RANDOM MIGRATION OF MOISTURE IN COMPOSITE MATERIALS

V. I. Barakhov, V. V. Chernyaev,
and V. I. Goncharov

UDC 541.18+539.217.1

The mathematical description of the migration of moisture in composites based on a Markov random process is analyzed. The physical aspect of the model is revealed by means of x-ray computational tomography. An expression is obtained for the pore-tortuosity coefficient.

The penetration of moisture in polymer composite materials consisting of a reinforcing filler and a polymer matrix has specific features associated with the laminar structure of the material, the alternation of tangential and spiral layers, and the presence of pores.

The process is random in character, and is determined by the random distribution of pores, cracks, and cleavages, their sizes and spatial orientations. As shown by tomographic investigation of the internal structure of composites [1], the basic channels of moisture penetration are formed at the intersection of two adjacent bands. The presence of a large number of random factors associated with the tension of the strip in winding, the percentage application of binder, the heat-treatment conditions, the spread of the characteristics of the initial components, and so on lead to the formation of paths of random moisture migration in composite materials.

Individual realizations of this random process may be observed by means of x-ray computational tomography. With the aim of revealing the macrokinetics of the process, a series of tomographic experiments are undertaken on the penetration of water in samples. The position of the sample remains constant. After repeated scanning of a fixed cross section with progressive penetration by water and the derivation of tomograms and matrices of linear attenuation coefficients (LAC) characterizing the density of each elementary cell, the initial scan is subtracted from each subsequent one. The macrokinetics of the penetration of water or moisture into the material may be judged from the variation in cell density. The results of one such experiment are shown in Fig. 1. Analyzing Fig. 1, it may be concluded that initially water penetrates into local defects of the outer layer of composite, propagating along the bands of reinforcing filler through pores and capillaries. Water migration in the first layer continues until a transverse defect is reached. The possibility of passing to the second layer then appears. The character of propagation here is as in the first layer. This process continues in the same way until the water reaches the other surface of the sample. Thus, random migration of water (moisture) occurs in composites, by motion of the water along the layers in the direction of the reinforcement in interband spaces which form channels of totally arbitrary form and cross-sectional dimensions and transition to the next layer on reaching a transverse defect.

Simultaneously with the capillary mechanism of moisture penetration, a diffusional mechanism must also be considered. Diffusion in a fixed elementary cell begins at the moment of appearance of the diffusing material in its capillaries. The random character of moisture migration in composites determines the randomness of the moisture-transfer parameters, one of which is the tortuosity. This parameter appears in the equation describing the behavior of the moisture—composite system and largely determines the accuracy of estimation of the output characteristics of the process. It is used to determine the effective diffusion coefficients [2]. Tortuosity is regarded as one of the probabilistic characteristics of moisture transfer in composites.

Two assumptions may be made for the given process:

1) the states in which the sample-moisture system resides are discrete, since the material may be divided into individual layers according to the winding scheme and sharp bound-

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 59, No. 5, pp. 801-807, November, 1990. Original article submitted October 2, 1989.

