A COMPARATIVE ANALYSIS OF MOISTURE TRANSPORT
MODELS AS APPLIED TO AN EPOXY BINDER

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The results of experimental and theoretical investigations into the kinetics of moisture sorption by a neat epoxy resin obtained from RAE Industries (Reapox 520, D523) are reported. The sorption process was realized in atmospheres with a constant relative humidity of 33, 53, 75, 84, and 97% and a temperature of 50°C. The results obtained showed that the diffusion behavior of epoxy resin did not obey Fick's law under the experimental conditions considered. Consequently, the application of a non-Fickian diffusion model was necessary. For this purpose, two-phase moisture sorption models, a model with a time-dependent diffusivity, a two-phase material model, as well as relaxation and convection models of anomalous diffusion, were considered. The model parameters were obtained from the approximation of experimental sorption data. A comparative analysis of the sorption models was performed, and the specific features of their applications were estimated. The two-phase material model and the model with varying diffusivity were found to be the most suitable ones due to a good agreement between calculation results and experimental data and the rather small (three or four) number of parameters, which make them more flexible and physically more justified than the classical Fick's model with its two parameters.

Introduction

The extensive application of epoxy resins is explained by their structural features and high operational properties, the ability to be cured in a wide temperature interval, the insignificant shrinkage, the non-toxicity in the cured state, the high values of adhesion and cohesion strength, and the chemical stability. In this connection, epoxy resins are used as binders to create materials with good physicomechanical properties. However, epoxy binders, as well as the majority of other ones, have a considerable drawback, namely a rather high moisture sorption, which noticeably degrades their functional, structural, and mechanical properties [1, 2].

Materials based on polymers are frequently exposed to a humid environment. Water molecules, as well as low-molecular substances, are able to move in a polymeric binder and change its physical properties. The key parameters determining the mechanism of moisture sorption are the chemical composition and microstructure of the polymers.

The moisture sorption in epoxy binders and composites based on them is investigated rather well. Different models have been suggested for describing the water sorption kinetics [3-10]. It is usually assumed that the moisture sorption in epoxy

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binders proceeds by diffusion according to Fick's law [3, 11]. Such a model, which suits well the initial stage of moisture sorption, is often inadequate for describing the moisture sorption process as a whole. The moisture sorption can activate different processes in a material, which, in turn, affect the water sorption kinetics (chemical reactions, leaching of low-molecular components, etc.). Therefore, the purpose of this study is to estimate the applicability of different moisture transport models to describing experimental data on water sorption in epoxy binders and to determine the most adequate ones.

Materials and the Experimental Procedure

We investigated a Reapox 520 epoxy binder presented by the RAE Industries company. The cure process was performed in four steps. First, the binder was cured at 20°C for 7 days. Then, the material was held for 24 h at a temperature of 40°C, annealed at 130°C, and rapidly cooled down to 50°C.

The specimens were made in the form of thin plates $50 \times 20 \times 2$ mm in size, so that to favor the one-dimensional diffusion. They were moistened in atmospheres with various humidity $\varphi = 34, 53, 75, 84,$ and 97%, at a temperature of 50°C, which were created by using saturated solutions of $MgCl_2$, $Mg(NO_3)_2$, $NaCl$, KCl, and K_2SO_4.

The specimens were weighed periodically, and their mass increment $m(t) - m_0$ against the initial mass m_0 was used to find the moisture content during sorption

$$w(t) = \frac{m(t) - m_0}{m_0}.$$

Sorption Models

Let us clear up the applicability of basic sorption models to describing the moisture sorption process in the epoxy binder.

Classical model with a constant diffusivity

In this model [3], it is assumed that moisture sorption occurs only by diffusion. According to the first Fick's law, the diffusant flow density j is directly proportional to the gradient of its concentration c:

$$j = -D\,\mathrm{grad}\,c, \tag{1}$$

where D is the diffusivity, describing the rate of moisture sorption, which is independent of moisture concentration. For a nonstationary state, with account of the mass conservation law, the second Fick's equation is valid. For the case of a one-dimensional diffusion along the x axis, when the specimen thickness is smaller than its length and width, it has the form

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}, \tag{2}$$

where c is the moisture concentration in the specimen at the instant of time t.

