Journal of Engineering Physics and Thermophysics, Vol. 77, No. 2, 2004

NUMERICAL MODELING OF THE DIFFUSION-LIMITED KINETICS OF FORMATION OF A THIN FILM FROM A POLYMER SOLUTION. 1. CONSTANT COEFFICIENT OF DIFFUSION

S. B. Kashevskii

UDC 541.64:532.72

By the method of numerical modeling, the kinetics of formation of a thin film from a polymer solution has been investigated. The regularities of the change in the thickness of a polymer layer and the concentration field in the process of drying as a function of the initial concentration of the polymer, the initial thickness of the layer, the value of the coefficient of mutual diffusion, and the concentration-dependent rate of evaporation of a solvent have been found.

Molding of films is one technique of mass processing of polymers [1] in which one uses heating of a metal tape and blowing of the polymer surface, which determines the complex multistage character of mass-exchange processes of formation of a film [2]. One problem in the field of film materials is the production of filled films, in particular, conductive polymer adhesives and spacers [3]. The conductivity of such films is attained by introduction of a finely dispersed conductive filler into the fluid polymer composition. The percolation properties of the material depend on the character of the structure of filler particles which is formed in the process of hardening [4]. The process of formation, apart from the particle interactions, is determined by the kinetics of change in the properties of the polymer matrix [5]. Allowance for the kinetics of the properties of a polymer binder is pressing in modeling [6] and practical implementation [7, 8] of the process of dissipative electromagnetic texturing of a disperse filler, which is carried out by the action of a rotating magnetic field on the hardened composition. Unlike the regular processes of molding of polymer films, the formation of structured composite films is a fairly slow heating- and blowing-free process. This makes it unnecessary to consider convective diffusion in a film, which substantially simplifies this problem as compared to the problem of mass molding [2]. At the same time, quite detailed information on the diffusion-limited stage of the process is required, which is absent from the literature on molding and is the subject of this investigation. The problem of the investigation lies in finding the regularities of a change in the thickness and the concentration field in a drying film of a polymer solution with allowance for the initial concentration of the polymer and the thickness of the solution layer and the concentration-dependent rate of evaporation of the solvent and the coefficient of diffusion of the polymer. Together with additional information on the concentration dependence of the solution viscosity, which can be obtained experimentally with the magneto-optical method [9], the studied characteristics of the process yield a total volume of the initial data for modeling of the processes of structurization of a disperse filler.

Formulation of the Problem. We consider a binary solution of a polymer in a low-molecular-weight liquid. It is assumed that the polymer and the solvent can be mixed in any proportion. The content of the polymer is characterized by the mass concentration c. The solution is applied as a uniform layer onto an impermeable horizontal surface. The upper surface of the layer is free. At the initial instant of time, the thickness of the layer is equal to H_0 and the concentration of the polymer is equal to c_0. The layer thickness decreases at the initial instant of time in the process of evaporation, whereas the excess of the polymer, formed on the surface, is transferred deep into the layer by diffusion. The problem lies in finding the regularities of the shrinkage $H(t)$ and the space-time variation in the concentration $c(z, t)$ for a fairly wide range of variation of the system's parameters. Along with the already introduced H_0 and c_0, they are the local-concentration-dependent coefficient of mutual diffusion of the polymer and the solvent $D(c)$, the density of the solution ρ, and the coefficient of mass transfer from the layer surface β.

A. V. Luikov Heat and Mass Transfer Institute, National Academy of Sciences of Belarus, 15 P. Brovka Str., Minsk, 220072, Belarus. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 77, No. 2, pp. 141–147, March–April, 2004. Original article submitted September 1, 2003.