0022-0841/90/5905-1427$12.50

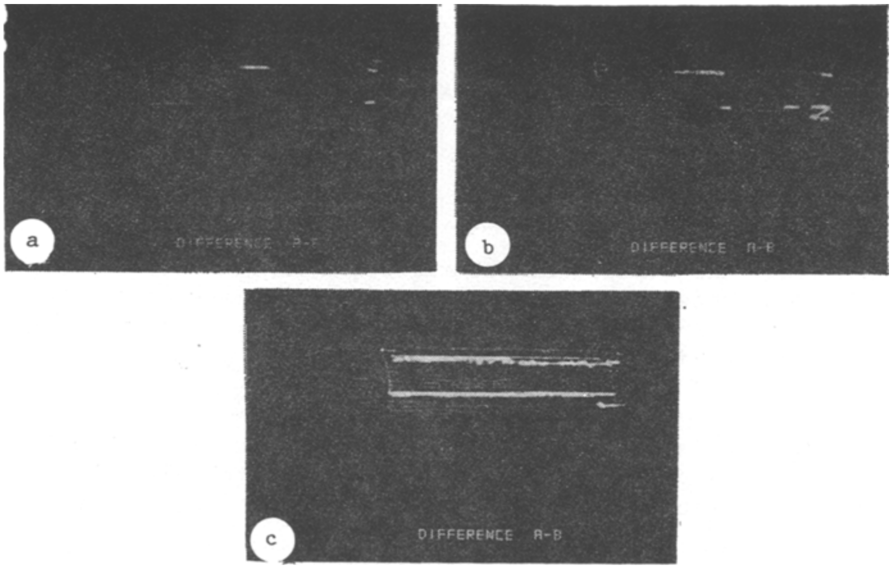

Fig. 1. Tomograms corresponding to subtraction of images of the cross section of an organic-plastic sample in the experimental investigation of water propagation: a) at time Δt_1 = 380 sec; b) Δt_2 = 840 sec; c) Δt_3 = 3780 sec.

aries of the beginning and ending of residence of the system in each state may be noted; their set forms a sequence ("chain") with continuous time;

2) for each time $t = \tau$, the probability of any discrete state S_{i+1} in the future ($t > \tau$) depends only on its state S_i at present and does not depend on how long it has been in this state.

Therefore, the sequence of states of the system corresponds to the condition of an ordinary flux of events. Transitions of the system from state to state occur at random times, which cannot be determined solely from its state, and the probability of transition from one state to another at time Δt is $\lambda_{ij}\Delta t$ [3]. Thus, the penetration of moisture in a composite may be interpreted as a Markov random process with discrete states and continuous time, under the assumption that the real flux of events is replaced by a Poisson flux.

In accordance with the laminar structure of the composite determined by the winding scheme, the penetration of moisture may be divided into the following individual states: S_1, the initial "dry" state of the material; S_{i+1}, the state of the material with moisture in pores of the layers 1, 2,...,i (i = 1, 2,..., n); S_d, the state of the material characterized by the diffusion of moisture. Transition from one state to another occurs randomly here. A graph of states of water migration in a composite with the given probability densities of transition $\lambda_{i,i+1}$ from state S_i to state S_{i+1} is shown in Fig. 2. As is known, the process described by the scheme of a Markov random process with discrete states and continuous time is characterized by the probability $P_k(t)$ and the mean residence time t_k of the system in each of its states. The probability of its residence in each of the states in Fig. 2 is described by the Kolmogorov system of equations [2]

$$\dot{P}_1(t) = -\lambda^*_{1,2}P_1(t); \quad \dot{P}_2(t) = \lambda_{1,2}P_1(t) - \lambda^*_{2,3}P_2(t);$$
$$\cdots\cdots\cdots\cdots\cdots\cdots$$
$$\dot{P}_i(t) = \lambda_{i-1,i}P_{i-1}(t) - \lambda^*_{i,i+1}P_i(t); \tag{1}$$
$$\cdots\cdots\cdots\cdots\cdots$$
$$\dot{P}_n(t) = \lambda_{n-1,n}P_{n-1}(t) - \lambda^*_{n,d}P_n(t); \quad \dot{P}_d(t) = \sum_{i=1}^{n} P_i(t)\,\lambda_{id},$$

where $\lambda^*_{i,i+1} = \lambda_{i,i+1} + \lambda_{i,d}$. At any time t, the normalizing condition

$$\sum_{i=1}^{n} P_i(t) + P_d = 1 \tag{2}$$

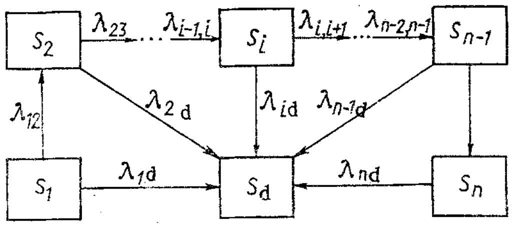

Fig. 2. Graph of states of the composite—moisture system.

