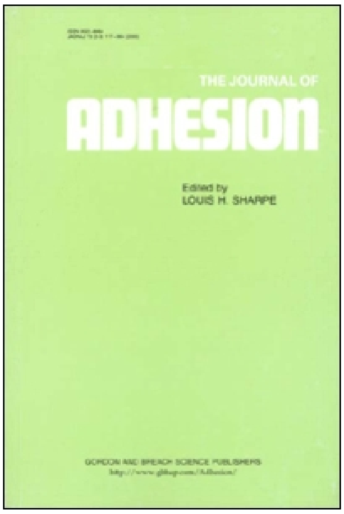

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Kinetics of Sorption Processes in the Course of Polymer Composite Formation

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Kinetics of Sorption Processes in the Course of Polymer Composite Formation*

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The important mechanism of interface layer formation in polymer composite materials is a sorption interaction between polymer fillers and binder components. The structure and properties of the interface layer will be dependent on the kinetics of the sorption. The kinetics of diffusion of some low molecular compounds including epoxies into aramide fibers are studied by the method of isothermic calorimetry. Discrepancy of the kinetics from Fickian was found. Theoretical consideration showed the cause of it could be the structural inhomogeneity of the sorbents. Experimental and theoretical data evidencing that the heterogeneous structure of the sorbent is the cause of the time dependence of the diffusion coefficient are presented in this paper.

Keywords: Polymer composite materials; polymer fiber structure; polymer filler-binder component interaction; interface layer formation; sorption processes; diffusion kinetics in inhomogeneous polymer bodies

INTRODUCTION

Polymer fibers as composite fillers differ significantly from mineral (glass) fibers by their ability to sorb liquid substances. Their structure and properties can be changed in the process of composite formation, especially in the case when thermoreactive binders are used. The undersurface layer of the fibers undergoes the most significant changes. Besides,

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*One of a Collection of papers honoring Yuri S. Lipatov on the occasion of his 70th birthday, 10 July 1997.

components of a binder can penetrate into fiber with different rates. As a result, a matrix gradient structure can be formed around fibers. That is why the sorption kinetics can define the structure of the formed interface layer and, consequently, the adhesion interaction in polymer composites. Originally, these problems were considered by Lipatov and coworkers [1]. Their investigations dealt mainly with thermodynamic aspects of interphase formation in composites. Here we focus on the kinetics of the sorption processes.

The salient feature of the supermolecular structure of fibers used as sorbents is their inhomogeneity. That is why it is impossible to describe the sorption kinetics with a simple diffusion equation. Instead of a single diffusion coefficient, $\mathbf{D}$, there is a set of local ones, $\mathbf{D}_i$, with values dependent on local densities and thermodynamic parameters of the sorbent-sorbate interaction.

If densities of structural elements are considerably different, and a part of them (*e.g.*, the crystal phase in semicrystalline polymers) is inaccessible for a sorbate transfer, then the diffusion of low molecular substances generally are assumed to occur in limited regions of an amorphous phase. This leads to decrease of the effective diffusion coefficient, nevertheless, the sorption kinetics is described by Fick's law. In this case, the structure heterogeneity, *i.e.* the fraction of accessible (amorphous) volume in semicrystalline polymers and tortuosity of a diffusion path, is taken into account by correction of the diffusion coefficient with a numerical factor [2, 3].

If the fraction of forbidden diffusion path is high, *i.e.* in the vicinity of a percolation threshold, the main peculiarity of diffusion kinetics is the time-dependence of the diffusion coefficient [4]; *i.e.*,

$$\mathbf{D} = \mathbf{D}_0 \cdot \mathbf{t}^{-\mathbf{n}} \tag{1}$$

here $\mathbf{D}_0$ is a proportionality coefficient, $\mathbf{n} = 3\mathbf{d}_f$, where $\mathbf{d}_f$ is the fractal dimension of the critical cluster.

The deviation of diffusion kinetics from Fick's law could occur also when the structural heterogeneity is related to a few types of sorption equilibria (*e.g.*, those obeying Henry's and Langmuir's isotherms) [5, 6]. This kind of structural heterogeneity is considered in the dual mode sorption model [7–9].

If the local densities of structural elements do not differ drastically, the transfer of a sorbate can occur simultaneously in several structural elements (diffusion channels). For example, diffusion coefficients of water into globular and interglobular regions of epoxy resins differ by no more than one order of the magnitude [2]. Obviously, in this case the sorption process should be characterized by a set of transfer coefficients. However, there are practically no works analyzing the kinetic features of these processes. Most of the works have dealt with cases in which in the course of the sorption the sorbent structure changed or the sorbate accumulated (See, for example, reviews [3, 9]).