The solution to Eq. (2) for a plane-parallel plate of thickness h, with initial $c\,(0 \le x \le h, t = 0) = c_0$ and boundary $c\,(x = 0, x = h, t > 0) = c_\infty$ conditions, is the series [3]

$$c(x,t) = c_\infty - 2\frac{(c_\infty - c_0)}{\pi}\sum_{k=1}^{\infty}\frac{[1-(-1)^k]}{k}\sin\left(\frac{k\pi}{h}x\right)\exp\left[-\left(\frac{k\pi}{h}\right)^2 Dt\right]. \tag{3}$$

Integrating Eq. (3) across the plate thickness, we come to an expression for determining the moisture content in the specimen:

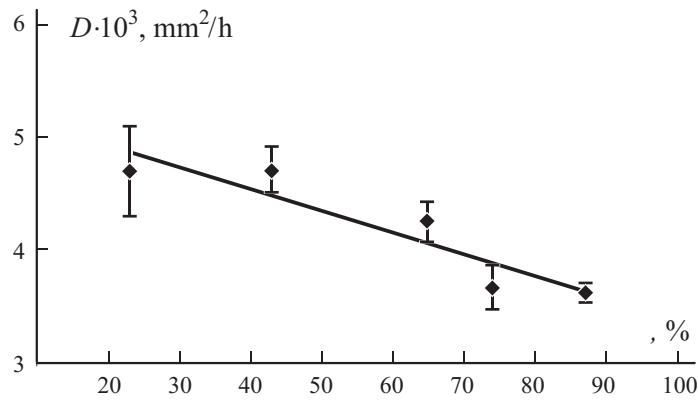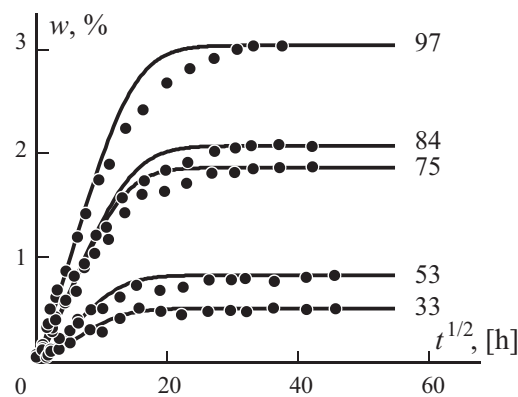Fig. 1. Diffusivity D vs. the relative humidity φ of environment.

Fig. 2. Changes in the specimen mass with time at different values of φ (numbers next to the curves): experimental data (dots) and calculations by Fick's model (4) (curves).

$$w(t) = w_\infty - 2(w_\infty - w_0) \sum_{k=1}^{\infty} \frac{[1-(-1)^k]^2}{k^2} \exp\left[-\left(\frac{k\pi}{h}\right)^2 Dt\right].$$

(4)

Here, w_∞ is the equilibrium moisture content in the specimen. Thus, the model considered contains two material characteristics as parameters: the diffusivity D and the equilibrium moisture content w_∞. In numerous studies (e.g., [3]), it is shown that, if the sorption curve is drawn on a diagram whose abscissa axis is $\sqrt{t}$, the initial section of this diagram will be a straight line passing through the origin of coordinates. Then, using experimental data, the diffusivity can be determined from its inclination:

$$D = \frac{h^2 \pi}{16t} L^2,$$

(5)