1062-0125/04/7702-0421 ©2004 Plenum Publishing Corporation

The expression for the shrinkage rate is obtained from the equation of variation of the mass of the layer of unit area

$$\frac{dH}{dt} = -\frac{j_s}{\rho_s} . \tag{1}$$

The relation for j_s will be obtained in the following manner. In evaporation of the solvent, a layer of saturated vapor with concentration $c_{v,s}$ is formed directly above the film surface. The vapor flow is determined by the conditions of transfer from the surface layer (diffusion and convection) and is in direct proportion to the concentration of the saturated vapor $j_s = \beta c_{v,s}$ by virtue of the linearity of the transfer equations. We take into account that the concentration of the saturated vapor is in direct proportion to its pressure P, which is known to decrease with increase in the concentration of the substance dissolved. For a nonvolatile substance in the region of low concentrations the decrease in the pressure of the saturated vapor is in proportion to the amount of the substance dissolved in a given weight amount of the solvent (Raoult's law), i.e., $\Delta P/P = -Q/q$. Thus, in a diluted solution, we have $j_s = \beta c^0_{v,s}(1 - Q_\Sigma/q_\Sigma)$, where $c^0_{v,s}$ is the concentration of the saturated vapor of a pure solvent. To generalize this dependence to polymer solutions of arbitrary concentration we replace the quantity Q by the number of monomer links in a unit volume of the solution Q_1 and the quantity Q/q by $Q_1/(q + Q_1)$. In this case we have $j_s = \beta c^0_{v,s}(1 - Q_{1\Sigma}/(Q_{1\Sigma} + q_\Sigma))$. According to this relation, the solvent flow tends to zero with increase in the concentration of the polymer. Using $Q_1 = \rho c/m_1$ and $q = \rho(1 - c)/m_s$, where m_1 is the mass of a polymer link and m_s is the mass of a solvent molecule, we write

$$j_s = \beta c^0_{v,s}\left(1 - \frac{c_\Sigma}{c_\Sigma + (1 - c_\Sigma)\dfrac{m_1}{m_s}}\right) = \beta c^0_{v,s}\gamma , \quad \gamma = \frac{1 - c_\Sigma}{c_\Sigma \dfrac{m_s}{m_1} + (1 - c_\Sigma)} . \tag{2}$$

With account for (2), the equation for the rate of shrinkage of the layer takes the form

$$\frac{dH}{dt} = -w_0\gamma . \tag{3}$$

According to (3), the layer of a pure solvent ($c_\Sigma = 0$) evaporates over the period $T = H_0/w_0$, which will be used further as the characteristic time of the problem.

The distribution of the polymer in the drying layer obeys the differential equation of balance of the polymer mass

$$\frac{\partial(\rho c)}{\partial t} = -\operatorname{div}(j + v\rho c) .$$

The density of the solution depends on the concentration of the polymer. However, this dependence is of no decisive importance and to reduce the number of parameters and to simplify an analysis of the results we set ρ = const. This condition is observed rigorously if the density of the polymer is equal to the density of the solvent and the volume of the mixture of any concentration is equal to the sum of volumes of the components (ideal solution). The equality of the polymer and solvent densities yields the absence of the motion of the liquid as a whole ($v = 0$), since the polymer flow is compensated for with the oppositely directed solvent flow. Using Fick's law for the diffusion polymer flow and taking into account that the concentration depends only on the coordinate z, we obtain

$$\frac{\partial c(z, t)}{\partial t} = \frac{\partial}{\partial z}\left[D(c)\frac{\partial c(z, t)}{\partial z}\right]. \tag{4}$$

We write the boundary conditions for (4). At the lower boundary, we have the impermeability condition

$$\left.\frac{\partial c}{\partial z}\right|_{z=0} = 0 . \tag{5}$$

The boundary condition of the free surface will be found from the equation of balance of the polymer mass in a thin surface layer. Taking into account that a change in the polymer mass in this layer occurs only by diffusion through its lower boundary ($z = \zeta$), we have

$$\frac{d}{dt}\int_{\zeta}^{H(t)} c dz \equiv c_{\Sigma}\frac{dH}{dt} + \int_{\zeta}^{H}\frac{\partial c}{\partial t} dz = -D(c)\frac{\partial c}{\partial z}\bigg|_{z=\zeta} .$$

Letting ζ tend to H, we obtain the boundary condition in the form

$$c_{\Sigma} w_0 \gamma = D(c_{\Sigma})\frac{\partial c}{\partial z}\bigg|_{z=\Sigma} . \tag{6}$$

