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Polymer Science 2025/26

Course Notes of Chapter 4.3

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1. Large Deformation in the Solid State: Plasticity vs. Brittle Rupture

Most plastics are used in their glassy or semi-crystalline solid state, where conformational mobility is strongly restricted and elasticity is dominated by van der Waals interactions. Their behavior at large deformation determines whether a part will fail in a ductile or brittle manner.

Some polymers (HDPE, PC) can undergo large irreversible strains, while still exhibiting a modulus on the order of 1–3 GPa. Others (PS, PMMA) fail after only a few percent strain, often through crazing which leads to brittle facture. **The competition between plastic flow and crazing is governed primarily by entanglement density.**

In structural applications, plasticity is often desired: it dissipates energy, stabilizes cracks by forming a large plastic zone, and predictable stress-strain behavior. Brittle crazing, in contrast, absorbs little energy and promotes crack growth.

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2. Plasticity of Polymers

2.1 General Features

Metals and some ceramics are also capable of plastic deformation, but polymers differ in several fundamental ways (Slide 316):

- **the elastic/plastic transition in polymers is not sharp** because polymer deformation is strongly **viscoelastic** and depends on **time and temperature**.
- **plastic deformation can be partially recovered:** by heating above T_g, the entanglement network regains mobility and the material relaxes towards its undeformed state.
- **all plastic deformation is constrained by chain connectivity:** Polymer segments do not move independently and even very large plastic strains require the coordinated motion, stretching, reorientation, or disentanglement of whole chain segments.

2.2 Plastic Necking and the Role of Entanglements

In a tensile test at constant strain rate, the nominal stress ($\sigma = f/A_o$) rises until a maximum (**yield point**) and then drops as a **neck** forms, i.e. the deformation becomes strongly localized. This geometric instability occurs because plastic deformation is approximately volume-conserving (the yield stress is typically 1–2 orders of magnitude lower than Young's and bulk modulus), so that the nominal stress falls beyond the yield stress.

A convenient way to formalize this geometric instability is through the **Considère construction** (Slide 320). For a material deforming at a constant strain rate, a neck will form when $d\sigma_r/d\lambda = \sigma_r/\lambda$. This condition states: if σ_r cannot increase as fast as the material is being stretched, uniform deformation becomes unstable and localization (necking) begins.

For some glassy materials, an intrinsic yield drop is observed at which the true stress ($\sigma_r = f/A$) decreases. This is related to ageing effects, when the sample is kept for some time below T_g (Slide 323), during which the polymer gradually densifies and its free volume decreases, which increases the yield stress. However, once deformation begins, the local strain softens the material because plastic flow creates free volume faster than it can relax. The sudden increase in free volume causes a temporary reduction in the flow stress.

A key observation is that after the neck forms, the true stress rises again at large stretch ratios λ_c. This stabilizes plastic flow and causes the neck to propagate, instead of the sample failing immediately as metals often do. For many amorphous polymers:

$$\lambda_c \propto \sqrt{M_e} \quad . \tag{1}$$

Thus, the maximum extensibility of the entanglement controls plastic stability. Polymers with $M < 2M_e$ cannot stabilize a neck and therefore behave in a brittle manner.

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2.3 General Yield Criteria

Plastic flow in polymers is mostly **shear-controlled** for which criteria like **Von Mises** can be used. Unlike metals, however, polymer yield stress depends strongly on **hydrostatic pressure**:

$$\sigma_y = \sigma_{y0} + \mu p \qquad \text{with} \qquad p = -\frac{\sigma_1 + \sigma_2 + \sigma_3}{3} \quad . \tag{2}$$

Here, the negative sign ensures that tensile loading corresponds to negative hydrostatic pressure. Compression (positive pressure) therefore raises the yield stress by suppressing local cavitation or conformational changes (much different for elastomers, where the local shear barriers are zero). This effect is particularly pronounced in polymers because their compression modulus, K, is about two orders of magnitude lower than for most metals.

