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

Polymer Science 2025/26

Exercise 13 – Solutions

1. The least expensive semicrystalline polymers (iPP, HDPE, LDPE) are relatively ductile, but often not rigid enough for engineering applications. Other semicrystalline polymers such as PET, PPS, or PEEK show much higher stiffness and heat resistance and are therefore widely used as engineering materials.

   a) What is the fundamental difference between these two groups of semicrystalline polymers?

   The key difference is the T_g of the amorphous phase:

   - **iPP, HDPE, and LDPE have a T_g well below 0 °C. Their amorphous regions are rubbery at room temperature and contribute very little to overall stiffness. The modulus therefore reflects almost exclusively the crystalline phase, resulting in moderate rigidity often too low for certain technical applications.**
   - **PET, PPS, and PEEK have high T_g (typically > 80–150 °C). Their amorphous regions are glassy at room temperature and therefore stiff. The total modulus is determined by both the glassy amorphous and the crystalline phases, yielding engineering-level rigidity.**

   b) Polyoxymethylene (POM, polyacetal) has a glass transition below 0 °C, yet it behaves as an engineering polymer. Draw its repeating unit and explain why its crystallization behavior compensates for the low T_g.

   POM has the repeating unit –O–CH_2–. It is highly regular, linear, and crystallizes extremely well with very fast crystallization kinetics and high crystallinity. Even though its $T_g \approx -80$ °C is very low, the very high crystallinity (up to ~80%) dominates mechanical behavior. POM has therefore a stiffness (2.5–3.5 GPa) typical of engineering polymers.

2. Polycarbonate (PC) can crystallize, yet in practice it used almost exclusively as a fully amorphous polymer. Why is PC not considered a semicrystalline engineering polymer? Why is PC nevertheless classified as an engineering polymer, unlike inexpensive glassy polymers such as PS and PMMA?

   Tip: revisit the Chapter 5.3.

PC crystallizes extremely slowly under typical processing conditions (extrusion, injection, thermoforming, etc.). Cooling rates are far too fast for significant crystallization, so that the solidified polymer remains fully amorphous.

PC is an engineering polymer because of its remarkable toughness and ductitlity, even in the glassy state. Unlike PS and PMMA, PC undergoes stable shear yielding rather than brittle crazing, has an excellent impact resistance and good thermal stability ($T_g \approx 150$ °C). Thus, PC combines a high T_g with toughness, which very few amorphous polymers provide.

Note: most high T_g semicrystalline engineering polymers crystallize slowly due to their rigid molecular structure (but not Nylons, which can be considered more flexible in that regard).

3. PET has excellent mechanical and barrier properties at low cost.

   a) Why is PET not widely used in injection molding of large-series articles?

   PET crystallizes slowly. For high-throughput injection molding, the mold must cool and solidify parts as rapidly as possible to render manufacturing profitable. If PET is ejected too early:

   - **it continues to crystallize outside the mold, resulting in warpage, distortion, internal stresses.**
   - **post-shrinkage cannot be compensated because no packing pressure is applied outside the mold.**
   - **with $T_g \approx 70$ °C, partially crystalline parts are dimensionally unstable during service or storage.**

   Fast-crystallizing PET grades exist (e.g. Rynite from DuPont), but require nucleating agents (additives that promote the nucleus formation for polymer crystallization) and are more expensive.

   b) Why do these arguments not apply to PET bottles produced by injection stretch blow molding?

PET bottles are produced from a fully amorphous preform. In stretch blow molding, the preform undergoes strong biaxial orientation, which:

- **dramatically increases nucleation density**
- **promotes rapid non-spherulitic crystallization**
- **yields transparent, strain-induced semicrystalline structures suitable for bottles.**

Thus, crystallization is fast enough to support large-scale production.

c) Copolyesters such as PETG (copolymers of terephthalic acid with ethylene glycol and cyclohexane dimethanol) are similar in price to PET. Could PETG substitute PET in all applications?

