Lecture №13. Diffusion processes in polymeric materials. General regularities of diffusion processes in polymers

Aim: Consider the mechanism of diffusion of the substance dispersed in some polymeric capillary-porous materials. Describe abnormal diffusion in polymers. To characterize the main types of manifestations of anomalous diffusion.

Lecture summary: Consider the mechanism of diffusion of the substance dispersed in some polymeric capillary-porous materials.

Diffusion in polymers is significantly influenced by both the properties of the polymer itself and the properties of the substance to be distributed (diffusant). The chemical nature and molecular weight distribution of macromolecules, the degree of crosslinking, the presence and nature of the plasticizer, the state of the polymer is highly elastic or glassy, the degree of crystallinity, the presence of filler, etc., have a significant impact on the diffusion of a substance in a polymer. In a highly elastic state, essential segmental mobility macromolecules ensure the normal course of diffusion processes, whereas during the transition to the glassy state due to inhibition, the oscillatory motion of macromolecules segments diffusion decreases by several orders of magnitude. The properties of the diffusant — the molecular weight, the shape of the molecules, and their donor-acceptor characteristics — also strongly influence the diffusion process and the nature of the interaction of the substance to be distributed and the polymer framework.

With abnormal diffusion in polymers, the diffusion coefficient at a constant temperature depends not only on the concentration, as it should be when the process is subject to Fick's law. The reason for the abnormal diffusion in polymers are processes occurring during the interaction of the diffusant with the polymer. For example, swelling of a polymer, depending on the process conditions (temperature, concentration), the structure of the polymer adsorbent (globular, fibrillar or various intermediate conformations), its state (glassy or highly elastic), may be the main cause of anomalous diffusion.

Anomaly, as shown by numerous studies, is inherent mainly in polymers as it is in the glassy state. It is manifested the more significantly, the lower the polymer temperature compared to the glass transition temperature, the more “good” solvent is the substance to be dispersed in relation to the material, the higher the solvent concentration and the longer the structure relaxation time for this polymer.

If the change in the structure of the polymer with a change in concentration is insignificant or occurs very quickly, and also in such a case when the diffusant is not wetting, then a diffusion anomaly is not observed. Structural changes take equilibrium values, which are functions of concentration and temperature. The process of diffusion in isothermal conditions in this case is described by a coefficient of mass conductivity that depends only on the concentration, and at the initial part of the kinetic curve the square root ratio is:

$$M(\tau) / M_0 = k\sqrt{\tau}, \quad (1)$$

where M (τ), M_0 are the amount of sorbed or desorbed substance, respectively, at time τ and at the end of the process.

With significant, but slowly proceeding structural changes, the process can proceed in two stages - first, rapid sorption with a mass diffusivity coefficient that depends only on concentration, then anomalous sorption (or desorption) from the pseudo-equilibrium state to the state of true equilibrium.

In fig. 3 presents four types of anomalies. A two-stage sorption process (Fig. 3a) is characteristic of the cellulose acetate – acetone system, and anomalous diffusion with an S-shaped curve (Fig. 3b) is characteristic of cellulose acetate – methylene chloride or gelatin – water systems. A feature of this type of system is the presence of an inflection point on the sorption curve and the fact that the desorption process is initially faster than the sorption process.

The sorption kinetics curve with a maximum (Fig. 3c) is characteristic of the anomalous sorption of polymers with a rigid structure of molecules, when relaxation processes proceed extremely slowly. The absorption of the diffusant weakens the intermolecular bonds of the polymer and contributes to the completion of the structure relaxation process, which is accompanied by a decrease in the free volume of the polymer, which leads to a decrease in sorption.

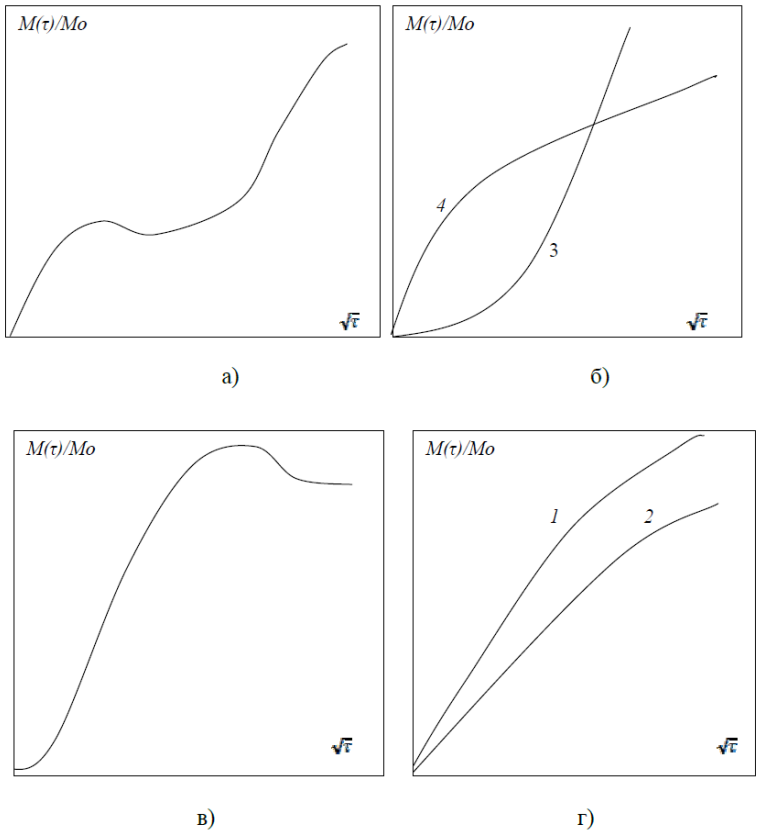

Fig. 3. Types of anomalous diffusion: a) two-stage; b) - S – shaped; c) - with a maximum; d) - pseudonormal (1 - normal diffusion, 2 - pseudonormal diffusion, 3- sorption, 4 - desorption)

The fourth type of sorption curve (Fig. 3d) has the usual form, but the kinetic curve is more extended in time (pseudonormal) compared to the curve described by Fick's law. It should be borne in mind that the course of the curve (two-stage, S-shaped, with a maximum or pseudonormal) for the same system depends on the initial concentration. For example, for water sorption by cellulose with an increase in the initial concentration, the shape of the sorption curve changes in the following sequence: S-shaped, pseudonormal, two-stage, S-shaped.

In general, the following main types of manifestation of anomalous diffusion are distinguished: a) the occurrence of sorption hysteresis due to a change in the sorption capacity of the polymer; b) a change in the diffusion coefficient during the process, caused not only by a change in concentration, but also due to a conformational change in polymer macromolecules; C) the occurrence of the stress state in the polymer, caused by the mutual influence of the swollen and non-swollen parts of the polymer; d) the appearance of the structural orientation of macromolecules in the direction of diffusion; e) the effect of the initial non-isotropic structure of the polymer in thickness, caused by the conditions of obtaining the polymer during crystallization, as well as during thermal or mechanical processing. All these manifestations in varying degrees are essential in the processes of drying, adsorption or sorption processes.

Questions to control:

1. Consider the mechanism of diffusion of the substance dispersed in some polymeric capillary-porous materials.
2. Description abnormal diffusion in polymers.
3. Characterization the main types of manifestations of anomalous diffusion.

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