The present work deals with analysis of sorption kinetics in heterogeneous polymer structures where structural transitions are excluded and the final concentration of the sorbates is low. Therefore, we can neglect these factors.

EXPERIMENTAL

Commercial fibers based on aromatic polyamides with similar molecular structure were used as sorbents. PABI fibers were prepared by precipitation from a liquid-crystalline solution of poly(amide benzimidazole) [10]. According to the results of X-ray diffraction [11], these fibers contain amorphous and mesomorphic regions; the latter give meridional reflections typical for nematics. Terlon^{TM} fibers analogous to Kelvar^{TM} [12, 13] were obtained from crystalline poly-*p*-phenylene terephtalamide (PPTA) [10] and had a 90% crystallinity. Armos^{TM} fiber was prepared from PPTA-PABI copolymer with 60% of PABI [14].

Water vapor, liquid water and epoxy resin DGEBA were used as sorbates. An isothermal calorimetric method was used to study the sorption kinetics. Details of the experiments were published in [15–17]. Note that the kinetics of sorption of liquid substances was studied using the ordinary method. In the case of vapor sorption, an experimental setup comprising two coupled calorimeters was used. One of them recorded the sorbate uptake by measuring the heat of evaporation. The other registered the heat of sorption directly. To determine the diffusion coefficient, the entire thermokinetic curve of the sorption process was analyzed. The "time interval method" developed by us was used to solve this problem [15].

EXPERIMENTAL RESULTS

On Figure 1 the thermokinetic curves of the sorption of liquid water by aramid (1–3) and glass (4) fibers are presented. The initial rates of the process are similar in all cases. It corresponds to the surface adsorption; according to the results of low-temperature krypton adsorption, the values of the specific areas of all fibers are similar ($\approx 0.2\ m^2/g$). However, after some period of time the rate of heat release for a glass fiber became practically zero, while the sorption process in polymer fibers proceeds at sufficiently high rates. This means that in the latter case volume sorption takes place.

On Figure 2 the kinetic curves of sorption of water vapor and heat release are presented. As one can see, the shape of these curves is not Fickian. The differential specific heat of sorption depends on the penetration depth of a sorbate (Fig. 3). Perhaps this is evidence of a gradient heterogeneous structure of the fiber skin-layer.

The diffusion coefficients (**D**) determined by the interval method decrease with time (Fig. 4). There is a sudden jump on the curve **D(t)** at a time about 1000 s. This corresponds to a penetration depth of around 0.1 of the fiber radius. Obviously, different structure densities

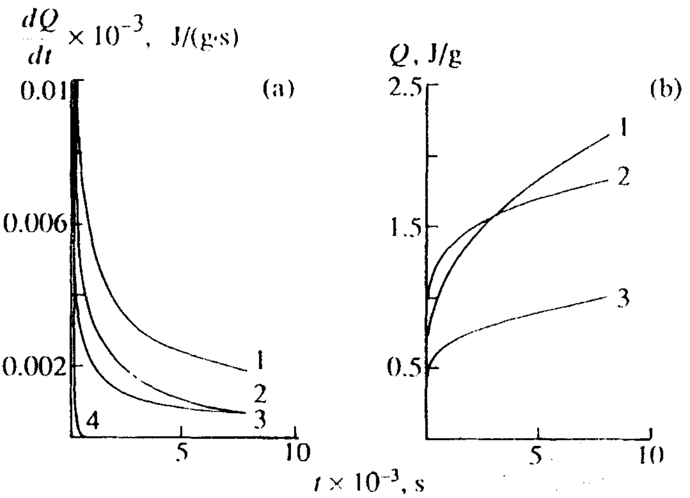

FIGURE 1 Differential (a) and integral (b) kinetic curves of liquid water sorption by aramid (1- PABI, 2- Terlon™, 3- Armos™) and glass (4) fibers.