We pass to a fixed region with the use of the transformation $r = z/H(t)$. Having introduced the dimensionless time $\tau = t/T$, the layer thickness $h(t) = H(t)/H_0$, and the diffusion coefficient $d(c) = D(c)/D_0$, we transform the equations and boundary conditions (3)–(6):

$$\frac{dh}{d\tau} = -\gamma, \quad \frac{\partial c}{\partial \tau} = \frac{\partial c}{\partial r}\frac{r}{h(\tau)}\gamma + A\frac{1}{h^2(\tau)}\frac{\partial}{\partial r}\left[d(c)\frac{\partial c}{\partial r}\right],$$

$$\frac{\partial c}{\partial r}\bigg|_{r=0} = 0, \quad c_{\Sigma}\gamma(c_{\Sigma}) = A\frac{d(c_{\Sigma})}{h(\tau)}\frac{\partial c}{\partial r}\bigg|_{r=1}, \quad A = \frac{D_0}{w_0 H_0}. \tag{7}$$

Here the dimensionless parameter A is the ratio of the time of evaporation of the layer of a pure solvent of thickness H_0 to the characteristic time of diffusion equalization of the concentration.

In the case of infinitely mixing polymer and solvent, the change in the coefficient of mutual diffusion with concentration of the solvent $c_s = 1 - c$ is characterized by convex dependences with a weak maximum [10]. Such dependences can be approximated by the function

$$\log D = A + \frac{Bc_s}{1 + Fc_s^2}, \tag{8}$$

containing the fitting coefficients A, B, and F. We can find them for a specific system with the use of the known values of the diffusion coefficient in the limits $c_s \to 0$ ($D = D_1$) and $c_s \to 0$ ($D = D_0$) and the value of the concentration of the solvent $c^s_{\max}$, which corresponds to the maximum diffusion coefficient (Fig. 1). We obtain that $A = \log D_1$, $B = \frac{(c^s_{\max})^2 + 1}{(c^s_{\max})^2}\log Z$, $F = \frac{1}{(c^s_{\max})^2}$, and $Z = \frac{D_0}{D_1}$. Passing from the concentration of the solvent to the concentration of the polymer ($c_s = 1 - c$, $c^s_{\max} = 1 - c_{\max}$), we should take into account that the initial coefficient of diffusion will be $D|_{c_s \to 0} = D_0$ and not $D|_{c_s = 1} = D_1$. Thus, the expression for the diffusion coefficient has the form

$$D/D_0 = d(c) = Z^{\Psi}, \tag{9}$$

where $\Psi = \frac{(1-c)[(1-c_{\max})^2 + 1] - (1-c_{\max})^2 - (1-c)^2}{(1-c_{\max})^2 + (1-c)^2}$.

Figure 1 gives the dependence $D(c_s)$ for dibutylphthalate (the points are the experimental data of [10] and the curve is the approximating function).

Finite-Difference Scheme. The diffusion equation in (7) has been solved with the explicit difference scheme on a uniform grid. The right-hand side of this equation for each instant of time has been approximated by the relation

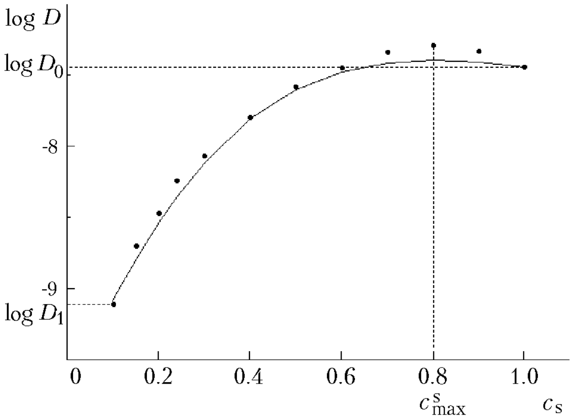

Fig. 1. Approximation of the dependence of the diffusion coefficient. log D, cm^2/sec.

