Lecture 9.

Theme. The structure of crystalline and amorphous polymers. Supramolecular structures of crystalline and amorphous polymers. Three physical states of amorphous polymers.

Aim: generate the following learning outcomes:
- to distinguish the types and methods of supramolecular organization of macromolecules;
- - to identify conditions for the formation of the crystalline structure of polymers.
- represent thermomechanical curves for amorphous polymers;

Purpose:

To understand the **molecular and supramolecular structures** of crystalline and amorphous polymers and to explore the **three physical states** of amorphous polymers and their relation to polymer properties.

Lecture content:
Structure and basic physical properties of polymer bodies.
Features of the molecular structure of polymers and principles of packaging of macromolecules.
Amorphous and crystalline polymers.
Conditions necessary for polymer crystallization. Crystallization temperature and melting point.
Structure and supramolecular organization of crystalline polymers. Differences and similarities in the structural organization of crystalline and amorphous polymers.
Properties of amorphous polymers. Three physical states.
Thermomechanical curves of amorphous polymers.

Main Questions:

1. What are the structural differences between crystalline and amorphous polymers?

2. What is meant by supramolecular structure in polymers?
3. How are crystalline and amorphous regions organized on the macromolecular scale?
4. What are the three physical states of amorphous polymers?
5. How does the degree of crystallinity affect polymer properties?

Key Theses:

1. Crystalline Polymers

- **Crystalline polymers** have **regular, ordered arrangements** of polymer chains in certain regions, forming **crystallites**.
- Crystallization occurs when polymer chains **fold or pack closely**, forming **lamellae**, which further aggregate into **spherulites**.

Features:

- High density and mechanical strength.
- Sharp melting temperature (Tm).
- Limited chain mobility.
- Example: **Polyethylene (PE), Polypropylene (PP)**.

Crystalline structure characteristics:

- Chains may adopt **extended or folded conformations**.
- **Crystallinity is never 100%** in polymers; real materials are **semi-crystalline**, with amorphous regions between crystallites.

2. Amorphous Polymers

- **Amorphous polymers** lack long-range order; chains are arranged **randomly** and entangled.
- They do not exhibit a sharp melting point but have a **glass transition temperature (Tg)**.

Characteristics:

- Lower density than crystalline polymers.
- Flexible chains in rubbery or molten states.
- Transparent in many cases due to lack of crystalline domains.
- Examples: **Polystyrene (PS), Poly(methyl methacrylate) (PMMA)**.

3. Supramolecular Structures of Polymers

- **Supramolecular structure** refers to the **organization of polymer chains beyond the molecular scale**, including crystallites, amorphous regions, and entanglements.

Crystalline polymers:

- Composed of **crystallites** (ordered regions) embedded in an **amorphous matrix**.
- Lamellar thickness and spherulite size determine mechanical and optical properties.

Amorphous polymers:

- Chains form **random coils** or loosely entangled networks.
- May exhibit **temporary physical cross-links** via entanglements or intermolecular interactions.

4. Three Physical States of Amorphous Polymers

1. **Glassy state (T < Tg):**
   - Chains are frozen in a rigid, brittle state.
   - Polymers behave like solids with high mechanical strength but low flexibility.
2. **Rubbery state (T > Tg but below Tm for semi-crystalline polymers):**
   - Chains have rotational mobility and can stretch elastically.
   - Polymers exhibit **entropy-driven elasticity**.
   - Examples: natural rubber, silicone elastomers.
3. **Viscous (melt) state (T >> Tg):**
   - Chains gain sufficient mobility to flow like a viscous liquid.
   - Enables processing methods such as extrusion and injection molding.

Transition temperatures:

- **Glass transition temperature (Tg):** marks glassy → rubbery transition.
- **Melting temperature (Tm):** marks crystalline → melt transition in semi-crystalline polymers.

5. Importance of Crystalline and Amorphous Structures

- **Mechanical properties:** Higher crystallinity → higher strength, rigidity, and chemical resistance.

- **Optical properties:** Amorphous polymers tend to be transparent; crystallinity causes opacity.
- **Thermal properties:** Crystalline domains define melting behavior; amorphous regions define Tg.
- **Processing:** Chain mobility in amorphous regions facilitates shaping; crystallinity determines final structural stability.

Control Questions:

1. What is the difference between crystalline and amorphous polymers at the molecular level?
2. Define supramolecular structure in polymers.
3. What are crystallites and spherulites?
4. Name for which polymers the transition to a crystalline state is not possible under any external conditions.
5. Name the factors on which the kinetics of crystallization depends.
6. Name the phase states in which polymers can be located.
7. What are the three physical states of amorphous polymers?
8. How does the glass transition temperature (Tg) differ from the melting temperature (Tm)?
9. How does the degree of crystallinity affect mechanical and optical properties?
10. Give examples of semi-crystalline and fully amorphous polymers.
11. List the main differences between the thermomechanical curve of an amorphous polymer and a similar curve of a low molecular weight amorphous/crystalline substance.

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