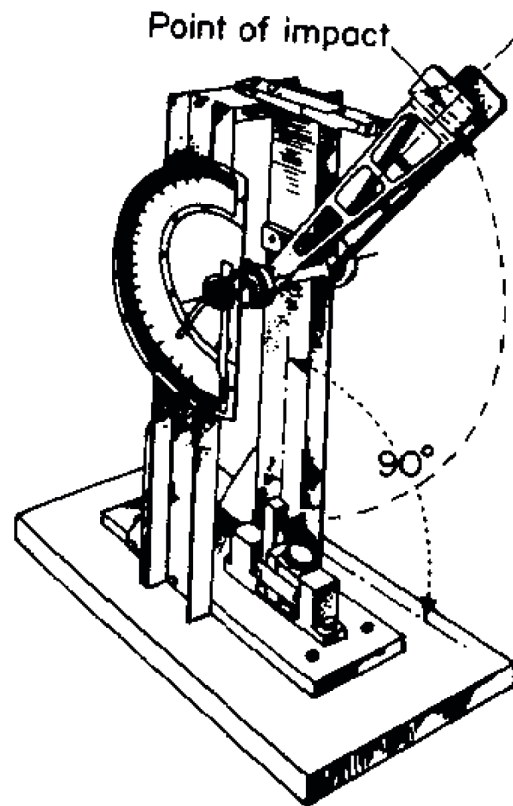
FIGURE 9-4

Impact testing (notched Izod). Original and final heights h_1 and h_2 of hammer determine strength of sample of thickness d held in vise.

$$\text{Impact strength} = (h_1 - h_2) \frac{W}{d}$$

Total energy to cause rupture, or toughness/tenacidade,
i.e. the area under the stress-strain curve

Resistance to impact



(d)

Tear test (teste de rasgão)

Teste de rasgão: “trousers tear test”

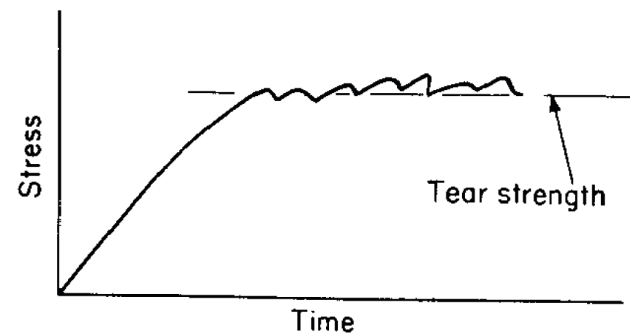


FIGURE 9-3
Typical trousers tear test diagram.

Cellophane example: stress needed to rupture a film **vs** the stress needed to propagate a tear

References

- “Principles of Polymer Systems”, 2ed., F. Rodriguez, McGraw-Hill-Int. Student Ed., 1983
- “Introduction to Polymer Science and Technology: An SPE Textbook”, H.S. Kaufman e J. J. Falcetta, eds., John Wiley & Sons, 1977.
- “Polymers: Chemistry & Physics of Modern Materials”, 2. Ed., J.M.G. Cowie, Nelson Thornes Ltd, 2001.