$$\left[\frac{\partial c}{\partial r}\frac{r}{h(\tau)}\gamma(c_N)\right]_i \approx \frac{c_{i+1}-c_{i-1}}{\delta_x}\frac{\delta_x j}{h}\gamma(c_N),$$

$$\left[\frac{\partial c}{\partial r}\frac{r}{h(\tau)}\gamma(c_\Sigma)\right]_i \approx \frac{c_{i+1}-c_{i-1}}{\delta_x}\frac{\delta_x j}{h}\gamma(c_N),$$

$$\left[\frac{\partial}{\partial r}\left[d\frac{\partial c}{\partial r}\right]\right]_i \approx \frac{1}{\delta_x}\left(\frac{d_{(i+1)/2}(c_{i+1}-c_i)}{\delta_x}-\frac{d_{(i-1)/2}(c_i-c_{i-1})}{\delta_x}\right)=\frac{1}{\delta_x^2}\left(d_{(i+1)/2}(c_{i+1}-c_i)-d_{(i-1)/2}(c_i-c_{i-1})\right).$$

Thus, for the internal nodes ($i = 1, \ldots, N-1$) the relationship between the values of the concentration at the present instant of time, $c1$, and the previous values, c, is yielded by the following relation:

$$c1_i = c_i + \frac{R\delta_x^2 j}{2h}(c_{i+1}-c_{i-1})\gamma + \frac{AR}{h^2}\left[d_{(i+1)/2}(c_{i+1}-c_i)-d_{(i-1)/2}(c_i-c_{i-1})\right],$$

here $R = \delta_t/\delta_x^2$.

The coefficients of mutual diffusion $d_{(i+1)/2}$ and $d_{(i-1)/2}$ are determined from formula (9); however it is necessary to prescribe the values of the concentration of the polymer at the same points ($c_{(i+1)/2}$ for determination of $d_{(i+1)/2}$ and $c_{(i-1)/2}$ for $d_{(i-1)/2}$). We obtain these values, expanding the polymer concentration in a Taylor series:

$$c_{(i+1)/2} = \frac{3}{4}c_i + \frac{3}{8}c_{i+1} - \frac{1}{8}c_{i-1}, \quad c_{(i-1)/2} = \frac{3}{4}c_i - \frac{1}{8}c_{i+1} + \frac{3}{8}c_{i-1}.$$

For the external nodes ($i = 0, N$) the equations for the boundary conditions in system (7) yield the following relationship for the concentration values: $c_0 = c_1$ at the impermeable (lower) boundary and

$$c_N = \frac{(\phi c_{N-1}+\phi-1-M\phi c_{N-1})-\sqrt{(\phi c_{N-1}+\phi-1-M\phi c_{N-1})^2-4\phi c_{N-1}(\phi-1-M\phi)}}{2(\phi-1-M\phi)},$$

$$M = \frac{m_{\mathrm{s}}}{m_1}, \quad \phi = \frac{Ad_N}{h\delta_x}.$$

on the free surface.

