Lecture 11.

Theme. Mechanical properties of polymers in glassy and crystalline states. The phenomenon of forced elasticity

Aim: generate the following learning outcomes:
- to characterize the polymer in a glassy state.

Purpose:

To understand the **mechanical behavior of polymers** in glassy and crystalline states, and to study the **phenomenon of forced elasticity**, which occurs under applied stress and contributes to polymer deformation and recovery.

Lecture content:
Glassy state. Features of polymer glasses.
Forced elasticity and stretching isotherms. The mechanism of forced elastic deformation. The limit of forced elasticity.
The fragility of polymers.

Main Questions:

1. What are the mechanical properties of polymers in the glassy state?
2. How do crystalline regions influence mechanical behavior?
3. What is forced elasticity and under what conditions does it occur?
4. How are mechanical properties related to polymer structure, configuration, and conformation?
5. How does temperature affect mechanical behavior in glassy and crystalline polymers?

Key Theses:

1. Mechanical Properties of Polymers in Glassy State

- Occurs **below Tg** for amorphous polymers or **below Tm** for crystalline regions.
- **Chains have very limited mobility**, so deformation is mostly **elastic** but **brittle**.

Characteristics:

- High **modulus of elasticity** (stiffness).
- Low **elongation at break**.
- Fracture occurs **without significant plastic deformation**.
- Example: **Polystyrene (PS), PMMA below Tg**.

Factors affecting glassy-state mechanics:

- Molecular weight (higher → stiffer).
- Chain entanglement (increases toughness).
- Cross-linking (increases stiffness, reduces elongation).

2. Mechanical Properties of Polymers in Crystalline State

- Crystalline regions **provide rigidity and strength**, while amorphous regions offer **limited flexibility**.
- Semi-crystalline polymers show a combination of **elastic and plastic behavior** depending on stress and temperature.

Characteristics:

- High **tensile strength** due to ordered packing of chains.
- Some **plastic deformation** is possible in amorphous regions between crystallites.
- Mechanical properties strongly depend on **degree of crystallinity** and **lamellar thickness**.
- Example: **Polyethylene (PE), Polypropylene (PP)**.

3. Forced Elasticity (Stress-Induced Elasticity)

- **Forced elasticity** occurs when a polymer is **stretched above Tg or partially below Tg**, causing temporary alignment of chains along the stress direction.
- It is a **time-dependent and reversible phenomenon**, driven by **entropy and chain conformation changes**.

Mechanism:

1. Polymer chains uncoil or straighten under applied stress.
2. Chains remain extended temporarily even when the stress is removed.
3. Over time, thermal motion allows chains to **return to random coil conformation**, restoring initial dimensions.

Significance:

- Explains the **elastic recovery** of stretched polymers below Tg.
- Important in **fiber drawing, rubber elasticity, and polymer processing**.

Examples:

- **Glass fibers stretched at elevated temperatures.**
- **Polystyrene and polyethylene films stretched below Tg.**

4. Relationship Between Structure and Mechanical Behavior

- **Glassy polymers:** rigid, brittle, limited deformation.
- **Crystalline polymers:** strong, partially plastic, dependent on crystallinity.
- **Forced elasticity:** highlights the role of chain mobility, entropy, and temporary chain alignment.
- **Chain flexibility, entanglements, and cross-links** influence both elastic and plastic response.

Summary Table:

State	Chain Mobility	Deformation Type	Stress Response	Example
Glassy	Very low	Elastic, brittle	High modulus, low elongation	PS below Tg
Crystalline	Low in crystallites, moderate in amorphous regions	Elastic + plastic	Strength increases with crystallinity	PE, PP
Forced Elasticity	Temporary alignment	Reversible	Stress-induced recovery	Stretched polymer films

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Control Questions:

1. What are the main mechanical properties of polymers in the glassy state?
2. How do crystalline regions influence strength and plasticity?
3. Define forced elasticity and explain its mechanism.
4. How does polymer chain flexibility affect forced elasticity?
5. Give examples of polymers showing forced elasticity.
6. How does temperature affect mechanical properties in glassy and crystalline polymers?
7. What is the relationship between crystallinity and tensile strength?
8. Draw and explain the stretching isotherms of the polymer below the brittleness temperature, above the brittleness temperature in the glassy state.

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