where $L = \dfrac{w(t) - w_0}{w_\infty - w_0}$ is the change in the moisture content $w(t) - w_0$ in the specimen by the instant of time t, normalized to its maximum value. The second parameter of the model — the equilibrium moisture content — as a rule, is found experimentally as the maximum moisture content achieved in the specimen. We should note here that, according to Eq. (4), this maximum is achieved only asymptotically at $t \to \infty$, which in practice leads to an error in determining w_∞. The relation between the diffusivity found by Eq. (5) and φ of the environment is shown in Fig. 1.
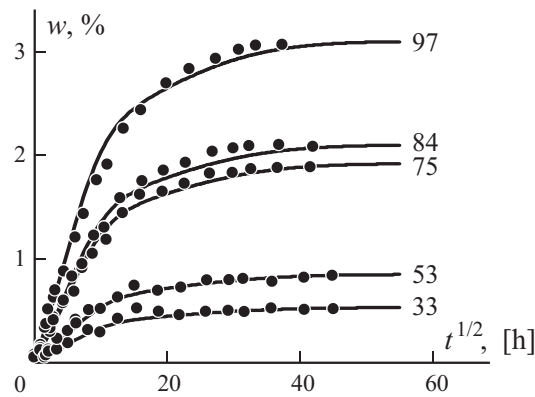
Fig. 3. Changes in the specimen mass with time at different values of   (numbers next to the curves): experimental data (dots) and calculations by Eq. (6) (curves).

The results from calculating the moisture content by Eq. (4) and experimental data for atmospheres with various humidity are shown in Fig. 2. It is clear that the Fick's model describes well the process of moisture sorption in a low-humidity atmosphere, but when the relative humidity exceeds 75%, the moisture sorption process slows down in the middle part of sorption curve.

In other words, the value of moisture sorption rate used in the calculation is overestimated, since the model disregards the processes of interaction between the moisture and polymer, swelling, etc., which accompany the process of moisture sorption. It is seen that the adequacy of Fick's model declines with increasing relative humidity of environment, since the diffusion mechanism becomes less dominating, and other mechanisms, such as the interaction between the polymer and the diffusant and/or relaxation processes, start to affect the moisture transport in the polymer [12]. The alternative models of moisture sorption which can be used to explain the deviation of moisture transport in polymers from the classical diffusion mechanism with a diffusivity independent of moisture concentration, take into account different subtle differences in the moisture sorption process in each particular case.

A model taking into account the two-phase state of absorbed moisture in the material

This model, known as the Langmuir model, is described, for example, in [4, 5]. According to this model, the anomalous moisture sorption in epoxy binders can be explained on the assumption that the absorbed moisture exists in two — free and bound — phases. The free-phase molecules diffuse with a diffusivity independent of diffusant concentration and are absorbed (become bound) with a probability   in a unit time. The molecules leave the bound state with a probability   in a unit time. Therefore, the process of diffusion is described by the same equation of diffusion (2), which is only modified and now takes into account the two-phase state of moisture in the material.

According to this model, the moisture content in a material, as a function of time $w(t)$, depends on four parameters: D, w, and the probabilities   and   and is expressed by the formula

$$w(t) \quad w \quad 1 \quad \text{—} \exp(\quad t) \quad \frac{2}{2} \sum_{k \; 0} \frac{[1 \quad (\quad 1)^k \,]^2 \exp\left[\quad \frac{k^2}{h}^2 Dt \right]}{k^2} \; .$$

(6)

The results of calculations by the Langmuir model, depicted in Fig. 3, show a better description of the sorption curve with account of the two-phase nature of moisture in the epoxy binder. This in turn means that, although the moisture sorption process could proceed by diffusion, some part of the water molecules absorbed was connected with polymer molecules, but some part was free.
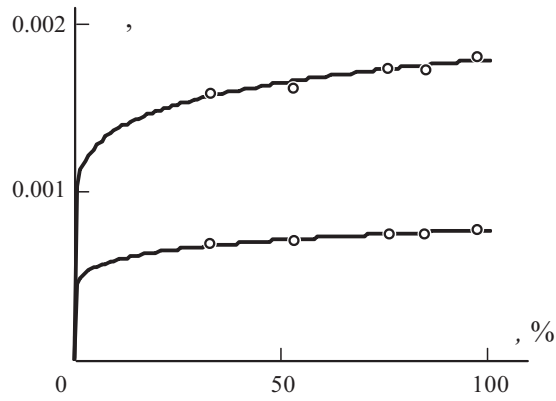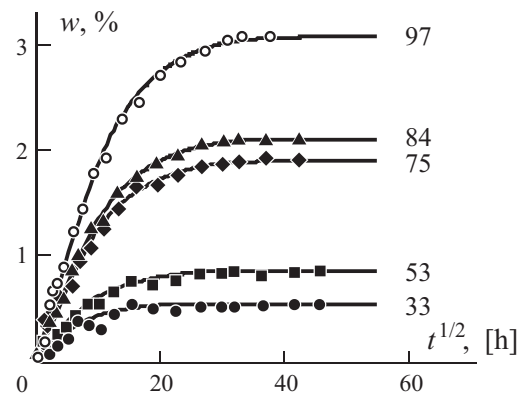
Fig. 4. Probabilities   and   vs. .