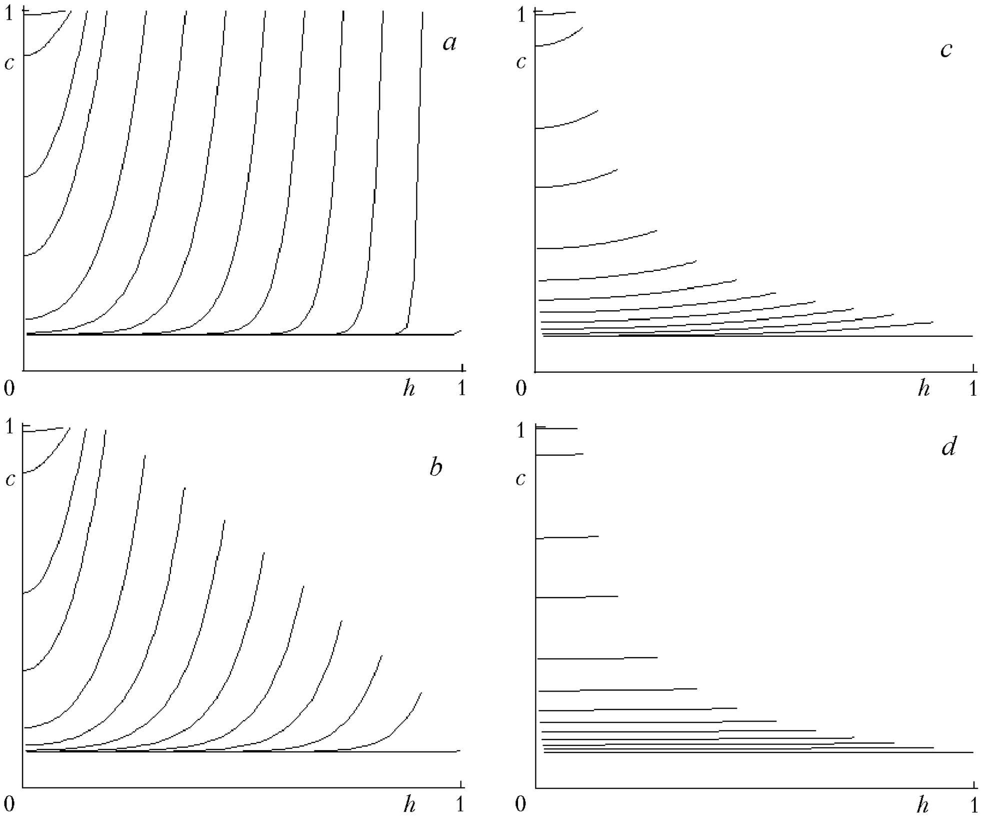

Fig. 2. Concentration distribution of the polymer over the layer thickness for different values of the parameter A: a) A = 0.01; b) 0.1; c) 1; d) 10.

The relationship between the value of the layer thickness at the present instant of time $h1$ and this value at the previous instant of time h is obtained from the equation for the rate of shrinkage of the layer (see system (7)) in the form

$$h1 = h - R\delta_x^2\gamma\,.$$

Kinetics of Drying of the Polymer with a Constant Coefficient of Diffusion. Setting the diffusion coefficient to be constant (B = 1), we consider the influence of the initial concentration of the polymer c_0, the relation of the molecular masses of the solvent and the polymer M, and the relation of the times of evaporation of a pure solvent and of diffusion equalization of the concentration A on the process of formation of a polymer film.

Figure 2 illustrates a variation in the concentration profile in the process of drying for different values of A for fixed c_0 (0.1) and M (0.001). For each A 13 profiles are presented; the first 12 profiles have been derived as the relative thickness of the layer $h_r = (h - c_0)/(1 - c_0)$ decreased by $\Delta h_r = 0.1$, and the last profile has been derived upon the evaporation of 99% of the solvent. The instants of time at which the profiles have been derived are given in Table 1. As we see, whereas the distribution of the polymer concentration over the layer thickness remains nearly uniform in the process of formation of the film in the case of intense diffusion ($A > 1$), the polymer begins to collect on the layer surface with decrease in the diffusion intensity, which leads to the formation of a crust and increases the duration of the process.

Figure 3 (the times are summarized in Table 2) shows the variation in the concentration profile for different values of M and A for a fixed c_0 (0.1). As we see, for large A ($A > 1$) the concentration distribution is weakly sensitive to how strongly the masses of the polymer and solvent molecules differ. For small A an increase in the molecular weight of the polymer leads to the formation of a crust on the drying-layer surface and a decrease in the drying time. The latter is explained by the fact that the evaporation rate, as shown in Fig. 4, increases with decrease in M.

TABLE 1. Values of the Times That Correspond to Different Profiles (see Fig. 2)

Profile No.	Fig. 2a	Fig. 2b	Fig. 2c	Fig. 2d
1	0.00	0.00	0.00	0.00
2	0.09	0.09	0.09	0.09
3	0.27	0.18	0.18	0.18
4	0.55	0.27	0.27	0.27
5	0.94	0.36	0.36	0.36
6	1.44	0.45	0.45	0.45
7	2.05	0.54	0.54	0.54
8	2.76	0.63	0.63	0.63
9	3.58	0.72	0.72	0.72
10	4.52	0.82	0.82	0.82
11	5.11	0.87	0.86	0.86
12	6.00	0.96	0.89	0.89
13	6.97	1.06	0.90	0.90