is valid here, and the initial conditions are written in the form (t = 0)

$$P_1(0)=1,\quad P_2(0)=P_3(0)=\ldots=P_n(0)=P_d(0)=0. \tag{3}$$

Taking account of Eq. (3), the solution of Eq. (1) for the probabilities $P_1(t),\ldots,$ $P_n(t)$ takes the form

$$P_k(t)=\sum_{j=1}^{k}\frac{\prod_{i=1}^{k-1}\lambda_{i,i+1}}{\prod_{i=1}^{k}(\lambda^*_{i,i+1}-\lambda^*_{j,j+1})}\exp(-\lambda^*_{j,j+1}t)+\alpha_k\exp(-\lambda^*_{nd}t); \tag{4}$$

when k = 1

$$\frac{\prod_{i=1}^{k-1}\lambda_{i,i+1}}{\prod_{i=1}^{k}(\lambda^*_{i,i+1}-\lambda^*_{j,j+1})}=1;\quad \lambda^*_{i,i+1}\neq\lambda^*_{j,j+1},$$

where

$$\alpha_k=\begin{cases}\dfrac{\prod_{i=1}^{k-1}\lambda_{i,i+1}}{\prod_{i=1}^{k}(\lambda^*_{i,i+1}-\lambda^*_{n,d})} & \text{when } k=n,\\ 0 & \text{when } k=1,\ 2,\ \ldots,\ n-1.\end{cases}$$

It follows from the normalizing condition in Eq. (2) that

$$P_d=1-\sum_{k=1}^{n}P_k(t). \tag{5}$$

The mean residence time of the system in each of the states in Fig. 2 is determined from the formula [3]

$$\bar{t}_k=\int_0^\infty P_k(t)\,dt, \tag{6}$$

which may be written in the following specific form, taking account of Eq. (4)

$$\bar{t}_k=\frac{\prod_{i=1}^{k-1}\lambda_{i,i+1}}{\prod_{i=1}^{k}\lambda^*_{i,i+1}}. \tag{7}$$

Setting $\lambda_{id}=0$, i = 1, 2,..., n, it follows that

$$\lambda_{k,k+1}=1/\bar{t}^0_k;\quad \lambda_{id}=\frac{1}{\bar{\Theta}_i}. \tag{8}$$

It follows from Eq. (8) that the probability density of transition of the system from state S_i to state S_{i+1} is the inverse of the mean residence time of the system in the preceding state. This time may be estimated by tomography of the given cross section with reconstruction of the image from the size of the elementary cells corresponding to the thickness of the wound layer. An aqueous solution of X-ray contrast material is chosen as the diffusing material. To eliminate "illumination," it is replaced before each tomographic measurement by a compensator liquid with an LAC close to the mean LAC of the sample. After multiple scanning of the sample cross sections with a layer thickness of 1-2 mm, coronal reconstruction is employed.

Note that Eqs. (4)-(7) are derived for the general case when $\lambda^*_{i-1,i} \neq \lambda^*_{i,i+1}$. However, situations in which some or all of the densities $\lambda^*_{i,i+1}$ (i = 1, 2,..., k − 1) are equal may be encountered. In the most probable case in which any two are equal (consider the case $\lambda^*_{12} = \lambda^*_{23}$, for example), the solution of Eq. (1) is written in the form

$$P_1(t) = \exp(-\lambda^*_{12}t); \tag{9}$$

$$P_2(t) = \lambda^*_{12} t \exp(-\lambda^*_{12}t); \tag{10}$$

$$P_k(t) = a_k \exp(-\lambda^*_{12}t) + \sum_{j=1}^{k} \frac{\prod_{i=1}^{k-1} \lambda^*_{i,i+1}}{(\lambda^*_{12} - \lambda^*_{j,j+1})^2 \prod_{i=3}^{k} (\lambda^*_{i,i+1} - \lambda^*_{j,j+1})} \times$$
$$\times \exp(-\lambda^*_{j,j+1}t) + b_k \exp(-\lambda^*_{n,d}t); \tag{11}$$

$$a_k = \prod_{i=1}^{k-1} \lambda^*_{i,i+1} \left[\frac{t}{\prod_{i=1}^{k} (\lambda^*_{i,i+1} - \lambda^*_{12})} - \right.$$
$$\left. - \sum_{j=3}^{k} \frac{1}{(\lambda^*_{j,j+1} - \lambda^*_{12}) \prod_{i=3}^{k} (\lambda^*_{i,i+1} - \lambda^*_{12})} \right];$$