Fig. 5. Changes in the mass of specimens with time at different values of   (numbers next to the curves): experimental data (dots) and calculations by Eq. (7) (curves).

The growing values of the parameters   and   with increasing humidity of environment, shown in Fig. 4, points to the increased possibility of transition of water molecules from the bound state into the free one and back. It is seen that, since the possibility for water molecules to become bound is much lower than to become free, the process of interaction between water and polymer can be presented as a constant migration of diffusant molecules from the bound state into the free one.

A model taking into account the two-phase nature of the material

In the model known as the Jacob's–Jones model [6], it is assumed that the material consists of two phases of different density and, accordingly, different sorption properties. It is assumed that the moisture sorption process in both the phases proceeds simultaneously and obeys Fick's law. The possibility of formation of chemical bonds between water and polymer molecules is neglected.

The moisture content in each phase of the material is expressed by the formulas

$$w_1(t) \quad w_{1} \quad 2\frac{(w_{1} \quad w_0)}{2}\sum_{k \quad 1}\frac{[1 \quad (\quad 1)^k]^2}{k^2}\exp \quad \frac{k}{h}^2 D_1 t \quad,$$

$$w_2(t) \quad w_{2} \quad 2\frac{(w_{2} \quad w_0)}{2}\sum_{k \quad 1}\frac{[1 \quad (\quad 1)^k]^2}{k^2}\exp \quad \frac{k}{h}^2 D_2 t \quad,$$
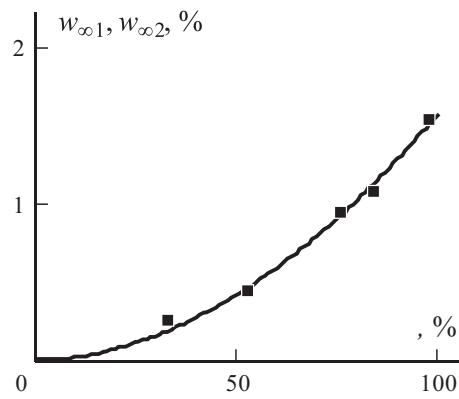
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Fig. 6. Sorption isotherms of two phases. The values of $w_{\infty 1}$ and $w_{\infty 2}$ (dots) are obtained by approximating the sorption curve by Eq. (8) at $w_1 = 2.55$, $k = 0.73$, and $f = 0.59$ (see Fig. 5).
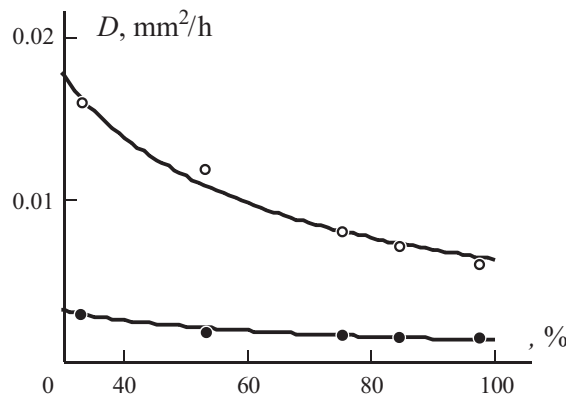

Fig. 7. Diffusivity of the phases D_1 (○) and D_2 (●) vs. φ.

which contain four unknown parameters, namely the equilibrium moisture content and the diffusivity of each of the phases. The total moisture content in the specimen is

$$w(t) = w_1(t) + w_2(t), \tag{7}$$

where $w_1(t) = \dfrac{\Delta m_1}{m_0}$ and $w_2(t) = \dfrac{\Delta m_2}{m_0}$; Δm_1 and Δm_2 are the mass increments of the phases with respect to the specimen mass.