TABLE 2. Values of the Times That Correspond to Different Profiles (see Fig. 3)

Profile No.	Fig. 3a			Fig. 3b			Fig. 3c		
	$M = 0.001$	$M = 0.1$	$M = 1$	$M = 0.001$	$M = 0.1$	$M = 1$	$M = 0.001$	$M = 0.1$	$M = 1$
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.10	0.10	0.12	0.10	0.10	0.11	0.10	0.10	0.11
3	0.20	0.21	0.26	0.20	0.20	0.23	0.20	0.20	0.23
4	0.30	0.31	0.41	0.30	0.31	0.35	0.30	0.30	0.34
5	0.40	0.42	0.58	0.40	0.41	0.47	0.40	0.41	0.46
6	0.50	0.54	0.75	0.50	0.51	0.60	0.50	0.51	0.58
7	0.60	0.65	0.94	0.60	0.61	0.73	0.60	0.61	0.71
8	0.70	0.78	1.14	0.70	0.72	0.86	0.70	0.71	0.84
9	0.80	0.91	1.36	0.80	0.82	1.01	0.80	0.82	0.98
10	0.91	1.05	1.61	0.90	0.93	1.20	0.90	0.93	1.16
11	0.97	1.13	1.79	0.95	0.99	1.33	0.95	0.98	1.29
12	1.07	1.25	2.09	0.99	1.05	1.56	0.99	1.04	1.52
13	1.18	1.39	2.46	1.00	1.10	1.86	1.00	1.09	1.89

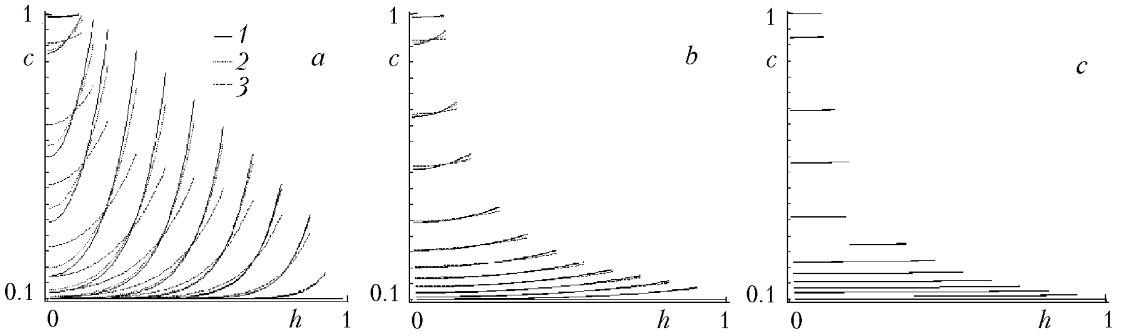

Fig. 3. Variation in the polymer-concentration distribution in passage from a low-molecular-weight polymer to a high-molecular-weight polymer: a) A = 0.1; b) 1; c) 10 [1) M = 0.01; 2) 0.1; 3) 1].

Let us consider what parameters influence a variation in the layer thickness with time. Figure 5 shows the variation in the thickness of the drying layer for different values of the initial concentration in it and the parameters A and M. As we see, in the case of a high-molecular-weight polymer the initial concentration of the polymer c_0 exerts

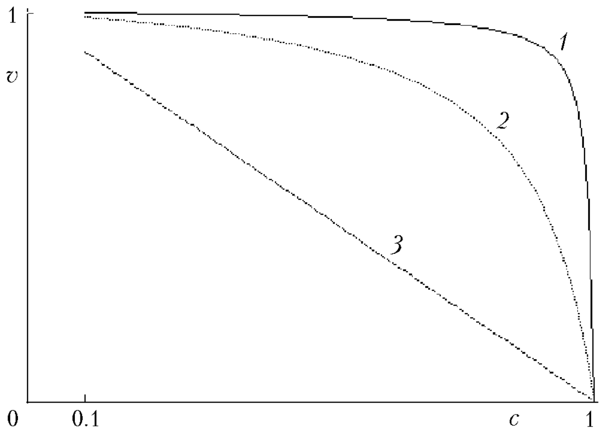

Fig. 4. Variation in the evaporation rate in passage from a high-molecular-weight polymer to a low-molecular-weight polymer: 1) M = 0.01; 2) 0.1; 3) 1.