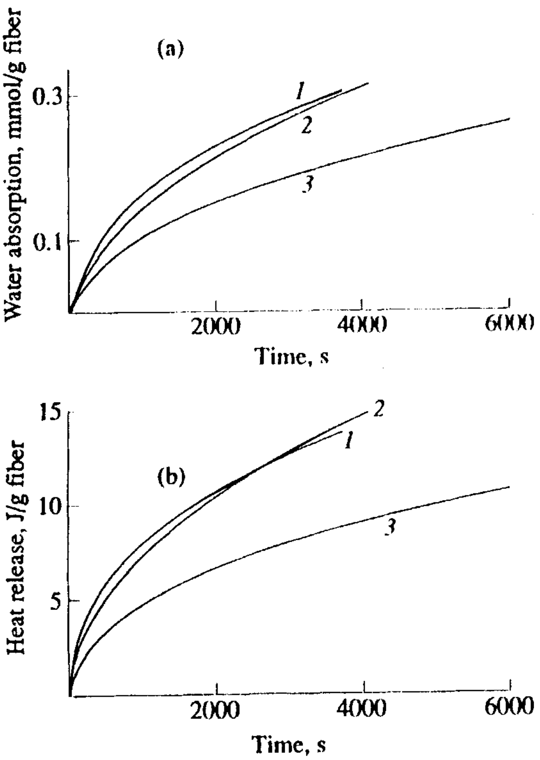

FIGURE 2 Kinetic curves of water vapor sorption (a) and heat release (b). Fibers: 1- Terlon, 2- Armos, 3- PABI.

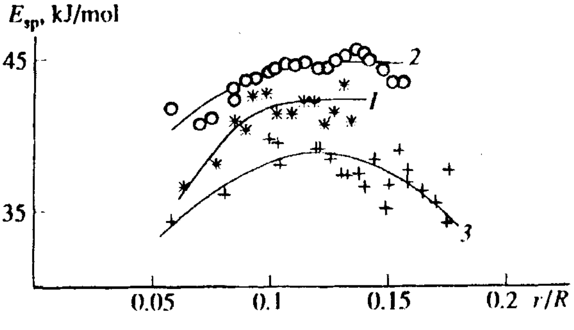

FIGURE 3 The change of specific differential heat with depth of penetration of water vapor into fibers: 1- Terlon, 2- Armos, 3- PABI.

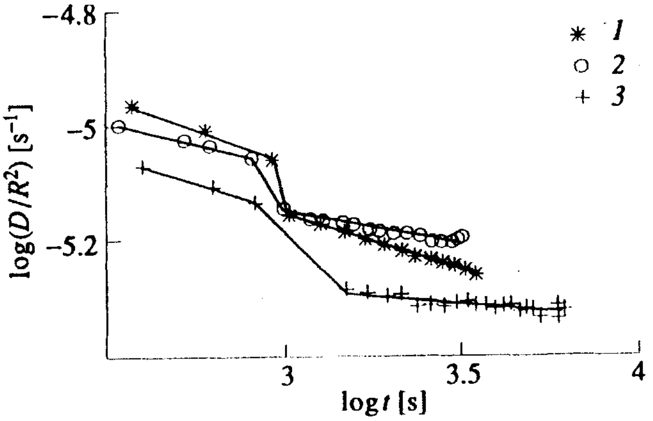

FIGURE 4 The dependence of diffusion coefficient (D/R^2) on time. Values of D/R^2 have been determined by treatment of sorption kinetic curve (Fig. 2).

of the fiber skin-layer and of the core are responsible for this fact. Note that a decrease of the diffusion coefficient with time is observed for both the fiber skin-layer and the core.

Similar time dependencies were obtained in studies of the processes of sorption of liquid substances, water and epoxy resin. However, in this case the beginning of a thermokinetic curve cannot be used for calculation of the diffusion coefficient because of methodological limitations. Note that in all experiments the dependence **D(t)** could be expressed by Eq. (1). Before analysing the reasons for the time dependence of the diffusion coefficient, some remarks should be made.

1. In reality, the proposed interval method for the analysis of the kinetic curves allows one to determine a change of diffusion coefficient in the course of the sorption process. The equation for diffusion with a time-dependent diffusion coefficient is transformed to the usual Fick's equation [18], provided that τ is determined as:

$$\tau = \int_0^t \mathrm{D(x)dx} \qquad (2)$$

A solution obtained for dummy time, τ, can be analysed by comparison with the experimental curve. As far as τ is time dependent, a relatively narrow time interval must be considered. If $\tau = \varphi(\mathbf{t})$ then

$$\mathbf{D(t) = d\varphi/dt + \varphi(t)} \tag{3}$$

Consequently, the dependence **D(t)** can be determined using the function $\varphi(\mathbf{t})$.

2. Though the decrease of the diffusion coefficient during the process does not exceed half an order of magnitude, this decrease is sufficient to consider the curves as non Fickian. Moreover, the differences in diffusion coefficients should be taken into account because the data are obtained from the same kinetic curve.

