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Course Notes of Chapter 5

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1. Introduction: Polymer Blends

Polymer blends combine existing polymers to create materials with tailored mechanical, thermal, or barrier properties without the cost or difficulty of synthesizing new polymers. Two key questions determine blend performance:

- **Are the polymers miscible?**

Flory-Huggins theory predicts that **most high-molar-mass polymers are immiscible** because their entropy of mixing is extremely small. Yet, some commercial blends are miscible (e.g. PS/PPO, PVC/PCL) due to favorable **specific intermolecular interactions** such as hydrogen bonding or π-π stacking (Slides 382 and 383).

- **If immiscible, what morphology forms during processing?**

Immiscible blends phase-separate. The resulting morphology (droplets, fibrils, co-continuous structures) depends on thermodynamics (spinodal/binodal), processing history (shear, cooling rate), interfacial tension, and viscosity ratio between phases. The morphology strongly influences mechanical properties such as toughness.

Copolymers behave differently because chemically distinct blocks are covalently connected. **Random copolymers are always homogeneous**, **block copolymers undergo microphase separation** and form ordered nanoscale structures (lamellae, cylinders, spheres), making them excellent compatibilizers, tougheners, and functional nanomaterials.

2. Thermodynamics of Polymer Mixing

A blend is miscible if the Gibbs free energy of mixing is negative:

$$\Delta G_\mathrm{m} = \Delta H_\mathrm{m} - T\Delta S_\mathrm{m} < 0 \quad , \tag{1}$$

where T is temperature, ΔH_m is the (molar) enthalpy change during mixing, and ΔS_m is the (molar) entropy change. For mixtures based on small molecules, the entropy term strongly favors mixing. **For polymers, however, the entropy change is very small**. Therefore, **miscibility is governed primarily by enthalpy**.

- **the Mixing Entropy**

Using the Flory-Huggins lattice model, the entropy of mixing per lattice site is:

$$\Delta S_\mathrm{m} \propto \frac{\phi_1}{N_1}\ln(\phi_1) + \frac{\phi_2}{N_2}\ln(\phi_2) \tag{2}$$

with volume fractions ϕ_i and degrees of polymerization N_i. For polymers, $N_i \gg 1$, so both terms become very small. Thus, entropy cannot overcome an unfavorable enthalpy, which is why most polymer blends are immiscible.

- **the Mixing Enthalpy**

Flory-Huggins theory evaluates the enthalpy based on pairwise contact energies u_ij. The mixing enthalpy per lattice site is:

$$\Delta H_\mathrm{m} = \frac{z}{2}\phi_1\phi_2(2u_{12} - u_{11} - u_{22}) \quad , \tag{3}$$

where z is the coordination number and the factor ½ avoids double counting the pair interactions. The **Flory-Huggins interaction parameter** χ is defined as:

$$\chi = \frac{z}{2}\frac{(2u_{12} - u_{11} - u_{22})}{\mathrm{k}T} \quad . \tag{4}$$

Here, χ is normalized with respect to kT in which case it becomes a dimensionless quantity. χ expresses how unfavorable “unlike” contacts are relative to like-like contacts. **A positive χ increases ΔG_m and promotes immiscibility.**

An experimentally accessible estimate of χ can be obtained using solubility parameters. For a pure substance, the molar cohesive energy is obtained by summing all pairwise interactions in one mole:

$$E_\mathrm{coh}^{ii} = -\frac{z}{2}\mathrm{N_A}u_{ii} \quad \rightarrow \quad u_{ii} = -\frac{2}{z\mathrm{N_A}}E_\mathrm{coh}^{ii} \,. \tag{5}$$

By convention, u_{ii} is taken negative for attractive interactions. Insertion into Equation (4) gives:

$$\chi = \frac{1}{\mathrm{k}T\mathrm{N_A}}\left(-2E_{\mathrm{coh}}^{12} + E_{\mathrm{coh}}^{11} + E_{\mathrm{coh}}^{22}\right) = \frac{1}{\mathrm{R}T}\left(E_{\mathrm{coh}}^{11} + E_{\mathrm{coh}}^{22} - 2E_{\mathrm{coh}}^{12}\right) \quad . \tag{6}$$

A standard approximation for the interaction between dissimilar sites is based on their geometric mean:

$$E_{\mathrm{coh}}^{12} \approx \sqrt{E_{\mathrm{coh}}^{11} E_{\mathrm{coh}}^{22}} \quad . \tag{7}$$

Using the definition for the solubility parameter (see Slide 130):

$$\chi = \frac{1}{RT}\left(E_{\mathrm{coh}}^{11} + E_{\mathrm{coh}}^{22} - 2\sqrt{E_{\mathrm{coh}}^{11} E_{\mathrm{coh}}^{22}}\right) = \frac{1}{RT}\left(\sqrt{E_{\mathrm{coh}}^{11}} - \sqrt{E_{\mathrm{coh}}^{22}}\right)^2 = \frac{V_0}{RT}(\delta_1 - \delta_2)^2 \quad . \tag{8}$$