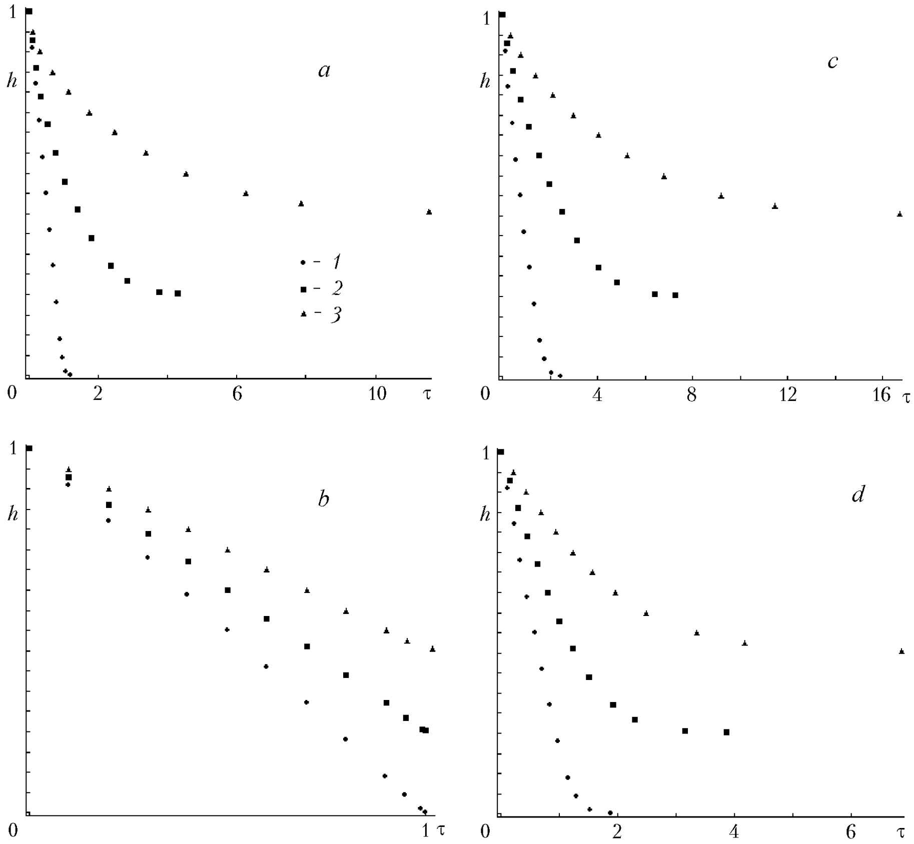

Fig. 5. Variation in the thickness of the solvent layer with time: a) A = 0.1 and M = 0.001; b) 10 and 0.001; c) 0.1 and 1; d) 10 and 1 [1) c_0 = 0.1; 2) 0.3; 3) 0.5].

a substantial influence on the process of formation of a polymer film in retarded diffusion ($A < 1$). This influence decreases when $A > 1$ and is insignificant even when A = 10. In the case of a low-molecular-weight polymer c_0 has an effect for all the A values considered, but, as the diffusion intensity increases, the time of formation of the film decreases.

