Discipline: Actual problems of chemistry of polymer composites

Lecture 9.

Theme: Plasticization of Polymer Composites: Types, Methods, Thermodynamics

---

Objective:

To understand the **concept, types, and methods of plasticization** in polymer composites, and to explore the **thermodynamic principles** underlying plasticization.

Key Questions:

1. What is plasticization in polymer composites?
2. What are the types of plasticizers and plasticization methods?
3. How does plasticization affect polymer composite properties?
4. What thermodynamic factors govern the plasticization process?
5. How are plasticizers selected for specific polymer composites?

Lecture Content:

- **Definition of Plasticization:**
  - Plasticization is the **process of increasing the flexibility, ductility, and processability** of polymer composites by adding a plasticizer.
  - Plasticizers are **low-molecular-weight or oligomeric compounds** that **reduce intermolecular forces in the polymer matrix**, allowing chains to move more freely.
- **Types of Plasticizers:**
  1. **Primary (External) Plasticizers:**
     - Added during processing to **enhance flexibility and workability**.
     - Examples: phthalates, adipates, citrates.
  2. **Internal Plasticizers:**
     - Incorporated **chemically into the polymer chain** during polymerization.
     - Permanent effect on flexibility without migration.
  3. **Reactive Plasticizers:**
     - Participate in **chemical reactions** with the polymer, forming bonds.

        - Improve flexibility while maintaining durability.
- **Methods of Plasticization:**
    - **Physical Blending:** Mixing polymer with plasticizer under heat or shear.
    - **Chemical Modification:** Covalent bonding of plasticizer moieties into polymer chains.
    - **Solvent-Induced Plasticization:** Using solvents to temporarily reduce polymer viscosity for processing.
- **Thermodynamics of Plasticization:**
    - Governed by the **interactions between polymer and plasticizer molecules**.
    - **Free energy of mixing (ΔG_mix):** Must be negative for spontaneous plasticization.
      $\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$
        - ΔH_{mix}: enthalpy of mixing (interaction energy)
        - ΔS_{mix}: entropy of mixing (increased chain mobility)
    - Plasticizer **reduces glass transition temperature (Tg)** by increasing chain mobility.
    - Compatibility between polymer and plasticizer is critical to prevent **phase separation**.
- **Effects on Polymer Composites:**
    - Increased **flexibility, elongation, and toughness**.
    - Reduced **brittleness and stiffness**.
    - Enhanced **processability** during molding, extrusion, or film formation.
    - Potential drawbacks: plasticizer migration, reduced thermal stability, decreased mechanical strength.
- **Selection Criteria for Plasticizers:**
    - Compatibility with polymer matrix
    - Desired flexibility and mechanical properties
    - Thermal and chemical stability
    - Non-toxicity for food, medical, or consumer applications
- **Applications:**
    - PVC composites for flexible tubing, films, and cables.
    - Rubber and elastomer composites for seals and gaskets.
    - Biodegradable polymer composites in medical devices.

Key Short Theses:

1. Plasticization increases flexibility and processability of polymer composites.
2. Types: **primary (external), internal, and reactive plasticizers**.
3. Methods include **physical blending, chemical modification, and solvent-induced plasticization**.

4. Thermodynamics: plasticization requires **favorable free energy of mixing** and polymer-plasticizer compatibility.
5. Plasticizers reduce **glass transition temperature (Tg)** and improve chain mobility.
6. Effects: enhanced flexibility, toughness, and processability; potential risks include migration and reduced thermal stability.
7. Selection of plasticizers depends on **polymer type, intended application, and performance requirements**.

Control Questions:

1. Define plasticization in polymer composites.
2. What are the main types of plasticizers and their differences?
3. Describe three methods of plasticization.
4. How does plasticization affect the glass transition temperature?
5. What thermodynamic factors govern plasticization?
6. What are the main benefits and potential drawbacks of plasticization in composites?
7. How should plasticizers be selected for a specific composite application?

Recommended references

Main literature:

1. Introduction to Polymer Science and Chemistry: A Problem-Solving Approach, Second Edition 2nd Edition / by Manas Chanda, CRC Press; 2nd edition (January 11, 2013)
2. Polymer Chemistry 2nd Edition / by Paul C. Hiemenz, Timothy P. Lodge, CRC Press; 2nd edition (February 15, 2007)
3. Semchikov Yu.D. High-molecular compounds: Textbook for universities. Moscow: Academy, 2003, 368.
4. S. Thomas, K. Joseph, S.K. Malhotra, K. Goda, M.S. Sreekala. Polymer composites. – Wiley-VCH, 2012. – 829 p.
5. Irmukhametova G.S. Fundamentals of polymer composite materials technology: textbook for universities; Al-Farabi Kazakh National University. - Almaty: Kazakh University, 2016. - 175 p.

Additional literature:

1. Polymer composite materials (part 1): a tutorial / L.I. Bondaletova, V.G. Bondaletov. - Tomsk: Publishing house of Tomsk Polytechnic University, 2013. - 118 p.

2. Polymer composite materials: structure, properties, technology. Edited by Berlin A.A. - St. Petersburg, Publishing house "Profession", 2008. - 560 p.
3. Polymer composite materials: structure, properties, technology: a tutorial / M.L. Kerber et al.; under the general editorship of A.A. Berlin. - St. Petersburg: Profession, 2009.- 556, [4] p.
4. Bataev, A.A. Composite materials. Structure, production, application: a tutorial. manual / A. A. Bataev, V. A. Bataev. - M.: Logos, 2006. - 397, [3] p. - (New University Library).