The calculation by Eq. (7), presented in Fig. 5, agrees with experimental data rather well for all the values of φ, which means that the epoxy binder can be two-phase. It is known that epoxy resins contain both areas with a sufficiently perfect and dense spatial network and poorly cross-linked regions, which can be regarded as a two-phase structure of the material. This model does not take into account possible changes in the material microstructure during the sorption process, which can be expressed in a worse description of sorption curves with increasing relative humidity of the environment, as seen from Fig. 5. Nevertheless, it can be used for an objective estimation of sorption characteristics of materials with a nonuniform structure.

An advantage of the given model is the possibility of describing the equilibrium moisture content by the Guggenheim–Anderson–De Boer equation [6]

$$w_\infty = w_1 \frac{kf\varphi}{(1 - f\varphi)[1 + (k-1)f\varphi]}, \tag{8}$$
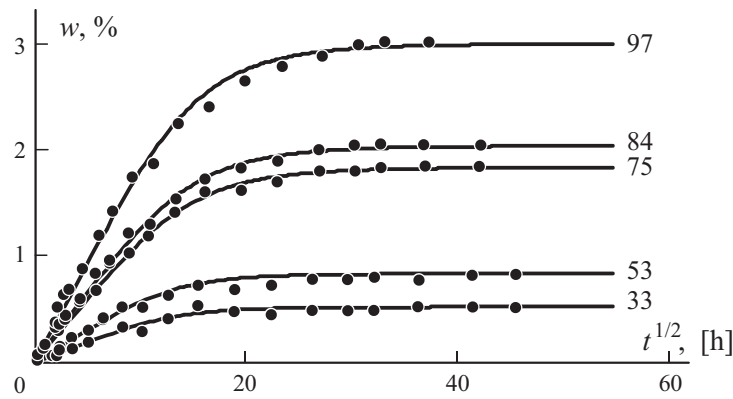
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Fig. 8. Approximation of experimental sorption data according to the model with a time-variable diffusivity for different   (numbers next to the curves).

where w_1 is the moisture content connected with the more hydrophilic phase, k is the factor of bond strength between water and polymer molecules, and f is the ratio between the chemical potentials of an indirectly bound diffusant molecule and a diffusant molecule in the free liquid state. The low values of f (f 1) indicate that the polymer is hydrophobic. It is assumed in this case that sorption ability of both material phases is equal, w_1 w_2.

As seen from Fig. 6, formula (8) is good for describing the sorption isotherm. In turn, it follows from Fig. 7 that the diffusivity in the different phases differs several times. Probably, this reflects the real material structure, with areas of relatively small and high permeabilities. The account of two-phase nature of the system allows one to improve the description of the sorption curve.

A model with a time-dependent diffusivity [7]

According to this model, owing to the physical processes going on in the material (primarily, the plasticization and associate changes in the relaxation character, as well as aging, aftercure, etc.), the diffusivity decreases with time in proportion to its current value:

$$\frac{dD}{dt} \quad D(t).$$

The solution of this equation is D $D_0 e^{\quad t}$. This model contains three parameters — the diffusivity at the initial instant of time D_0, the equilibrium moisture content w , and the coefficient   describing the rate of change in diffusivity.