As one can see from experimental data (Figs. 3, 4) the investigated polymer fiber have complex gradient structures. In this case, the penetrant transfer can be considered as a set of parallel, consecutive and parallel-consecutive processes with a possibility of exchange between diffusion channels.

MODEL OF A PARALLEL DIFFUSION

The simplest model of a parallel diffusion is proposed [19] to describe diffusion in a polymer body with isolated channels in the direction of flow. The diffusion flow as a whole is represented by a sum of partial diffusions. Obviously, this model is suitable for polymers with developed supermolecular structure, if diffusion coefficients related to different structural regions are essentially distinguishable. Clearly, this model appears to be rather artificial. Nevertheless, this model permits one to establish a mutual consistency between partial values of diffusion coefficients and the average ones obtained under different experimental conditions. The analysis of some well-known methods of evaluation of diffusion coefficients follows below.

1. Steady-state flow

The diffusion equation for steady-state flow can be written as:

$$\partial \mathbf{c}/\partial \mathbf{t} = \Sigma \mathbf{D}_i \partial^2 \mathbf{c}_i/\partial \mathbf{x}^2 = 0 \tag{4}$$

The apparent diffusion coefficient determined under these conditions is an arithmetic mean, *i.e.*,

$$\langle \mathbf{D} \rangle = \Sigma \omega_i \mathbf{D}_i \tag{5}$$

where ω_i is a fraction of structure elements in which the process is characterized by diffusion coefficient $\mathbf{D}_i$.

2. Time-lag Method

By this method, the diffusion coefficient is calculated from the time to reach a steady state (τ_{st}). The mechanism of parallel diffusion connects this value with the distribution function of diffusion coefficients in a more complicated manner:

$$\tau_{st} = \frac{\mathbf{l}^2}{6} \cdot \frac{\Sigma \mathbf{D}_i^{-1} \cdot \omega_i \cdot \mathbf{M}_i}{\Sigma \omega_i \cdot \mathbf{M}_i} \tag{6}$$

Here $\mathbf{l}$ is the sample size, and the $\mathbf{M}_i$ are partial ultimate sorbate concentrations. So, the experimental diffusion coefficient is determined as the arithmetic mean of the reciprocal values of the partial ones:

$$\langle \mathbf{D}^{-1} \rangle = \Sigma \omega_i \mathbf{D}_i^{-1} \tag{7}$$

Thus, the time τ_{st} is governed by the smallest diffusion coefficient.

These examples show that the conclusion about the effect of heterogeneity of polymer structure on diffusion process can be made only by comparison of results obtained under different conditions of the experiment.

3. Non-steady State

Complete information about the diffusion mechanism can be obtained from the analysis of the kinetics of a non-steady-state sorption process. To describe the kinetics of parallel diffusion the direct summation of the rates of the partial processes should be made using the known equations for diffusion rates. Mathematically, the dependence

D(t) is a result of averaging over all rates:

$$\mathbf{D(t)} = \Sigma \mathbf{D}_i \omega_i \mathbf{w}_i / \Sigma \omega_i \mathbf{w}_i \tag{8}$$

Here $\mathbf{D}_i$, ω_i and $\mathbf{w}_i$ are partial values of diffusion coefficients, process contributions and rates, respectively.

On Figure 5 are shown the calculated curves of **D(t)** for a flat specimen. The physical sense of **D(t)** decreasing with time is that each of the parallel processes is terminated the earlier, the higher the corresponding diffusion coefficient. To each of the processes corresponds its own time of completion of a process. At every moment, the average value of the diffusion coefficient depends on the degree of completion of each process. In the beginning, all of them make a contribution corresponding to their statistical weights; the contribution of the slow processes increases with time. The initial parts of the curves are different and depend on the set of ω_i; $\mathbf{D(t)} \rightarrow \mathbf{D}_{\min}$ when $\mathbf{t} \rightarrow \infty$ in any case. Thus, the function **D(t)** comprises the total information on the diffusion mechanism and testifies to a heterogeneity of polymer structure.

