Lecture 10.

Theme. Relaxation phenomena in polymers. Deformation properties of polymers in highly elastic state. Viscous state of polymers

Aim: generate the following learning outcomes:
- to formulate the nature of the highly elastic state;
- to identify the causes and consequences of relaxation phenomena in polymers;
- correlate the effect of exposure time and temperature on relaxation time;
- describe the mechanism of viscous flow;

Purpose:

To understand the **time-dependent relaxation behavior** of polymers, the **mechanical behavior** in the highly elastic state, and the properties of polymers in the viscous (flowing) state.

Lecture content:

Highly elastic condition (HES). Thermodynamics and molecular mechanism of highly elastic deformation.
The entropic nature of high elasticity. The relationship between the equilibrium elastic force and elongation. The lower limit of the molecular weights required for the manifestation of high elasticity.
Relaxation phenomena in polymers. Relaxation of tension. Relaxation time.
Dependence of relaxation time on temperature.
Hysteresis phenomena during mechanical testing of polymers. Mechanical losses and the nature of their occurrence. Coefficient of mechanical losses. The principle of temperature-time superposition.
Viscous state. The mechanism of viscous flow. Polymer flow curves.
Dependence of the viscous flow temperature on the molecular weight. Anomalies of viscous flow.
Molding of polymer products in the viscous flow mode.

Main Questions:

1. What are relaxation phenomena in polymers and why do they occur?
2. How do polymer chains respond to stress in the highly elastic state?
3. What defines the viscous behavior of polymers?
4. How are deformation and relaxation related to chain mobility and temperature?
5. What is the significance of relaxation phenomena for polymer applications?

Key Theses:

1. Relaxation Phenomena in Polymers

- **Relaxation** is the time-dependent return of a polymer to equilibrium after removal of stress or strain.
- Occurs due to **reorientation, rotation, or slippage of polymer chains** and segments.

Types of relaxation:

1. **Mechanical relaxation:** gradual decrease of stress under constant strain (stress relaxation).
2. **Viscoelastic creep:** gradual increase of strain under constant stress.
3. **Thermal relaxation:** polymer chains gain mobility with temperature changes, especially near Tg.

Factors affecting relaxation:

- **Temperature:** higher temperature → faster relaxation.
- **Molecular weight:** higher molecular weight → slower relaxation.
- **Chain flexibility and entanglement:** more flexible and loosely entangled chains relax faster.

Importance:

- Determines **service life** and **mechanical stability** of polymer materials.
- Critical for **rubbers, coatings, adhesives, and polymer composites**.

2. Deformation Properties of Polymers in Highly Elastic State

- **Highly elastic state** occurs above Tg in amorphous polymers or in lightly cross-linked elastomers.

- Polymer chains can **stretch significantly** and return to their original shape due to **entropy elasticity**.

Key features:

- Stress is proportional to the degree of chain extension (entropic origin).
- Deformation is **reversible** if chains are not chemically damaged.
- Behavior is typical for **rubbers and elastomers**.

Mechanism:

- Chains uncoil and align under stress.
- Upon release, thermal motion drives chains back to a random coil conformation.

Examples:

- Natural rubber: large reversible strains (~500%).
- Silicone elastomers: stable over wide temperature ranges.

3. Viscous State of Polymers

- **Viscous state** occurs at temperatures well above Tg or Tm for semi-crystalline polymers.
- Polymer chains have sufficient mobility to **flow under applied stress**.

Features:

- Time-dependent deformation (creep) is significant.
- Material behaves like a **highly viscous liquid**.
- Flow is influenced by molecular weight, entanglement, and temperature.

Applications:

- Melt processing (extrusion, injection molding).
- Coatings, adhesives, and films requiring shaping in molten state.

Relationship between states:

- Polymers can transition between **glassy → rubbery → viscous** states depending on temperature and stress.
- Relaxation phenomena and viscoelasticity dominate mechanical behavior near the transitions.

4. Relationship Between Relaxation, Elastic, and Viscous States

Property	Glassy State	Highly Elastic (Rubbery) State	Viscous (Melt) State
Chain mobility	Low	Moderate	High
Deformation	Mostly brittle	Large, reversible	Flow, permanent
Stress response	Immediate	Entropic elasticity	Viscous, time-dependent
Temperature	$T < Tg$	$Tg < T < Tm$	$T > Tm$

- Relaxation phenomena explain **time-dependent stress and strain** in all states.
- Highly elastic deformation is **reversible**, while viscous flow is **permanent**.

Control Questions:

1. What are relaxation phenomena in polymers and what causes them?
2. How do polymers deform in the highly elastic state?
3. Define the viscous state of polymers and its characteristics.
4. How do temperature and molecular weight influence relaxation times?
5. Formulate the reasons for the manifestation of relaxation phenomena in polymers.
6. List the side effects of the relaxation process in polymers.
7. What is entropy elasticity and which polymer state exhibits it?
8. Formulate the principle of temperature-time superposition.
9. Give examples of applications where viscous flow is important.
10. Draw and explain the stretching isotherms of the polymer in a viscous state.
11. How are the glassy, rubbery, and viscous states related in terms of polymer chain mobility?

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