To reduce the diffusion equation to Eq. (2) with a constant diffusivity D, we use the principle of modified time, by analogy with the change in D under a nonstationary temperature [13]:

$$dt \quad e^{\quad t} dt, \quad t \quad \int_0^t e^{\quad t} dt \quad \frac{1 \quad e^{\quad t}}{}. \tag{9}$$

Then, the diffusion equation takes the form

$$\frac{C}{t} \quad D_0 \quad C. \tag{10}$$

Using the earlier-found solution (4) to Eq. (2) and replacing t with t , according to Eq. (9), the solution to Eq. (10) for the one-dimensional case has the form
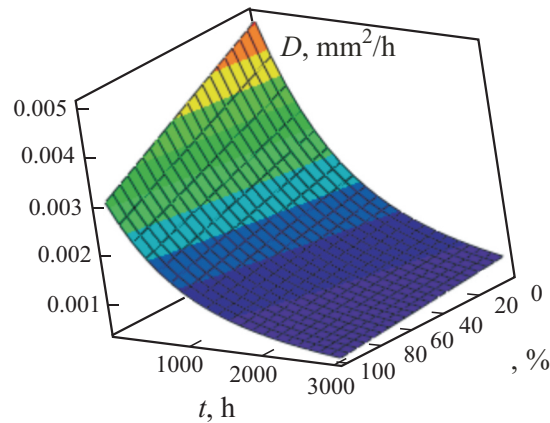
Fig. 9. Diffusivity D as a function of time t and the relative humidity φ of environment.

$$w \quad w \quad \frac{2(w \quad w_0)}{\sum\limits_{k \quad 1} \quad 2} \frac{[1 \quad (\quad 1)^k]^2}{k^2} e^{-\mu_k^2 F}, \tag{11}$$

where $F \quad \dfrac{D_0}{a}[1 \quad \exp(\quad \gamma t)]$; $\mu_k \quad \dfrac{k}{\quad}$; F is the Fourier criterion, $\gamma \quad 1/\quad$, and $\quad$ is the characteristic time of relaxation. A description of the sorption curve by Eq. (11) is shown in Fig. 8.

The diffusivity D as a function of time and the relative humidity of environment is shown in Fig. 9. It is seen that, at great times, the diffusivity tends to an infinitesimal value, which describes the saturated state of the system. During moisture sorption (for about 450 h) at $\varphi = 98\%$, $D_0 = 3.61 \cdot 10^{-3}$ cm^2/h, and $\quad = 0.002$, the diffusivity decreased 4-6 times. In general, due to the presence of three parameters, the model is relatively flexible and can describe the sorption curves rather well (Fig. 8).

Relaxation model of anomalous diffusion

This model [9] considers the time-dependent boundary conditions

$$\quad(t) \quad m_1 \quad (\quad_0 \quad \quad_1)\exp(\quad rt), \quad r \quad 0, \tag{12}$$

where $\quad$ and $\quad$ are the initial and limiting moisture concentrations and r is the constant of relaxation. The quantity $\quad$ is a characteristic of the supermolecular structure, reflecting the diffusant-caused structural transformations in the polymer. These transformations can be described by changing the equilibrium boundary conditions, i.e., by regarding them variable. Thus, for the boundary conditions $c(x,0) \quad c_0$ and $c(0,t) \quad c(h,t) \quad \quad(t)$, the moisture content in a plane-parallel plate of thickness h is calculated by the formula

$$w(t) \quad M_1 \quad (M_0 \quad M_1)\exp(\quad rt) \quad 8 \sum\limits_{k \quad 0} S_k, \tag{13}$$

where

$$S_k \quad \frac{V_0 n_k^2 \dfrac{D}{h^2} \quad V_1 r \quad \exp \quad n_k \dfrac{Dt}{h^2} \quad r(M_1 \quad M_0)\exp(\quad rt)}{n_k^2 \quad n_k^2 \dfrac{D}{h^2} \quad r},$$
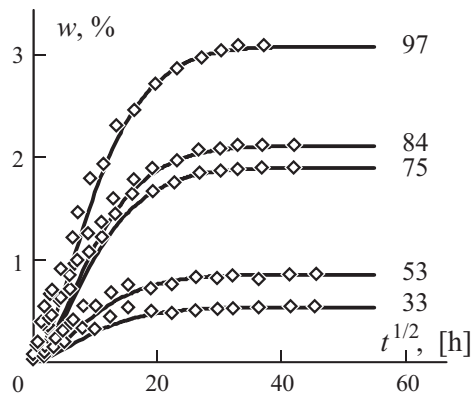
Fig. 10. Changes in the mass of specimens with time at different values of (numbers next to the curves): experimental data (dots) and calculations by relaxation model (13) (curves).