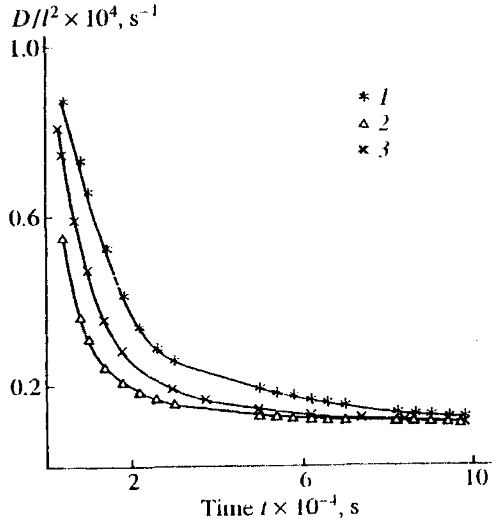

FIGURE 5 Time dependence of apparent diffusion coefficients. The diffusion coefficients of the parallel processes are $\mathbf{D}_i/l^2 \times 10^5$, s^{-1}: 1(**i** = 1), 3(**i** = 2), 10(**i** = 3); curves: 1- $\omega_1 = 0.6$, $\omega_2 = 0.3$, $\omega_3 = 0.1$; 2- $\omega_1 = 0.34$, $\omega_2 = 0.33$, $\omega_3 = 0.33$; 3- $\omega_1 = 0.1$, $\omega_2 = 0.3$, $\omega_3 = 0.6$.

The complexity of sorption kinetic laws does not allow one to obtain the function **D(t)** in an analytical form. The average value of a diffusion coefficient is obtained by extrapolation of **D(t)** to $\mathbf{t}=\mathbf{0}$.

$$\mathbf{D(0)} = \langle \mathbf{D} \rangle_t = \frac{\Sigma\, \omega_i \mathbf{M}_i \mathbf{D}_i^{3/2}}{\Sigma\, \omega_i \mathbf{M}_i \mathbf{D}_i^{1/2}} \tag{9}$$

Comparison of Eqs. (5) and (9) obtained under both steady-state and non-steady-state regimes shows that the latter expression is the average value of higher order than the arithmetic mean characterizing a steady-state flow. This distinction can be a proof that the process occurs in a heterogeneous medium.

The additional information on the features of a diffusion process can be obtained from consideration of diffusion rate dependencies on time in the coordinates $\mathbf{w} \cdot \mathbf{t}^{1/2} \rightarrow \mathbf{t}$. Actually, as shown in [17] for a plate, the initial part of a kinetic curve involves a plateau with a constant value $\mathbf{w} \cdot \mathbf{t}^{1/2}$

$$\mathbf{w} \cdot \mathbf{t}^{1/2} \rightarrow \Sigma \omega_i \mathbf{M}_i\, \mathbf{D}_i^{1/2} = \mathbf{M} \langle \mathbf{D}^{1/2} \rangle \text{ at } \mathbf{t} \rightarrow 0, \tag{10}$$

where $\mathbf{M} = \Sigma \omega_i \mathbf{M}_i$
And

$$\langle \mathbf{D} \rangle_w = \left\{ \frac{(\Sigma\, \omega_i\, \mathbf{M}_i\, \mathbf{D}_i^{1/2})^2}{\Sigma\, \omega_i \mathbf{M}_i^2\, \mathbf{D}_i^{1/2}} \right\}^2 \tag{11}$$

The ratio $\mathbf{D}_t/\mathbf{D}_w$ can serve as a measure of the width of diffusion coefficient distribution, *i.e.* an index for the degree of structure heterogeneity.

For a solid cylinder [19], the plateau on a kinetic curve degenerates into a point on the ordinate axis at $\mathbf{t} \rightarrow \mathbf{0}$. The tangent to the beginning of a kinetic curve intercepts a segment on the abscissa whose value is connected with the average value of a diffusion coefficient:

$$\mathbf{t}^{1/2} \cdot \langle \mathbf{D}^{1/2} \rangle = \frac{\Sigma \omega_i\, \mathbf{M}_i\, \mathbf{D}_i}{\Sigma \omega_i\, \mathbf{M}_i\, \mathbf{D}_i^{1/2}} \cdot \mathbf{t}^{1/2} = \frac{\mathbf{2}}{\pi^{1/2}} \tag{12}$$

The length of the segment intercepted by this tangent on the ordinate is defined by the expression:

$$\mathbf{w} \cdot \mathbf{t}^{1/2} \to \frac{2}{\pi^{1/2}} \cdot \Sigma\, \mathbf{M}_i\, \omega_i\, \mathbf{D}_i^{1/2} \tag{13}$$

Both Eqs. (12) and (13) present the average values of the root square of diffusion coefficients. However, it should be emphasized that the averaging is carried out on different moments of distribution of $\mathbf{D}_i$, and these values are not equal each to other. So, this way is suitable also to estimate a structural heterogeneity in cylindrical polymer bodies.

As to a sphere, the beginning of a kinetic curve is described by equations similar to (12) and (13), but in this case a factor 3 has to be used instead of a factor 2.

