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INVESTIGATION OF THE SORPTIVE PROPERTIES OF PIGMENTED POLYVINYL CHLORIDE

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The non-Fickian diffusion of water vapor through polyvinyl chloride (PVC) pigmented with kaolin was investigated. It is shown on the basis of the model proposed that the concentrational and time dependences of the effective diffusion coefficient of the PVC compound represent superpositions of the corresponding dependences of its structural components.

Keywords: *heterogeneous system, diffusion, effective diffusion coefficient, effective penetration coefficient, effective sorption coefficient, sorption.*

Introduction. The interest of the scientific community in the sorption of water by polymers is explained by the problems arising in the process of production of pigmented and reinforced polymeric materials [1] and in their use [2, 3]. Moreover, heterogeneous polymer systems based on PVC — one of the most multitonnage linear polymers — are used more and more widely in the home industry and abroad [4]. It should be noted that the mechanism of penetration of water vapor through the linear flexible chain polymers is as yet imperfectly understood [5]. It has been established that the structure of these materials changes in the process of sorption of moisture by them, which prevents the use of Fick's laws in full measure [6, 7] for description of the kinetics of their diffusion even though it is known that the diffusion coefficient of the indicated materials depends on their concentration [8, 9]. It was shown in [10, 11] that the introduction of microatomized pigments into the linear polymers makes the analysis of the diffusion of the heterogeneous polymer system even more complex because, in this case, it is necessary to take into account the appearance of the interphase boundary polymer–pigment.

The aim of the present work is to develop and analyze a mathematical model for description of the kinetics of moisture sorption in a heterogeneous polymer system and to obtain such systems with controllable properties.

Theoretical Model. Using the results of [1], we represent a PVC compound with a content of microatomized pigment φ lower than the critical one φ_{cr} in the form of a three-component system consisting of the pigment (P), the boundary layer (BL), and the polymer (Pol). At $\varphi \geq \varphi_{cr}$, the system degenerates into the two-component one: P–BL. In the case where $\varphi < \varphi_{cr}$, the heterogeneous polymer system is assumed to be colloidal [11]. We will assume that the sorbent at the interphase boundaries P–BL and BL–Pol represents a set of Langmuir pores and a Henry solution respectively [12]. This makes it possible, as in the case of analysis of the diffusion processes in flexible chain polymers [13], to use the model of sorption of a binary system.

According to the results of solution of the diffusion equations, the relative fraction of the sorbate in a semi-infinite plate of thickness l will be determined by integration of the local distribution of its concentration over the volume of the body [14]:

$$\frac{\Delta m}{\Delta m_s} = 1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{1}{(2j+1)^2} \exp\left[\frac{-(2j+1)^2 \pi^2 D t}{l^2}\right]. \tag{1}$$

The solution of (1) represents a rapidly converging series. At large values of the Fourier criterion for diffusion $\mathrm{Fo} = Dt/l^2$ we can restrict ourselves to the first term of the series. Then

$$\frac{\Delta m}{\Delta m_s} = 1 - \frac{8}{\pi^2} \exp\left[\frac{-\pi^2 D t}{l^2}\right]. \tag{2}$$

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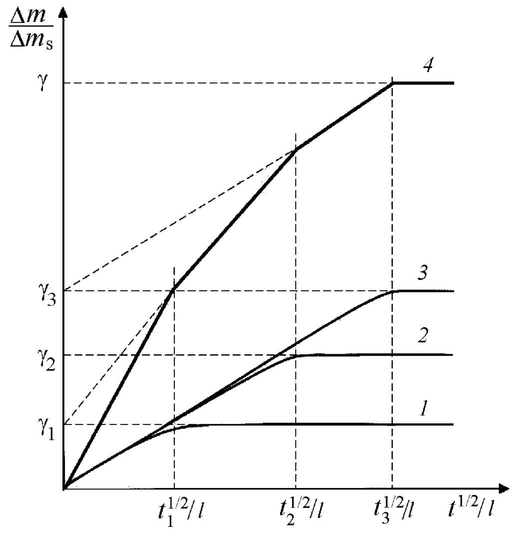

Fig. 1. Kinetics of sorption by components of the sorption process. γ, kg/kg; $t^{1/2}/l$, sec$^{1/2}$/m.

At small values of Fo, the relative fraction of the sorbate in the semi-infinite plate is determined by integration of its mass flow through the plate with respect to the time t [10]:

$$\frac{\Delta m}{\Delta m_s} = 4\sqrt{\frac{Dt}{\pi l^2}} . \tag{3}$$

In accordance with the model of the PVC compound, each component of the P–BL–Pol system is characterized by the effective coefficients of diffusion D_i, penetration P_i, and solubility h_i.