when k = 3

$$\prod_{i=3}^{k} (\lambda^*_{i,i+1} - \lambda^*_{12}) = 1,$$

$$b_k - \begin{cases} \dfrac{\prod_{i=1}^{k-1} \lambda^*_{i,i+1}}{(\lambda^*_{12} - \lambda^*_{nd})^2 \prod_{i=3}^{k} (\lambda^*_{i,i+1} - \lambda^*_{nd})}, & k = n, \\ 0 & \end{cases}$$

$$\lambda^*_{i,i+1} \neq \lambda^*_{nd}, \quad k = 3, 4, \ldots, n-1.$$

The mean residence time of the system in each state in Fig. 2 in this case may be determined from the formula

$$\bar{t}_k = \prod_{i=1}^{k-1} \lambda^*_{i,i+1} \left[\frac{2}{\lambda^{*2}_{12} \prod_{i=3}^{k} (\lambda^*_{i,i+1} - \lambda^*_{12})} - \right.$$
$$- \frac{1}{\lambda^*_{12}} \left(\sum_{j=3}^{k} \frac{1}{(\lambda^*_{j,j+1} - \lambda^*_{12}) \prod_{i=3}^{k} (\lambda^*_{i,i+1} - \lambda^*_{12})} \right) + \tag{12}$$
$$\left. + \sum_{j=3}^{k} \frac{1}{(\lambda^*_{12} - \lambda^*_{j,j+1})^2 \prod_{i=3}^{k} (\lambda^*_{j,i+1} - \lambda^*_{j,j+1}) \lambda^*_{j,j+1}} \right], \quad i \neq j.$$

If all the densities $\lambda^*_{i,i+1}$ are equal, the probabilities and mean residence times of the system in states $S_1,\ldots,S_n$ in Fig. 2 are as follows

$$P_k(t) = \frac{t^{k-1}}{(k-1)!} \exp(-\lambda^*_{12}t) \prod_{i=1}^{k-1} \lambda^*_{i,i+1},$$
$$k = 1, 2, \ldots, n; \quad i = 1, 2, \ldots, n-1; \tag{13}$$

$$\bar{t}_k = \frac{k}{\lambda^{*k}_{12}} \prod_{i=1}^{k-1} \lambda^*_{i,i+1}. \tag{14}$$

For quantitative estimation of the moisture-transfer parameters in the composites, it is expedient to convert from the probability of residence of the system in each state to the mean probability of moisture migration in each state. If the states $S_1, \ldots, S_n$ are regarded as one state of moisture migration over layers of the material S_M, the process may be reduced to two states S_M and S_d. Comparing the solution of the Kolmogorov equations for these two cases, an expression determining the mean moisture-migration probability in each state S_k may be obtained

$$\overline{P}_{Mk} = \exp(-\lambda_{kd}^* \bar{t}_k). \tag{15}$$

The random process in which the moisture "searches" for the next defect may be considered somewhat differently. Letting γ denote the mean number of observations in unit time, the probability P_m of obtaining an exactly specified number of observations m_0 in a search time t_S is expressed by the formula [4]

$$P_m = \frac{u^m}{m!} \exp(-u). \tag{16}$$

Here $u = \gamma t_S$ is the mean number of observations in search time t_S. In search theory, this quantity is called the search potential of observations in the search time

$$P_{m \geq 1} = 1 - \exp(-u). \tag{17}$$

Comparing Eqs. (15) and (17), a formula is obtained for the mathematical expectation of the mean number of observations in unit time in the k-th layer of composite

$$\gamma_k = \ln[1 - \exp(-\lambda_{kd}^* \bar{t}_k)]^{-\frac{1}{\bar{t}_k^0}}. \tag{18}$$

Using γ_k, the tortuosity (ε) may be determined; it is the ratio of the pore length to its projection on the direction of transfer. In the general case, the tortuosity factor characterizes all the inhomogeneities of the porous material: tortuosity and corrugation, the presence of tunnel pores, etc. [1]. Assuming equal rate of moisture propagation in the layers of material, it is found that

$$\varepsilon = 1 + \frac{L_x}{L_y} \frac{1}{n^2} \sum_{k=1}^{n} \gamma_k \sum_{k=1}^{n} \left(\frac{1}{\gamma_k}\right). \tag{19}$$

Analyzing Eqs. (15), (18), and (19), it may be concluded that the random process of moisture migration in composites is characterized by the presence of pores, cracks and cavities in the material, their size, mutual position, the characteristics of the laminar structure and reinforcement, and the component composition. The tortuosity depends on the porosity of the material, the pore distribution with respect to the radius, and the number of transverse defects.