APPLICATION OF THE MODEL TO ANALYSIS OF EXPERIMENTAL DATA

The model for determination of the effective diffusion coefficient in complex supermolecular polymer structures has been applied to treat experimental data [19]. The comparison of the different average of the diffusion coefficients, obtained from experimental dependencies $\mathbf{w} \cdot \mathbf{t}^{1/2} - \mathbf{t}$, $\mathbf{D}(\mathbf{t}) - \mathbf{t}$ (see Eqs. (9), (10), (12), (13)) allows one to choose the most probable sorption mechanism.

The dependence of sorption rate on time in the coordinates $\mathbf{w} \cdot \mathbf{t}^{1/2} - \mathbf{t}$ during the sorption process of water vapor by Terlon™ fiber is shown on Figure 6. As one can see, the curve has a straight segment whose extrapolation to both ordinate and abscissa axes allows one to find the desired diffusion coefficients. Note that the nonmonotonic pattern of the curve seems to be connected with the existing gradient structure of the fiber skin-layer.

To confirm this point of view, the experimental data on kinetics of sorption of water vapor into amorphous PEEK [20] have been treated according to the model of parallel diffusion. The diffusion parameters (**w**, **D**) as a function of time are shown in Figures 7 and 8. The average diffusion coefficients calculated from these data are displayed in Table I.

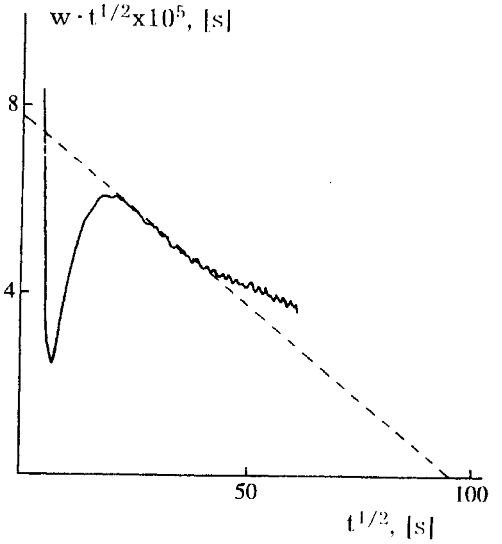

FIGURE 6 Kinetic curve of water vapor sorption by Terlon in coordinates: $w \cdot t^{1/2} - t^{1/2}$.

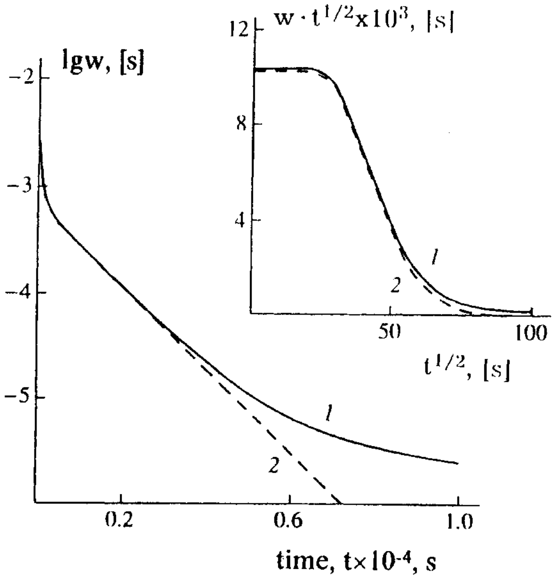

FIGURE 7 Kinetic curve of water vapor sorption by PEEK (The data are taken from [18]). Dashed lines correspond to Fick's law.

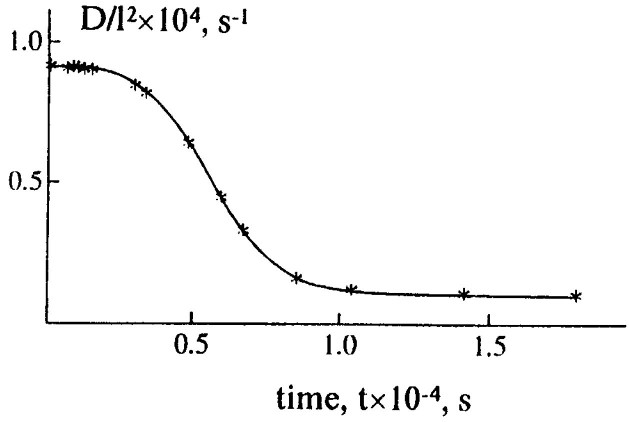

FIGURE 8 Time dependence of the apparent diffusion coefficient calculated from data of [18].