2.4 Molecular Models for Yielding in Glassy Polymers

Several phenomenological models capture the strong temperature and rate dependence of yield:

- **Eyring model**: plastic flow is activated over an enthalpy barrier reduced by stress (Slide 328). For a constant temperature, it predicts that

$$\sigma_y = A + B \ln \dot{\varepsilon} \quad . \tag{3}$$

  Plastic deformation is associated with an activation volume V^* that typically involves several repeat units. Secondary relaxations play therefore a major role in providing local mobility. While **conformational relaxations involving a limited number of bonds can subsist below T_g**, even when the strain is small, their relaxations become "frozen" at lower temperatures indicating distinct plasticity regimes below and above this temperature. **The activation of movements that correspond to secondary transitions is therefore very important for plasticity, which facilitate conformational changes that have a 'lubricating' effect** (Slides 329–331).

- **Argon model**: similar to Eyring but attributes barriers to **intermolecular elastic constraints** around a sheared segment (Slide 332).

- **Robertson model**: the barrier is of **intramolecular** nature (*trans–cis* rotations) and connected to WLF viscosity (Slide 333).

These models successfully reproduce trends but remain phenomenological. They do not yet incorporate entanglements or local relaxation spectra explicitly.

2.5 Yield of Semi-Crystalline Polymers

In semi-crystalline polymers, especially above T_g:

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- Yielding often begins by **lamellar slip** and the nucleation of a **dislocation** (see model of Young).
- Yield stress increases with **lamellar thickness** and **crystallinity**.
- At very large strains, the lamellae rotate and align, causing strong strain hardening and self-reinforcement which is not observed in glassy amorphous polymers.

Highly oriented fibers behave then as highly brittle in tension (no active slip systems remain), but can still show significant plastic deformation in compression thanks to twinning and slip bands. Unlike a glass or carbon fiber, in general, a polymer fiber does not break in compression. Indeed, organic fibers can absorb a lot of energy, hence their interest in applications such as bulletproof vests or impact resistant composites.

3. Crazing and Brittle Failure

3.1 Phenomenology of Crazes

Crazes are **localized, fibrillar microvoids** that form **only in tension**. They appear like small cracks but carry **significant load** because their faces are bridged by polymer nano-fibrils. A craze contains roughly 50% void volume (Slide 345).

Key points:

- craze formation **requires local plasticity**, but **macroscopic behavior becomes brittle** because the deformation is highly localized.
- transparency and solvent resistance decrease dramatically.
- crazes nucleate around local stress concentrators and propagate perpendicular to the tensile axis.

Because cavitation (void formation) requires **negative hydrostatic pressure**, crazing is suppressed under compression and absent in pure shear since cavitation requires negative hydrostatic pressure. A typical craze criterion is:

$$\varepsilon_c = A + \frac{B}{p} \quad , \tag{4}$$

where higher (more negative) hydrostatic tension promotes cavitation, i.e. ε_c gets reduced.

3.2 How Crazes Grow: Surface Drawing Model

Crazes can form and propagate only if the local stress concentrations remain high. To this end, it is necessary that the fibrillar regions already formed extend in the direction of the pull. **The stress at the head of the craze and its propagation speed are therefore controlled by the speed of craze expansion**.

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The propagation of a craze depends on the **pressure at the fibril base** determined by the capillary pressure at the void surfaces and the **ability to flow from the void head to the fibril base** (Slide 349). A maximum propagation rate exists at a characteristic fibril spacing D_0, where it can be shown that the stress needed to keep a craze propagating increases with surface energy (void formation requires new surface creation):

$$\sigma_c \propto \sqrt{\Gamma\, v^{1/n}} \quad . \tag{5}$$

To form the fibrils, the polymer chains must be extended to about $\lambda_{\max}$. This can occur by two microscopic mechanisms:

- **chain scission**: dominant in highly glassy, immobile conditions (low temperatures, high strain rate)
- **disentanglement**: possible when local mobility is higher (temperatures just below T_g, low strain rates, or comparably low molar masses)

The fibrils typically deform to $\lambda_{\max}$, implying that stable crazes require an intact entanglement network. If the entanglement density N_e is small, fewer entanglements must be broken to create voids:

$$\Gamma \propto d_e N_e U \quad . \tag{6}$$

Thus, polymers with low entanglement density (PS) easily undergo crazing, whereas for polymers with high entanglement density (PC), crazing is suppressed (necking is then favored) (Slide 352).