Results of calculating ε for the first three layers of a composite at different times characterizing the residence time of the moisture in each of the layers are shown in Fig. 3, where the subscript i corresponds to the given residence time in one of the three states,

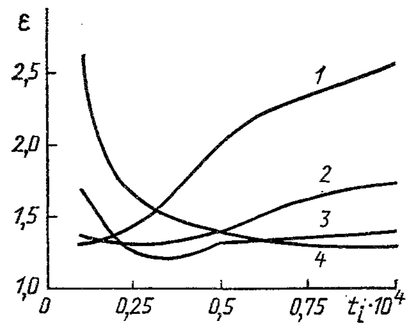

Fig. 3. Variation in tortosity as a function of the residence time in the i-th state (i = 1, 2, 3) with Q_i = 10 hr for the cases: 1) t_j = 0.1 hr; 2) 0.2; 3) 0.5; 4) 1.0 hr; j = 1, 2, 3; $j \neq i$; t_i, sec.

and j to two other states. The time intervals and mass-transfer coefficients obtained on samples of the composites analogous to that corresponding to the tomogram in Fig. 1 are considered. It follows from Fig. 3 that: assuming the best material has the least tortuosity, the most acceptable is that in which the layers are characterized by the same properties with respect to moisture migration. In this case, ε is a minimum, and depends only on the ratio L_x/L_y. With a purely diffusional process, $L_y = 0$, and hence ε is not determined. Increase in the difference between $\bar{t}_i^0$ leads to increase in ε. As shown by calculations, moisture migration characterized by the tortuosity is determined basically by the times $\bar{t}_i^0$ and is practically independent of $\bar{\theta}_i$. The results obtained may be extended to any number of layers.

Thus, the tortuosity factor of pores has been estimated as a random parameter of moisture absorption in composites. In the present case, it characterizes the pore space of the material over its whole volume and may be used in mathematical models of moisture transfer.

NOTATION

n, number of layers in material; $\bar{t}_k^0$, mean residence time in k-th state in Fig. 2, taking no account of internal diffusion; L_x, L_y, mass-transfer coefficients along x and y axes, respectively.

LITERATURE CITED

1. V. I. Barakhov, I. P. Dimitrienko, V. I. Goncharov, et al., Inzh.-Fiz. Zh., 51, No. 6, 1021-1027 (1986).
2. L. K. Kheifets and A. V. Neimark, Multiphase Processes in Porous Media [in Russian], Moscow (1982).
3. E. S. Venttsel', Investigation of Operations [in Russian], Moscow (1972).
4. V. A. Abchuk and V. G. Suzdal', Search for Objects [in Russian], Moscow (1977).

NONSTEADY TRANSFER AND DISPERSIONAL EFFECTS IN HETEROGENEOUS MEDIA

Yu. A. Buevich and V. A. Ustinov

UDC 536.242:532.546

A single transport equation taking account of the dispersion of effective conductivities and interphase exchange due to relaxation effects, as well as the inhomogeneity of the corresponding fields, is obtained in Laplace transforms. The asymptotes of this equation are considered.

1. The problem of adequate description of heat and mass transfer in heterogeneous and, in particular, granular media has been under intensive study for several decades now. Methods of engineering calculation based on semiempirical models have been proposed, leading to completely satisfactory results in many situations; see the review [1], for example. However, as yet there is no general theory indicating the regions of validity of these methods and models and extending them to processes in which nonsteady effects, sources, and sinks due to phase and chemical transformations and diverse nonlinear phenomena are of fundamental importance [2]. In practice, as before, the phenomenological model based on the concept of parallel transport in the two phases of a heterogeneous medium is most often used; this model leads to a system of two linear equations with constant coefficients [1, 3, 4] or to a single equivalent transport equation, which may be formally obtained from this system [5, 6].

The applicability of these equations is limited to processes which are very close to steady state. Generalization to a situation which is very unsteady is difficult in that

A. M. Gor'kii Ural State University, Sverdlovsk.

Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 59, No. 5, pp. 807-816, November, 1990. Original article submitted September 29, 1989.

0022-0841/90/5905-1432$12.50