TABLE I Values of the average diffusion coefficients (s^{-1}) obtained from the sorption kinetic curves (data from [18]). $\mathbf{D}^0$ is also taken from [18]; $\langle \mathbf{D} \rangle_t$ and $\langle \mathbf{D} \rangle_w$ were calculated using Eqs. (9) and (11)

Samples	$D^0 \times 10^5$	$\langle D \rangle_t \times 10^5$	$\langle D \rangle_w \times 10^5$
1	9.3	9.2	10.0
2	9.3	9.2	11.8

In this case, the kinetic curves were observed to deviate from Fick's equation: the value of **D** decreases with time. Nevertheless, the values of the different averages of the diffusion coefficients are seen to be practically the same. This means that the sorption process proceeds in a homogeneous structure. The conclusion of the authors [20] that the observed deviations from Fick's law are caused by relaxation retardation of the sorption process seems to be completely justified.

MODEL OF CONSEQUENT DIFFUSION

In bodies with gradient structure the consequent diffusion process has much importance. Note that the model of consequent diffusion does not take into account a real diffusion that proceeds in inhomogeneous systems as the parallel-consequent transfer between regions with different kinetic (diffusion coefficients) and thermodynamic characteristics.

Attempts to solve the problem of diffusion through inhomogeneous media have been made [2, 3, 8, 19]. Numerical methods were used for construction of concentration profiles. However, these data can not be obtained experimentally, especially in thin films and fibers. Generally, the kinetic parameters were evaluated by the time-lag method or/and steady-state characteristics [18]. For a Fickian process the retardation time, τ, obeys the relationship:

$$\tau = \mathbf{b}^2/6\mathbf{D},$$

where **b** is the film thickness.

As shown above, the diffusion coefficients obtained from time-lag data depend on their distribution in the body space if the parallel process takes place. Obviously, the analogous phenomenon has to manifest itself in the case of a consequent process as well.

The diffusion process through a film of thickness, **b**, and diffusant concentration, $\mathbf{c}_0$, on input and $\mathbf{c} = 0$ on output (boundary conditions) and $\mathbf{D(x)}$ being a function of coordinate **x** (one-dimensional diffusion) was treated in [22]. The soluion of the one-dimensional diffusion equation

$$\frac{\partial \mathbf{c}}{\partial \mathbf{t}} = \frac{\partial}{\partial \mathbf{x}}\left(\mathbf{D(x)}\frac{\partial \mathbf{c}}{\partial \mathbf{x}}\right) \tag{14}$$

can be described as:

$$\int_{\mathbf{x}}^{\mathbf{b}} \frac{\partial \mathbf{c(z,t)}}{\partial \mathbf{t}}\mathbf{dz} = \mathbf{D(b)}\frac{\partial \mathbf{c(b)}}{\partial \mathbf{x}} - \mathbf{D(x)}\frac{\partial \mathbf{c(x)}}{\partial \mathbf{x}} = \mathbf{q}_b - \mathbf{q}_x \tag{15}$$

where $\mathbf{q}_x$ is the flow rate through the section with coordinate **x**.

The equation for the output flow **Q(t)** is obtained by integration of Eq. (15) by **x** from **0** to **b**, and by **t** from **0** to **t**, *i.e.*,

$$\mathbf{Q(t)} = \int_0^t \mathbf{q}_b \mathbf{d}\tau = \int_0^t \mathbf{q}_b \mathbf{d}\tau + \int_{\mathbf{x}}^{\mathbf{b}} \mathbf{c(z,t)}\,\mathbf{dz}; \tag{16}$$

$$\int_0^b Q(t)dz = Q(t)b = \int_0^b dz \int_0^t q_x d\tau + \int_0^b dx \int_x^b C(z,t)dz; \qquad (17)$$

For $t \rightarrow \infty$ the output flow tends asymptotically to a steady-state one:

$$Q_a(t) = \frac{1}{b}\left\{ q_{st} t b + \int_0^b dx \int_x^b c_{st}(z)dz \right\}; \qquad (18)$$

where steady-state values of the flow and concentration are obtained from steady-state conditions:

$$q_{st} = D(x)\frac{\partial c}{\partial x} = const; \qquad (19)$$

$$c_{st}(x) = c_0 + q_{st} \int_0^x \frac{dz}{D(z)}; \qquad (20)$$

$$q_{st} = -c_0 \cdot \left[\int_0^b \frac{dx}{D(x)} \right]^{-1}; \quad \text{because of } c_{st}(b) = 0. \qquad (21)$$