Let us consider the influence of the three components of the indicated system on the kinetics of sorption of moisture in it. The sorption of moisture in the P–BL–Pol system is illustrated by the curves of partial sorption of phases 1, 2, and 3 in Fig. 1. According to the group-contribution method, the sorption curve has a more complex shape at the end of the diffusion in the three-component PVC compound due to the superposition of the sorptions of the P, BL, and Pol components participating in the process (curve 4). The existence of the three sorption regions is due to the change in the sorption of the penetrant of each structure-forming component and its completion. Because of this, by the character of the sorption in the heterogeneous polymer system, represented in the coordinates $\Delta m/\Delta m_s = f(\sqrt{t_i}/l)$, one can estimate the effective diffusion coefficient of each component. At the moment of quasi-saturation, $\Delta m_i/\Delta m_{si} = 1$. Substituting this expression into (3), we obtain

$$1 = 4\sqrt{\frac{D_i t_i}{\pi l^2}} ,$$

whence it follows that

$$D_i = \frac{\pi l^2}{16 t_i} , \tag{4}$$

where i is the number of a structure-forming component.

To estimate the mass fractions of the sorbate absorbed by each component of the composite, we will draw the tangents to the curve of the sorption kinetics of the heterogeneous polymer system. This makes it possible to estimate, by the points of intersection of the tangents with the axis $\Delta m/\Delta m_s$, the relative fraction of the sorbate γ_i, absorbed by an individual component and, correspondingly, its mass:

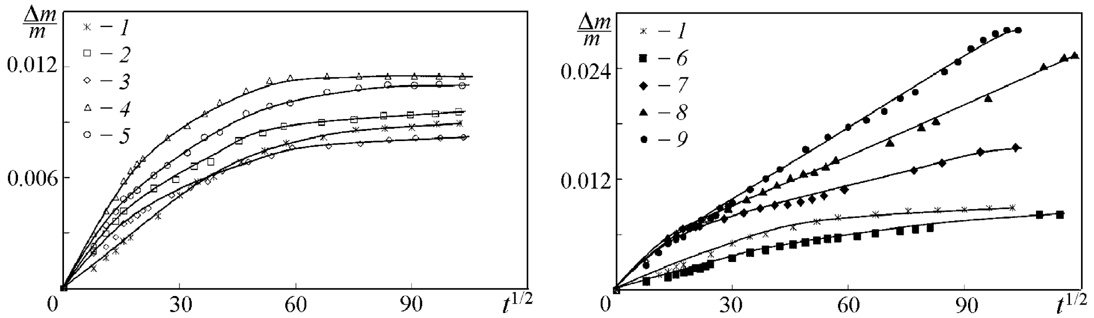

Fig. 2. Kinetic curves of sorption of distilled water by PVC–kaolin composites at different contents of the pigment: φ = 0 (1), 1 (2), 2 (3), 3 (4), 4 (5), 5 (6), 10 (7), 15 (8), and 20 wt. % (9). $\Delta m/m$, kg/kg; $t^{1/2}$, $\sec^{1/2}$.

$$\Delta m_{si} = \gamma_i \Delta m_s . \tag{5}$$

The effective sorption and penetration coefficients will be determined [10] as

$$h_i = \frac{C_i}{P_{H_2O}} = \frac{\Delta m_{si}}{VP_{H_2O}} = \frac{\Delta m_{si}}{mP_{H_2O}} \rho , \tag{6}$$

$$P_i = h_i D_i . \tag{7}$$

Then, using the superposition principle, we obtain

$$h = \sum_i h_i , \quad P = \sum_i P_i , \quad D(t) = \sum_i D_i \delta_i ,$$

where $i = 3$ at $\varphi < \varphi_{cr}$, $i = 2$ at $\varphi \ge \varphi_{cr}$, $\delta_i = \begin{cases} 1 , & t < t_i ; \\ 0 , & t \ge t_i . \end{cases}$

Results and Discussion. As a polymer matrix, we used C-6359 PVC subjected to suspension polymerization in accordance with the State Standard 14332-78 with a Fikintscher constant of 63 and a molecular mass of $1.4 \cdot 10^5$ obtained from a solution, which made it possible to remove the low-molecular impurities and the residues of the initiator and emulsifier.

The pigment was kaolin of the Prosyanovsk deposit, the particles of which have the hexagonal form. According to the macroscopic-analysis data, the kaolin particles are characterized by a wide size distribution. The sizes of the main-fraction particles range from 3 to 7 μm. The content of the pigment in the heterogeneous polymer system was investigated in the range of φ = 0–20 wt. %.

