School of Engineering
Institute of Materials
Laboratory of Macromolecular
and Organic Materials

Polymer Science 2025/26

Exercise 11

1. The true stress, σ_r, as a function of the strain, ε, for a certain polymer is given by

$$\sigma_r = \sigma_0 \varepsilon^b (1 + \varepsilon^{-0.99b})$$

   where σ_o = 100 MPa and b = 5. Determine the strain at which necking begins during a tensile test on this polymer? Is this necking process stable or unstable? Briefly explain your reasoning.

   Tip 1: it is much easier to solve this problem graphically, rather than analytically. You can use tools such as Excel, Origin, etc.

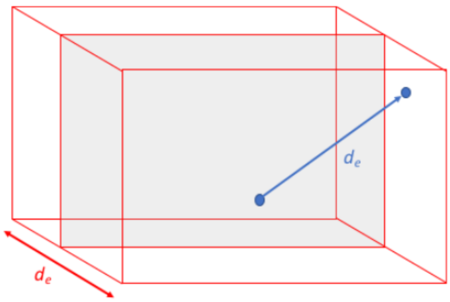
   Tip 2: use the Considère criterion (Slide 320). For the required differentiation of σ_r with respect to ε (or equivalently λ), use the product rule.

2. The yield strength of a polyethylene (PE) sample tested at 23 °C and at 0.001 s^{-1} is 30 MPa in uniaxial tension and 31.5 MPa in uniaxial compression. Assuming that the yield strength, σ_y, is a linear function of the hydrostatic pressure p, calculate the yield strength in uniaxial tension when an external hydrostatic pressure of 500 MPa is applied.

   Note: the external pressure is added to the material's existing stress state.

   Tip: hydrostatic pressure is compressive in nature, so it is negative for tensile deformation and positive for compression.

3. Consider a cuboid volume of an isotropic entangled polymer with an area equal to 1 and a thickness of d_e. How many entanglement points are in this volume according to the model of the entanglement network?



(i) Two entanglement points linked by a subchain are separated by a vector $\vec{d}_e$ whose root mean square length is equal to d_e. How many of these sub-chains pass through the inner surface unit of the polymer?

(ii) If U is the energy required to break a subchain and γ is the van der Waals surface energy of the polymer, what is the effective surface energy, Γ, when creating the voids of a craze at temperatures $T << T_g$?

(iii) Sketch the surface stretching mechanism for craze widening.

(iv) The rate of movement of the polymer from the heads of the voids to the bases of the craze fibrils and therefore the craze expansion rate, v, are proportional to ∇P^n, where n is an empirical constant and

$$\nabla P \approx \frac{P_2 - P_1}{D_0} = \frac{\sigma - \frac{4\Gamma}{D_0}}{D_0}$$

is the pressure gradient that drives the polymer from the head of the voids towards the base of the fibrils. σ is the applied stress, and D_o is the spacing of the fibrils. Show that the maximum craze widening speed for a given value of σ is obtained when

$$D_0 = \frac{8\Gamma}{\sigma}$$

and therefore, that the critical stress for widening of a craze at a speed v is

$$\sigma_c \propto \Gamma^{1/2}\, v^{1/2n}$$

(v) Explain why polystyrene (PS) shows a much more fragile behavior than polycarbonate (PC), when deformed in tension.

(vi) Is the craze formation via a disentanglement mechanism rather favored by (i) a low molar mass, (ii) a high strain rate, or (iii) high temperature? Explain!

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