$$V_0 \quad M_0 \quad C_0, \quad V_1 \quad M_1 \quad C_0, \quad n_k \quad (2k \quad 1), \quad M_0 \quad h_0, \quad M_1 \quad h_1, \quad C_0 \quad hc_0.$$

The calculation according to model (13), shown in Fig. 10, describes the sorption curves at great times rather well, but underestimates the rate of moisture sorption at the initial stage. Another drawback of this model is the presence of a great (five) number of coefficients, which complicate calculations and, in this case, have no exact physical meaning. Therefore, although this model accounts for the relaxation in materials which occurs under any boundary conditions, it is more suitable for describing the process of moisture sorption under a nonstationary humidity. An example of nonstationary humidity is a seasonally varying humidity of the environment.

Convection model of anomalous diffusion

Upon nonuniform moisture sorption, layers with different moisture contents can arise in the material, which leads to the appearance of a diffusant flow through the material. The process of moisture convection can be taken into account by supplementing the equation of diffusion (2) with an additional term:

$$\frac{c}{t} \quad D \frac{^2c}{x^2} \quad v \left| \frac{c}{x} \right|, \tag{14}$$

which describes the diffusant flow at a rate v. The solution of Eq. (14) is found for the initial and boundary conditions

$$c(x,0) \quad 0 \quad \text{and} \quad c(0) \quad c(l,t) \qquad _0. \tag{15}$$

For the equilibrium state, we have

$$D \frac{^2c}{x^2} \quad v \left| \frac{c}{x} \right| \quad 0, \tag{16}$$

where $c \quad (0) \quad c \quad (l,t) \qquad _0$. The solution to Eq. (16) is

$$c \quad (x) \quad \frac{_0 \; 1 \; \exp \; \frac{v}{D} \left| x \quad \frac{h}{2} \right|}{1 \; \exp \; \frac{vh}{2D}}. \tag{17}$$

As a result of integrating Eq. (17) across the specimen thickness, we find the limiting moisture content in the specimen

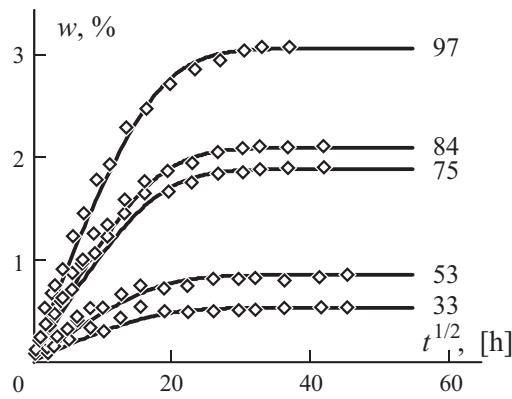$$w \quad \frac{M_0}{1 \; \exp} \quad \frac{\exp}{} \quad 1 \;, \tag{18}$$

Fig. 11. Changes in the mass of specimens with time at different values of (numbers next to the curves): experimental data (dots) and calculations by convection model Eq. (19) (curves).

where M_0 h $_0$ and $-\dfrac{vl}{2\,D}$ is the parameter determining the convection rate. It is logical that the solution of Eq. (14), with account of Eq. (15), at great times tends to solution (18).

Integrating the solution of Eq. (14) across the specimen thickness h, we come to the expression for moisture content in the specimen

$$w(t) \quad w \quad \frac{16 M_0 \; \coth 0.5}{1 \quad \exp}$$

$$\sum_{k \; 0} \frac{n_k [n_k \; \exp 0.5 \qquad {}^{k \; 1}]}{(\qquad n_k^2)^2} \exp \quad (n_k^2 \qquad {}^2)\frac{D}{h^2} t \quad , \tag{19}$$

where n_k $(2k \; 1)$.

