

## Polymer Science 2024/25

## Exercise 10 – Solution

1. The true stress,  $\sigma_r$ , as a function of the strain,  $\varepsilon$ , for a certain polymer is given by

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

where  $\sigma_0 = 100$  MPa and  $b = 5$ . Determine the strain at which necking begins during a simple tensile test on this polymer? Is this necking process stable or unstable? Briefly explain your reasoning.

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

**Necking begins when the material experiences plastic instability, which occurs when strain localizes in a region of the sample, leading to a decrease in stress. The onset of necking is typically identified when the slope of the nominal stress-strain curve becomes zero, indicating that the material is unable to resist further deformation in a localized region (see Slide 304).**

$$\frac{d\sigma}{d\varepsilon} = \frac{d\sigma}{d\lambda} = 0$$

**where  $\lambda = 1 + \varepsilon$ . Since nominal and true stress are related via  $\sigma = \frac{\sigma_r}{\lambda}$ , we can re-write the derivative of the nominal stress with respect to strain, and applying the quotient rule to differentiate  $\sigma = \frac{\sigma_r}{\lambda}$ :**

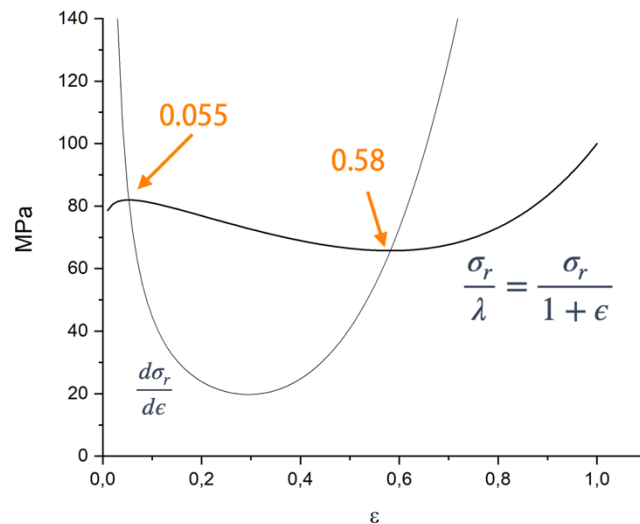
$$\frac{d\sigma}{d\lambda} = \frac{d}{d\lambda} \left( \frac{\sigma_r}{\lambda} \right) = \frac{\lambda \cdot \frac{d\sigma_r}{d\lambda} - \sigma_r \cdot 1}{\lambda^2} = \frac{1}{\lambda} \frac{d\sigma_r}{d\lambda} - \frac{\sigma_r}{\lambda^2}$$

**Because necking begins when the derivative  $d\sigma/d\lambda$  becomes zero, the criterion for plastic instability is:**

$$\frac{d\sigma_r}{d\lambda} = \frac{\sigma_r}{\lambda}$$

Graphically, we can just juxtapose the left-hand and the right-hand side and find where they intersect. For differentiation of the left-hand side, we use the product rule:

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



So, for  $\varepsilon > 5.5\%$ ,  $d\sigma/d\varepsilon$  becomes negative. Thus, a region which is slightly more distorted than the rest of the sample can continue to deform at a relatively low nominal stress. This stress decreases as the deformation progresses. There is therefore an instability and the appearance of a neck.

If the deformation is sufficiently large, it is possible that  $d\sigma/d\varepsilon$  becomes positive again. In the example above,  $d\sigma/d\varepsilon$  is positive for  $\varepsilon > 58\%$ . From  $\varepsilon = 58\%$ , it is easier to deform the regions surrounding the neck than the neck itself, and the neck becomes stable (otherwise it would continue to deform until it breaks, as in some metals).

- The yield strength of a polyethylene (PE) sample tested at 23 °C and at 0.001 s<sup>-1</sup> is 30 MPa in uniaxial tension and 31.5 Mpa in uniaxial compression. Assuming that the yield strength,  $\sigma_y$ , 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.

Let us assume a linear dependence between yield stress,  $\sigma_y$ , and the hydrostatic pressure  $p$  (see Slide 308):

$$\sigma_y = \sigma_{y0} + \mu p$$

where  $\sigma_{y0}$  is the yield strength under zero hydrostatic pressure and  $\mu$  is a material constant that determines the sensitivity of the yield stress to hydrostatic pressure. The hydrostatic pressure is defined as the average of the principal stresses:

$$p = \frac{\sigma_1 + \sigma_2 + \sigma_3}{3}$$

In uniaxial tension, there is no stress in the lateral directions, and the only nonzero stress is  $\sigma_1$  : thus the hydrostatic pressure at yield is:

$$p_{\text{tension}} = \frac{\sigma_1}{3}$$

At yield,  $\sigma_1 = \sigma_y$ , and since tension produces a negative hydrostatic pressure, we have

$$p_{\text{tension}} = -\frac{\sigma_y}{3} = -10 \text{ MPa}$$

In uniaxial compression, the hydrostatic pressure in compression is positive:

$$p_{\text{compression}} = \frac{\sigma_y}{3} = 10.5 \text{ MPa}$$

This allows to determine the material constants  $\mu$  and  $\sigma_{y0}$ :