So, the value of τ is [23]:

$$\tau = \frac{\int_x^b dx \int_0^b c_{st}(z)dz}{q_{st}\, b}; \qquad (22)$$

The general solution was obtained in [22] where it was shown that

$$\tau = \frac{\int_0^b [(x^2 dx)/(D(x))]}{2b} \qquad (23)$$

and

$$D_\tau^{-1} = \frac{3}{b^3} \int_0^b \frac{x^2 dx}{D(x)}; \qquad (24)$$

The effective diffusion coefficient from steady-state data can be obtained using Eqs. (21) and (22):

$$D_{st}^{-1} = \frac{1}{b} \cdot \int_0^b \frac{dx}{D(x)}; \qquad (25)$$

As one can see, the values of **D** obtained by different methods of averaging, naturally, are different. So, in the case of a consequent diffusion process we have the analogous result: the dependence of the diffusion coefficient on the method of its measurement.

CONCLUSION

The proposed method of analysis of sorption kinetics in a non-steady diffusion regime enables one to obtain useful information about the mechanism of sorption processes and, accordingly, about heterogeneity of polymer structure. To our mind, this approach is applicable to investigate different polymer bodies with complex supermolecular structure. Different average values of kinetic parameters of a sorption process (diffusion coefficient and ultimate concentration of sorbed substances) can be obtained from the beginning of the kinetic curve. The advantage of such an approach is obvious. Really, it allows one to characterize an initial state of a polymer while its structure has not been changed by interaction with a low molecular sorbate. Moreover, the direct comparison of the ultimate concentration of sorbed substance calculated from kinetic curves with one obtained from sorption equilibrium data allows one to estimate the influence of a sorbate on polymer structure.

The time dependence of the diffusion coefficient in heterogeneous bodies, as mentioned above, is assumed to be connected with the existence of fractal structures. Actually, such a structure should comprise channels (where diffusion can occur) and barrier regions (where the transfer is forbidden). But in this case the dependence $\mathbf{D} \sim \mathbf{t}^{-n}$, Eq. (1) can be valid only in the narrow structure interval near the percolation threshold. Obviously, such a situation should be rare. On the other hand, this time dependence stipulated by the availability of a spectrum of diffusion coefficients must be a general phenomenon. This explanation seems to be more preferable.

One more circumstance which has to be taken into account in consideration of diffusion processes in inhomogeneous polymers is the existence or absence of a solid surface (or, in other words, the rate of relaxation of the surface structure). Note, the meaning "surface" related to polymer solids implies a more or less thick layer: its thickness is much more than a monomolecular layer. If the relaxation process proceeds with sufficiently high rates, the structures at the surface and in the bulk will be identical. In this case, the equilibrium gas-polymer bulk will obeys Henry's law (taking into account the polymeric nature by using Flory-Huggins' theory). In the opposite case, when the rate of surface relaxation is rather low, one must consider the total equilibrium as based on the principle of detailed equilibrium:

gas–surface (I)

and

surface–bulk (II)

(I) obeys Langmuir or BET laws: $\mathbf{a} = \mathbf{f(p)}$, where **a** is surface concentration of sorbate, **p** is sorbate pressure.

(II) leads to: $\mathbf{c} = \mathbf{K} \cdot \mathbf{a}$ where **c** is bulk concentration of sorbate, **K** is the equilibrium constant. As a consequence, $\mathbf{c} = \mathbf{K} \cdot \mathbf{f(p)}$. This means that the bulk concentration of sorbate depends on the vapor pressure in the same manner as the surface concentration.

This conclusion is readily apparent from general thermodynamic concepts. Actually, the free energy of a system is connected with surface energy as:

$$\mathbf{F} = \mathbf{U} - \mathbf{TS} + \gamma \cdot \mathbf{A} \tag{26}$$

where γ is surface energy and **A** is surface area. Differentiation of Eq. (26) with respect to sorbate concentration, **c**, gives:

$$\mu_v = \mu_g + \mathbf{A} \cdot \partial \gamma / \partial \mathbf{c} \tag{27}$$

Here μ_v and μ_g are chemical potentials of the sorbate in the bulk and gas phases, respectively.

These considerations should be taken into account in analyzing the processes of sorption and transfer in polymer bodies.

Finally, we should like to underline once more that the sorption interaction between polymer fillers and binder components leads to formation of extended interface layers. Obviously, their structure and properties would determine the value of the adhesion interaction in composites. Therefore, the understanding of the kinetic features of the sorption processes occurring during composite formation is very important.

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