The composites were prepared by direct mixing of kaolin with the PVC in the T–p regime at T = 403 K and p = 10 MPa with subsequent cooling under pressure to room temperature with a rate of 3 deg/min in the form of films of thickness 130–150 μm and diameter 25 mm.

The sorption kinetics of the composites was measured under isobaric-isothermic conditions at a temperature of 293 ± 1 K and a water-vapor activity of 0.98 that was controlled with the use of an HIH-3610 device of the Honeywall firm (the measurement error was ±2% in the relative-humidity range 0–100%). The change in the mass of samples in the process of an experiment was determined gravimetrically with the use of modernized analytical VLR-200 balance and a V-630 cathetometer. The accuracy of measurements was ±2.5 μg. Prior to investigations, the samples subjected to processing were held in an exiccator with a ShSM silica gel. The sample being investigated was positioned in an exiccator containing distilled water.

Integral kinetic curves of sorption of water vapor by composites are presented in Fig. 2. They differ in character from the normal Fickian curves. It follows from the results obtained that, as the kaolin content increases to 3%,

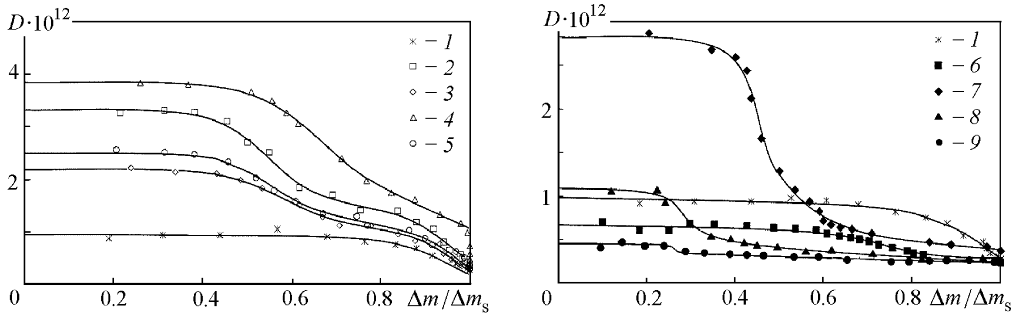

Fig. 3. Dependence of the effective diffusion coefficient on the relative mass of the absorbed water vapor. Designations 1–9 are identical to those in Fig. 2. D, m^2/sec; $\Delta m/\Delta m_s$, kg/kg.

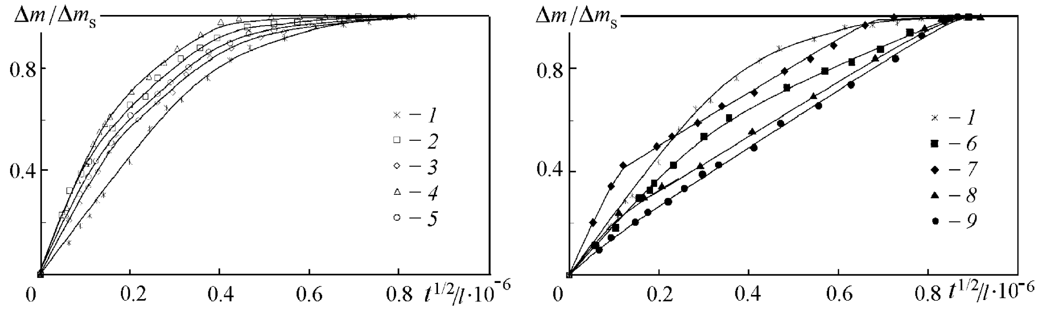

Fig. 4. Kinetic curves of the sorption of distilled water by PVC–kaolin composites in the coordinates of the Fick-equation solution. Designations 1–9 are identical to those in Fig. 2. $\Delta m/m_s$, kg/kg; $t^{1/2}/l$, $sec^{1/2}$/m.

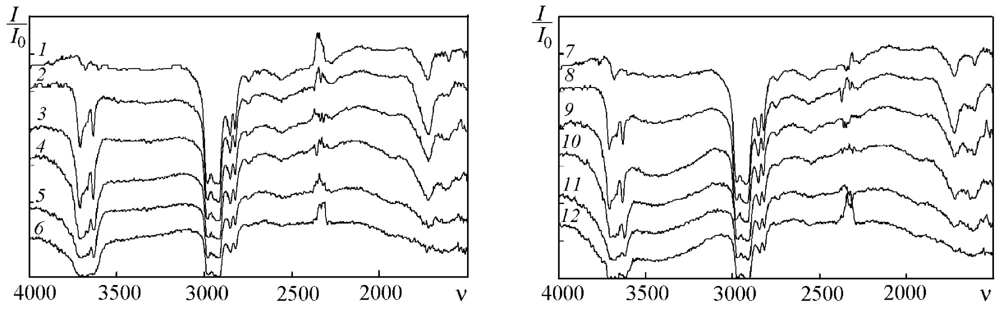

Fig. 5. IR spectra of the initial (1–6) and water-saturated (7–12) composites with a different content of the pigment: φ = 0 (1, 7), 2 (2, 8), 5 (3, 9), 10 (4, 10), 15 (5, 11), and 20 wt. % (6, 12). ν, cm^{-1}.