PETG is a random copolymer, and the incorporation of cyclohexane dimethanol interrupts chain regularity and suppresses crystallization. PETG is therefore fully amorphous and softens at its T_g = 70–80 °C, whereas semicrystalline PET melts at ~260 °C and retains stiffness well above 100 °C. Many PET applications require high heat resistance, dimensional stability above T_g, mechanical stiffness under load, all of which rely on the semicrystalline morphology of PET.

Therefore, PETG cannot replace PET in applications involving elevated temperatures or mechanical loads above ~70 °C. PETG is useful in applications where amorphous clarity and good processability matter (e.g. 3D printing, thermoforming), and where post-crystallization of PET would shrinkage and warping.

4. A manufacturer wants a dimensionally stable, high-heat styrenic material for electrical housings. Which material is more suitable: PPE/HIPS (Noryl-like blends) or SBS? Give a reason.

PPE/HIPS is the more suitable choice.

PPE has a very high T_g (~200–220 °C) but is difficult to melt-process on its own because it degrades at the required temperatures. Since PPE is miscible with the PS phase of HIPS, blending the two lowers the effective T_g to a still high but more manageable value, enabling melt processing while retaining excellent thermal stability.

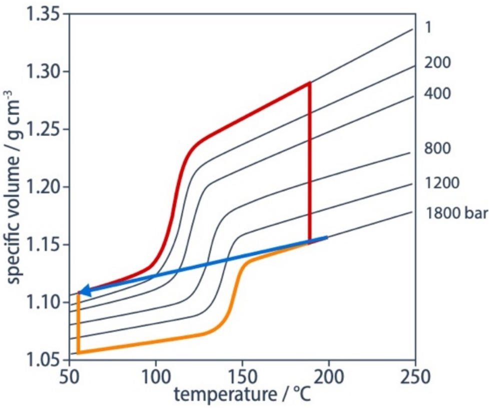
The PPE/PS remains glassy up to ~150 °C (depending on the composition), and the butadiene rubber particles from HIPS provide toughness. The resulting material offers a high heat deflection temperature, stiffness, low thermal expansion, and good processability, all essential for electrical housings.

By contrast, SBS is a styrene-butadiene thermoplastic elastomer with a rubbery midblock. It is soft and elastomeric at room temperature, and its heat resistance is limited by the T_g of the glassy PS end blocks. SBS therefore cannot provide the dimensional stability or heat resistance required for electrical housings.

5. A PVT diagram shows isobars at 1, 200, 400, 800, 1200 and 1800 bar.

a) Does the diagram belong to an amorphous or semicrystalline polymer?

The PVT curves show a volume discontinuity (step) due to crystallization. Amorphous polymers only show a slope change at T_g.



b) The polymer is injected into a closed mold at 200 °C under 1800 bar. At what temperature should the pressure be released to minize shrinkage? What happens if the pressure is released too early? (You can sketch the ideal change in specific volume versus temperature in the diagram above.)

To minimize shrinkage, the pressure should ideally be released gradually during the crystallization and solidification phase (blue line in the diagram).

If the pressure is released too early, the melt undergoes significant volumetric shrinkage (red line), leading to warpage, high internal stresses, surface defects, or possible caviation.

If the pressure is released only after the part has cooled to near the ejection temperature, the material shows some elastic recovery (volume expansion), but the overall shrinkage remains small (orange curve).

In practice, the melt is kept under constant packing pressure until the gate freezes. Once the gate solidifies, no further compensation of shrinakge is possible, and the final shrinkage is determined by the remaining cooling and crystallization inside the moulded part.

c) In real molds, temperature and pressure vary spatially. What consequences does this have for the microstructure of an injection-molded semicrystalline polymer?

Spatial gradients in temperature and flow history produce microstructural heterogeneity:

- **a highly oriented skin layer near the cold mold wall (frozen-in molecular orientation, shish-kebab structures)**
- **a fine spherulitic zone beneath the skin where nucleation is fast**

- **a coarse spherulitic core with slow cooling and low shear.**

This multilayer morphology strongly influences toughness, shrinkage, gloss, and anisotropy.