$$30 \text{ MPa} = \sigma_{y0} - \mu \times 10 \text{ MPa}$$

$$31.5 \text{ MPa} = \sigma_{y0} + \mu \times 10.5 \text{ MPa}$$

from which we get  $\mu = 0.073 \text{ MPa}^{-1}$  and  $\sigma_{y0} = 30.73 \text{ MPa}$ . In presence of an external pressure of 500 MPa, the yield strength is accordingly

$$\sigma_1 = \sigma_{y0} - \mu \frac{\sigma_1}{3} + \mu \times 500 \text{ MPa}$$

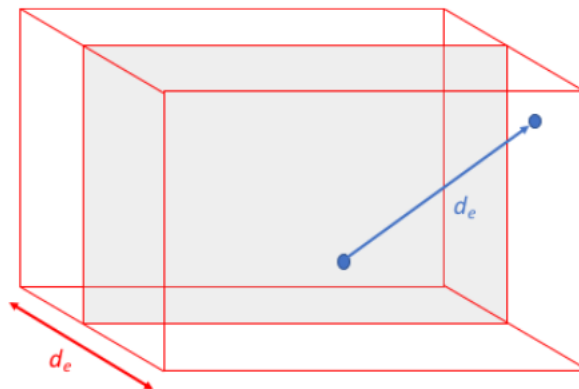
$$\sigma_1 = \frac{\sigma_{y0} + \mu \times 500 \text{ MPa}}{1 + \mu/3} = \frac{30.73 + 0.073 \times 500 \text{ MPa}}{1 + 0.073/3} = 65.63 \text{ MPa}$$

Note that here we are solving for the yield strength under pressure, which considers both the intrinsic hydrostatic pressure generated by the tensile stress state and the external applied pressure.

1. 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?

As a reminder, a cuboid is a rectangular solid figure that has six rectangular faces. The volume of our cuboid is therefore  $d_e$ . In terms of the entanglement network model for polymers, the entanglement density,  $N_e$ , is defined as the number of entanglement points per unit volume of the polymer. Thus, the total number of entanglements is given by the product of the entanglement density and the volume, i.e. for our cuboid it is simply given by  $N_e d_e$ .

- (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?



Take an entanglement point that is inside the box drawn above. As the vector  $\vec{d}_e$  can take any direction, the probability that it intersects the gray plane is 0.5 (half of the subchains will cross the plane due to the random orientation of the vector  $\vec{d}_e$ ). If the surface of the gray plane is 1, there are  $N_e d_e$  entanglement points in the box and only half of the subchains linked to these entanglement points will pass through the gray plane. Therefore  $N_e d_e / 2$  subchains pass through the unit area.

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

**$U$  must be shared between the two surfaces that we create. So**

$$\Gamma = \gamma + \frac{d_e N_e U}{4}$$

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

**See the notes / slide 331**

- (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  $\nabla P^n$ , 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.  $\sigma$  is the applied stress, and  $D_0$  is the spacing of the fibrils. Show that the maximum craze widening speed for a given value of  $\sigma$  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

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

**The maximum craze widening speed occurs, when the pressure gradient  $\nabla P$  is maximized. Hence, we define the first derivative of  $\nabla P$  with respect to  $D_0$ , using the quotient rule:**

$$\frac{d\nabla P}{dD_0} = \frac{\frac{4\Gamma}{D_0^2}}{D_0} - \frac{\sigma - \frac{4\Gamma}{D_0}}{D_0^2} = 0 \Rightarrow \frac{4\Gamma}{D_0} - \sigma + \frac{4\Gamma}{D_0} = 0 \Rightarrow D_0 = \frac{8\Gamma}{\sigma}$$

**If we substitute  $\frac{8\Gamma}{\sigma}$  for  $D_0$  in the expression for  $\nabla P$ , we get**

$$\nabla P = \frac{\sigma^2}{16\Gamma}$$

$$v \propto \nabla P^n \propto \left(\frac{\sigma^2}{\Gamma}\right)^n \Rightarrow \sigma \propto \Gamma^{1/2} v^{1/2n} \propto \left(\gamma + \frac{N_e d_e U}{4}\right)^{1/2} v^{1/2n}$$

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

The entanglement density,  $N_e$ , in PC is approximately 10 times higher than in PS. This implies that it is more difficult for the PC chains to slide past each other during deformation. So, the stress required to propagate a craze is much higher in PC and it therefore tends to undergo a more ductile behavior, where the polymer deforms plastically through necking rather than forming a craze. (The plasticity threshold is not directly influenced by  $N_e$ , but the formation of a craze becomes less favored compared to macroscopic necking if  $N_e$  is high).

- (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!

The formation of a craze via disentanglement depends on how easily polymer chains can slide past each other or “unwind” from entanglements.

Forced disentanglement is opposed by the friction of the chain against its tube. This friction will increase, if we increase the size of the chains and decrease if we increase the temperature (the mobility of the polymer increases). Since it is a friction, the forces that oppose the disentanglement will decrease as the strain rate is reduced. Thus, the formation of crazes by disentanglement is favored at low molar mass and a high temperature, but disfavored by a high strain rate.