the fraction of water in the system at equilibrium increases, which is due to the loosening of the PVC accompanied by its subsequent transformation into the boundary-layer state. In the region where the kaolin content is equal to 3–5% the moisture content is decreased, which is explained by the intensive ordering of the structure of the boundary layer under the action of the surface pigment [1]. In the case where the kaolin content exceeds 5%, the moisture content of the composite increases due to the loosening of the PVC structure.

Figure 3 presents the dependence of the effective diffusion coefficient calculated by the classical model (3) on the fraction of the absorbed water. The nonlinear change in $D = f(\Delta m/\Delta m_s)$ indicates that the composite experience structural changes that manifest themselves markedly as defects at $\varphi > 10\%$ of kaolin.

Analysis of the dependences $D = f(\Delta m/\Delta m_s)$ shows that they define three characteristic regions: the first and third regions are characterized by a constant value of the effective diffusion coefficient; the second region, the size of which is of the order of $\Delta m/\Delta m_s \approx 0.2$ independently of the pigment content, is characterized by a monotone decrease in D. It increases at $\varphi < 3\%$ and decreases at $\varphi > 3\%$.

Figure 4 presents the sorption kinetics of composites in the coordinates of Eq. (3). Extrapolation of the diffusion curves by straight lines allows the conclusion that, at a pigment content $\varphi < 5\%$, the diffusion of water in the composites is three-stage in character. According to [11], this is evidence that they have a three-component structure. At $\varphi > 5\%$ the diffusion curve degenerates into the two-stage one, which can be explained by the transformation of the Pol–BL–P system into the two-phase one.

The character of change in the structure of the heterogeneous polymer system in the case where the kaolin content falls within the range $0 < \varphi < 20$ wt. % can be also judged from the results of infrared (IR) spectroscopy investigations (Fig. 5). An increase in the content of the pigment in the PVC causes the transmission coefficient in the IR region of the spectrum to change, and, in the case of composites containing moisture, the characteristic absorption bands in the IR spectra of the PVC are not shifted. The absence of a pronounced chemical interaction between the moisture and the heterogeneous polymer system is evidence in favor of the correctness of the model selected for calculating the value of D.

Conclusions. Thus, the sorption properties of a heterogeneous polymer system based on PVC — a typical representative of the flexible chain polymers — can be calculated by the model proposed on the basis of the superposition principle with account for the heterophase property of the composite. This makes it possible to regulate the sorption properties of materials based on flexible chain polymers.

NOTATION

C_i, partial concentration of the sorbate in the ith phase, kg/m^3; D, effective diffusion coefficient of the heterogeneous polymer system, m^2/sec; D_i, effective diffusion coefficient of the ith phase, m^2/sec; h_i, effective solubility coefficient of the ith phase, kg/(m^3·Pa); I/I_0, transmission; i, number of phases of the heterogeneous polymer system ($i = 3$ at $\varphi < \varphi_{cr}$, $i = 2$ at $\varphi \geq \varphi_{cr}$); j, ordinal number of a term of a series; l, thickness of a sample being investigated, m; m, mass of the sample, kg; Δm, flow mass of the sorbate in the heterogeneous polymer system, kg; Δm_s, mass of the sorbate in the case of saturation; Δm_i, mass of the sorbate absorbed by the ith phase for the exposure time, kg; Δm_{si}, mass of the sorbate in the ith phase at equilibrium, kg; P_{H_2O}, partial pressure of the sorbate vapor in the environment, Pa; P_i, effective penetration coefficient of the ith phase, kg/(m·sec); p, pressure, Pa; T, absolute temperature, K; t, exposure time, sec; t_i, time of transformation of the ith phase into the quasi-equilibrium state, sec; V, volume of the heterogeneous polymer system, m^3; γ_i, relative fraction of the sorbate in the ith phase, kg/kg; δ_i, Kronecker symbol; ν, frequency of IR radiation, cm^{-1}; ρ, density of the heterogeneous polymer system, kg/m^3; φ, mass fraction of the pigment in the heterogeneous polymer system, %; φ_{cr}, critical mass fraction of the pigment, %. Subscripts: cr, critical; s, sorbate.

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