The same is true for the plastic deformation of semicrystalline polymers below T_g: highly entangled polymers (PET, PEEK) hardly craze. Above T_g, voids may form at amorphous/crystalline boundaries due to modulus mismatch. These "fibrillar deformations" facilitate the local plastic deformation of lamellae and are therefore often part of ductile plastic flow, i.e. they do not necessarily imply brittleness.

3.3 Crazes and Fracture

Crazes dramatically affect the fracture toughness. A single craze at the crack tip can still carry load. The critical mode-I stress intensity scales roughly with the force to break a single chain (Slide 357). **High-entanglement polymers (PC) therefore show much higher fracture toughness compared to low-entanglement polymers (PS), even when both craze.**

However, if the effective value of N_e is too high, as is the case of highly crosslinked polymers, no crazes at the crack tip are observed. Because $\lambda_{\max}$ also becomes very low, they cannot plastically deform and behave brittle. Therefore, thermosets (highly crosslinked materials) are, in general, very fragile.

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Rubber toughening: An isolated craze which forms at the head of the crack is not very dissipative because the plasticity is very localized. However, **the cracking resistance can be increased significantly, if the formation of multiple crazes or combinations of crazes and plasticity are favored, even in the most fragile polymers such as PS or PMMA**. Added nodules of a rubber or elastomeric particles serve as stress concentrators under tension. Thus, numerous crazes appear at relatively low overall stresses around a crack, leading to higher energy dissipation than in the presence of a single craze. In addition, the formation of voids associated with crazes as well as in elastomer nodules promote classical plasticity by relaxing three-dimensional stresses.

As the examples on Slides 362 show, this approach is not only very effective in glassy amorphous polymers but also in rather fragile semi-crystalline polymers like PP. It is, however, necessary that the size and spatial dispersion of the elastomer particles must be well controlled and the elastomer content is not too high so as to not reduce Young's modulus excessively.

4. Summary

- Yielding usually defined as the point where the slope of the stress-train curve becomes zero during the deformation of glassy or semicrystalline polymers. This often results in the formation of a stable neck with a draw ratio which is a materials parameter, characteristic of the entanglement network.
- σ_y decreases roughly linearly with T and decreasing deformation rate under certain conditions, in accordance with simple Eyring rate theory. However, the yield behaviour also strongly influenced by the presence of sub-T_g relaxations, in some cases providing a link between yielding and molecular structure.
- Semicrystalline polymers modelled in terms of crystallographic slip for $T > T_g$. For a constant degree of crystallinity, σ_y increases with lamellar thickness l. Thus, in general, polymers crystallized at higher temperatures have higher yield stresses.
- Crazes are crack-like defects which appear when certain polymers are tested in tension. The craze surfaces are spanned by highly drawn craze fibrils, which are load bearing. Crazing is nevertheless associated with brittle behaviour.
- Crazes form most readily in low entanglement density polymers. The formation of the craze fibrils requires loss of entanglements: the fewer entanglements there are, the less energy is consumed during fibrillation and the lower the crazing stress.
- The strength of a craze fibril and hence of the craze depends directly on the entanglement density. Low entanglement density polymers show little resistance to crack propagation and are fragile. However, although the energy dissipation due to one craze is small, and hence the toughness, it can be increased greatly by increasing the number of crazes at the crack tip. This is the basis of rubber toughening in PS and in PMMA.

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