- **the full Flory-Huggins Expression**

For a polymer blend, the Flory-Huggins equation is thus:

$$\Delta G_{\mathrm{m}} = \mathrm{k}T\left(\frac{\phi_1}{N_1}\ln(\phi_1) + \frac{\phi_2}{N_2}\ln(\phi_2) + \chi\phi_1\phi_2\right) \quad , \tag{9}$$

This result implies that the entropic contribution becomes negligible for high N_1 and N_2. Since χ is usually positive, ΔG_{m} should be positive for binary mixtures of high molecular weight polymers. **This implies that a homogeneous mixture between two polymers should always be thermodynamically unstable with respect to a macroscopically phase separated state.**

However, the Flory-Huggins model relies on many simplifications, such as the assumption of ideal chains (we do not consider the effect of the solvent on their conformations) with a constant volume and concentration of segments. More importantly, **miscibility may arise when new favorable interactions, especially specific intermolecular interactions, exist only in the mixture:**

- π-π interactions of benzene units. Example: PS/PPE (PPE: poly(phenylene ether) or PPO™)
- Hydrogen bonds. Example: PVC/PCL (PCL: poly(ε-caprolactone))
- Acid-base interactions
- Ionic interactions

These blends allow tuning T_{g} or modulus while maintaining transparency.

3. Immiscible Polymer Blends

Unlike a homogeneous system, a mixture or a block copolymer separated into two different phases will show two T_{g} as well as very inhomogeneous thermomechanical properties at the local level, which is essential for impact reinforcement or "rubber toughening" (see Chapter 4.3), and for the design of thermoplastic materials.

The morphology, that is, the way in which variations in properties are distributed in space, is also very important for the synergy between the properties of the different phases: gluing a block of an elastomer to a block of a glassy polymer will not have the same effect as dispersing the elastomer in the glassy polymer on a micrometer length scale.

3.1 Phase Diagrams and Phase Separation

In general, phase separation is quantified using a phase diagram, which allows to estimate the proportions and compositions of different phases present in a mixture at equilibrium. From Flory-Huggins theory, two curves are predicted:

- **binodal curve**: the two phases coexist (common tangent condition)
- **spinodal curve**: where $\Delta G_{\mathrm{m}}'' = 0$ marks the onset of immediate phase separation

Two mechanisms of phase separation are associated:

- **nucleation and growth** in the metastable region (between binodal and spinodal) associated with an activation barrier.
- **spinodal decomposition**: immediate phase separation, no activation barrier in the unstable region (inside the spinodal).

3.2 Morphology of Immiscible Mixtures

In practice, blends are usually processed in the melt (extrusion, mixing). The final morphology depends on:

- viscosity ratio of matrix and dispersed phase: the less viscous component is easy to deform and controls whether droplets, fibrils, or co-continuous structures form
- interfacial tension, which promotes coalescence.
- applied shear
- cooling rate

The low mobility of polymers leads to kinetically trapped morphologies, typically micron-scale dispersed droplets (Slide 379). Compatibilizers are used to prevent droplet growth.

Blends often coarsen (droplets grow) unless the interface is stabilized. Strategies in this regard include:

- block copolymers as compatibilizers (one block in each phase)

- reactive compatibilization (e.g. PA6 reacting with maleic-anhydride grafted PP)
- emulsion-polymerized rubber particles (used in PS and PMMA toughening)

These methods increase interfacial adhesion and prevent domain coalescence.

4. Copolymers

Random or “statistical” copolymers are homogeneous on the molecular scale because different monomers are covalently connected in random order along the chain. Their T_g lies between the T_g of the respective homopolymers. They are used to improve toughness, suppress crystallization (e.g. EPR, EPDM), or to tune processability (e.g. SAN).

Many toughened plastics (e.g. ABS) are built from random copolymers and rubber particles.

- random or "statistical" copolymers
- block copolymers (diblock or multiblock, linear or grafted).

By contrast, **block copolymers behave self-organize into periodic nanostructures like lamellae, cylinders, or spheres.** The final morphology depends on block volume fractions and χN. Applications include thermoplastic elastomers (TPEs) such as SBS (Slide X), their use as compatibilizers, templates for nanostructures, and functional surfaces and coatings.

4. Summary

- Polymer blends often phase separate because mixing entropy is extremely small.
- Miscibility requires favorable enthalpic interactions ($\chi < 0$).
- Phase diagrams reveal regions of stability (single phase), metastability, or instability.
- Morphology in immiscible blends is mostly determined by processing, not equilibrium.
- Compatibilization (block copolymers or reactive chemistry) is essential for stable morphologies.
- Block copolymers form ordered nanoscale structures due to microphase separation.