The results of calculations by Eq. (19), shown in Fig. 11, point to a rather good description of sorption curves at all stages of moisture sorption for all the atmospheres considered, but the great (five) number of coefficients complicates the calculation. Therefore, the application of the given model is justified only in the case of heavily swelling polymers, whose sorption capacity is high [9].

Comparison of Models

The sorption models considered in the present study reflect the process of moisture sorption in different ways, taking into account certain additional processes occurring in a material. These models describe experimental data rather well, but not always can we agree with the physical meaning laid in them for describing some particular situation, as in the case of convection and relaxation models of anomalous diffusion. Therefore, in each specific case, one must be guided not only by the results of good approximation, but also by the physical interpretation of the complex process of moisture sorption included in the models.

Figure 12 presents a comparison between all the models examined in this study for an atmosphere with the maximum relative humidity = 97%. To evaluate the correspondence between the calculations and experimental results, the sum of all absolute deviations s $\sum_i \left| w_i^e \quad w_i \right|$ of the calculation results w_i from the experimental data w_i^e was determined. It is seen that the presence of a greater number of parameters leads to a better description of experimental data. However, in choosing a suitable model, the number of parameters used in the model should also be considered.
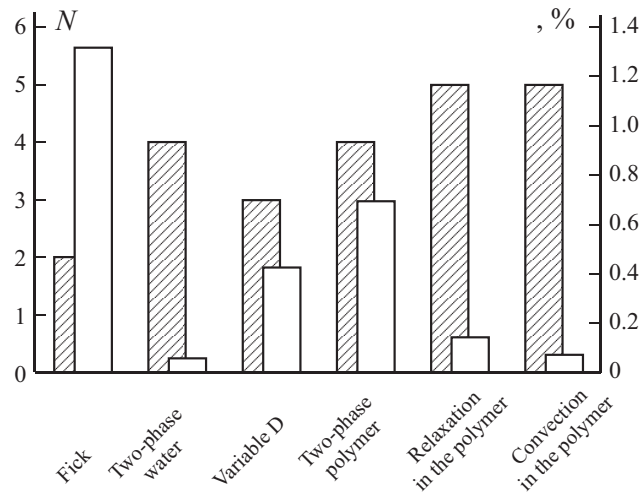
Fig. 12. Comparison of moisture sorption models at = 97%. *N* is the number of parameters
(▨), and is the absolute deviation, % (☐).

Consequently, the models most suitable for describing the kinetics of moisture sorption for the particular epoxy binder are the two-phase model taking into account the two-phase nature of materials and the model with a variable diffusivity. The latter one has only three parameters and agrees well with experimental results. The model with a two-phase material, in turn, is characterized by four independent parameters, but it has a good physical basis — the two-phase nature of the system, with corresponding values of diffusivity and equilibrium moisture content for each phase.

Conclusions

In this study, a comparative analysis of various moisture sorption models, based on different assumptions and boundary conditions and distinct physical interpretations of the process of moisture sorption, as applied to an epoxy binder moistened in atmospheres with different relative humidity has been carried out. It is shown that, with increased environmental humidity, the classical Fick's model is unable to adequately describe the process of moisture sorption, since it takes into account only the diffusion mechanism. In such cases, it is also necessary to consider the additional processes arising during moisture sorption in the material.

It is shown that a good approximation of experimental data not always evidence the validity of a model, even in the case where they are physically substantiated. For example, the Langmuir model and the model with a two-phase material are based on different physical interpretations of the process, each of them is physically admissible, and both give good approximations of experimental data. Consequently, the true applicability of a model can be confirmed by check tests including sorption–desorption cycles or sorption under nonstationary environmental conditions.

Most suitable for describing the sorption kinetics are found to be the model taking into account the two-phase nature of materials and the model with a variable diffusivity. These models give results agreeing rather well with experimental data and, in addition, contain a relatively small number of parameters, which make them more acceptable in practical applications.

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