Lecture №14. Diffusion phenomena in drying process in systems with a polymer solid phase

Aim: Describe the drying process involving polymers. Compare the process of removing liquids by drying from capillary-porous polymers with non-porous polymers. To characterize colloidal capillary-porous materials of polymeric nature by examples.

Lecture summary: In the drying process as a solid phase are often involved polymers, which in sorption and kinetic respect should be to be considered as non-porous: they absorb distributed in solid the phase of the substance occurs by the mechanism of absorption, and its migration-by molecular diffusion.

Studies show that polymers such as polyamides (-6, -66, -610, -12), polyethylene terephthalate, polypropylene, polycarbonate exhibit properties of non-porous materials. Lack of them genetically significant pores are confirmed by the fact that the sorption and desorption curves water vapor in these polymers are highly elastic in state, throughout the range of moisture φ coincide, and in the region of low values of φ ($\varphi \leq 0.3$) have a linear character corresponding to Henry's law; pairs are not miscible with the polymer of the liquid is almost not sorbed, and moisture absorption is accompanied by the contraction of the system. Negligible role of adsorption and capillary mechanisms condensation is also shown in experiments on the study of sorption in amides of n-hexane-a liquid practically insoluble in polyamide and having zero sorption.

The process of removing liquids by drying from capillary-porous compared with non-porous polymers characterized by other patterns. Common to these processes is that removal of various liquids by drying from the capillary-porous body due to the energy of its connection with the "skeleton" of the material-first removed free moisture and then more firmly bound. The study of the influence physical and chemical properties of moisture (which is understood as specified above, any liquid removed by drying) on the kinetics of the internal mass transfer is of great practical importance, as the production of polymers and other materials associated with the use of various organic solvents and their mixtures removed by drying.

The main physical and chemical properties of the liquid and its vapor, the viscosity $\boldsymbol{\eta}$ has an impact on the drying process, the surface tension $\boldsymbol{\sigma}$ and the density $\boldsymbol{\rho_{liq}}$, the vapor pressure in the air $\boldsymbol{\rho_{sat}}$, vapor diffusion coefficient in air **D**, dipole moment $\boldsymbol{\varepsilon_d}$, characterizing the polarity of the molecule of the distributed substance.

The effect of these parameters is manifested in different degrees by as the humidity of the dried material changes. As previously stated, with large moisture content, the main type of mass transfer is the capillary flow and, therefore, in this case, the following are important characteristics such as $\boldsymbol{\eta}$, $\boldsymbol{\sigma}$ and $\boldsymbol{\rho_l}$.

At low moisture content, the transfer of the substance in the microcapillary-porous material is carried out mainly by Stefan diffusion steam and additionally capillary and film flows. Under these conditions a large role should be played by the parameters **D**, $\boldsymbol{\rho_{sat}}$, $\boldsymbol{\varepsilon_d}$.

As noted earlier, as the moisture content of the material decreases, the role of the steam flow in the transfer of moisture increases, therefore, in the area of low humidity, the mass conductivity coefficient should depend on the diffusion properties of the vapor phase.

When drying microcapillary-porous materials in the period of falling drying rate intraporous the air is not in a state of thermodynamic equilibrium with the moisture of the material. This is evidenced by the fact that for these materials the drying rate, which decreases in time, is observed in the humid area and indicates a continuous decrease of vapor concentration at the interface of the "solid –medium" system in the considered period. This indicates the presence of internal evaporation in macro capillary-porous materials.

Colloidal capillary-porous materials of polymeric nature in their structural properties occupy an intermediate position between non-porous and capillary-porous materials, which predetermines intermediateness of their sorption and mass conduction properties. Experiments on the study of isotherms of sorption-desorption of water vapor on the latex film of Revultex showed the presence of sorption hysteresis in the whole range of moisture content φ. This is explained by the fact that this material contains both swelling moisture in globules and capillary bound moisture filling the gaps between the globules trapped during gel formation. In the process of drying (desorption), the volume of the latex film changes, as when capillary moisture is removed from the latex film, as a result of the high elasticity of the body frame, it is tightened up to complete merging of the globules and the disappearance of porosity. The continuous change in the porous structure of the film is reflected in a wide range of sorption hysteresis in the sorption-desorption isotherm of water vapor in this material.

Another example of a colloidal capillary-porous material is polystyrene. When cooling the melt of this polymer in the process of its production, a significant local decrease in the volume of the crystalline regions occurs, as a result of which a porous structure is formed. In water vapor sorption-desorption isotherms, Styron brand polystyrene hysteresis loop covers the entire region of relative humidity, which indicates the presence of both adsorption and absorption mechanisms for vapor absorption.

As experiments with this polymer have shown, the curves of the dependence of the mass conductivity coefficient K on the volume moisture content of the material C by the nature of concentration dependencies during drying (the decreasing nature of the function $k = f(C)\ \tau$ with small C) are similar to those for microcapillary-porous materials. This is due to a fairly rigid frame, which does not change much during drying.

In the region of high moisture contents, moisture transfer occurs predominantly by a capillary flow, and in the region of low moisture contents, it is caused mainly by the diffusion transfer mechanism, most likely by surface diffusion. The presence of a pore system, in contrast to latex, makes it possible to desorb a substance adsorbed in the polymer matrix into the pore space and then migrate through the pore channels to the surface of the body. Thus, it can be argued that according to the results of kinetic studies and mathematical modeling of the drying process of polystyrene, this material belongs to the first subgroup of the class of colloidal capillary-porous materials (Table 1).

Another polymeric material, celluloid, belongs to the second subgroup of the class of colloidal capillary-porous materials (Table 1), which is characterized by anomalous diffusion. This phenomenon is illustrated by the experimental data on the sorption of ethyl alcohol vapor by celluloid.

Sorption measurements showed that celluloid absorbs ethyl alcohol vapor in an amount substantially higher than the porosity of the material, i.e. the absorption of ethyl alcohol vapor occurs both in the pores and in the polymer matrix. The curves of the distribution of the mass fractions of ethyl alcohol through the thickness of the plate of celluloid have the usual form for such distributions. Unusual for them is the slow decrease in the surface concentration of ethyl alcohol in the sample during the entire drying time, which is not typical for a process controlled by internal diffusion.

The observed phenomenon can be justified as follows. The slow establishment of desorption equilibrium at the interface is explained by the tense state of the polymer: under the action of the swollen central core, the surface layers are stretched; tensile forces prevent desorption of ethanol molecules in the material. As drying occurs, the concentration difference across the thickness of the material decreases, the mechanical stresses relax, and the surface concentration decreases, approaching the equilibrium value.
In some cases, anomalous diffusion in polymers can be described with sufficient accuracy on the basis of the Fick's nonlinear differential equation, but in general, special mathematical models are required to describe it.

Questions to control:

1. Describe the drying process involving polymers.
2. Compare the process of removing liquids by drying from capillary-porous polymers with non-porous polymers.
3. Characterize colloidal capillary-porous materials of polymeric nature by examples.

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