It is noteworthy (Table 1) that the times of formation of the film are actually the same for A = 1 and A = 10. Consequently, the time tends to a certain asymptotic function of the initial concentration with increase in A. The existence of the asymptotics is motivated by the fact that the distribution of the polymer concentration over the layer

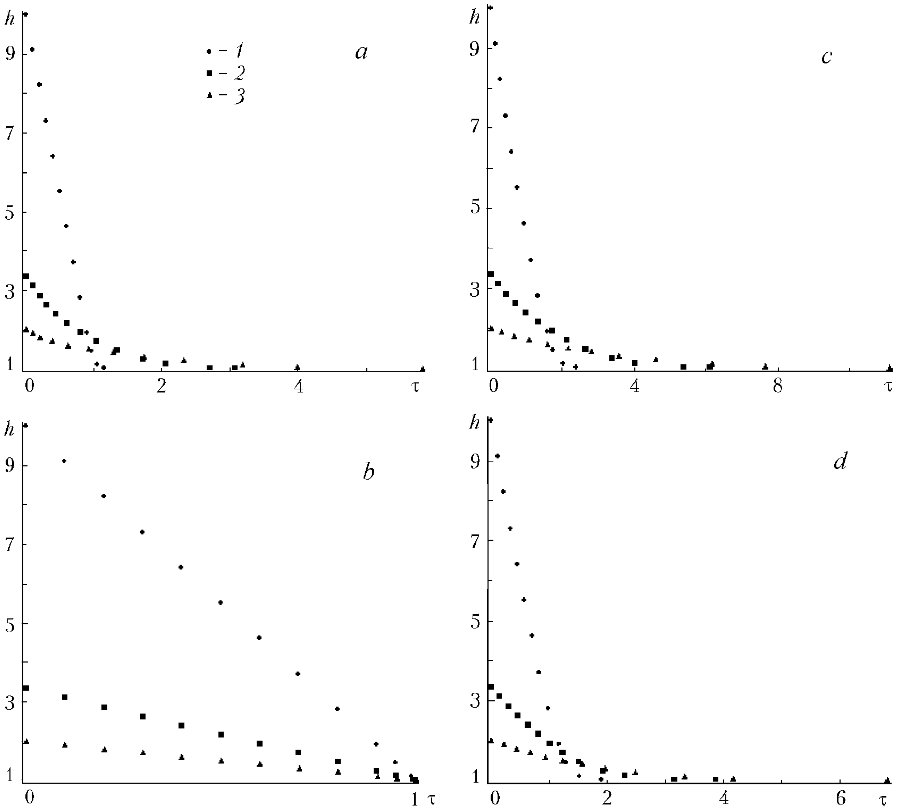

Fig. 6. Influence of the initial content of the polymer in the solution on the kinetics of formation of a film of prescribed thickness: a) A = 0.1 and M = 0.001; b) 10 and 0.001; c) 0.1 and 1; d) 10 and 1 [1) c_0 = 0.1; 2) 0.3; 3) 0.5].

in the process of evaporation remains uniform, in practice, for large A. This yields a direct relationship of the concentration and the layer thickness: $cH = c_0H_0$, or $c = c_0/h$, using which in the equation for the rate of shrinkage of the layer $dh/d\tau = -\gamma$, we obtain the asymptotic dependence sought in the form

$$h(\tau) + c_0 M \ln\left[\frac{h(\tau) - c_0}{1 - c_0}\right] = 1 - \tau\,. \tag{10}$$

As the characteristic time of formation of the film, we select the time τ_e in which 99% of the solvent evaporates; here, $h_r = 0.01$ and $h = 0.01 + 0.99c_0$. According to (10), we have

$$\tau_e = 0.99 + c_0\,[4.605M - 0.99]\,.$$

A comparison to the calculated data (A = 10, M = 0.001, and c_0 = 0.1) yields an error of 0.8%.

In the calculations performed, the initial thickness of the film was assumed to be fixed and the thickness of the produced film H_f was determined by the initial concentration of the polymer. To produce a film of prescribed thickness one can use either a large amount of the solvent with a low concentration of the polymer (i.e., a layer of large thickness) or the opposite. This brings up the question: what is more profitable from the viewpoint of the formation of the film?

Figure 6 illustrates the dependence of the time of formation of the film of thickness H_f on the initial thickness of the layer for different values of the parameters A and M. As we see, in the case of a high-molecular-weight polymer (M = 0.001) and retarded diffusion ($A < 1$) the formation time increases with decrease in H_0. The reason is that, when H_0 values are low, the initial concentration of the polymer is high, which promotes the formation of a crust on the layer surface (Fig. 7). As A increases, the influence of the initial layer thickness on the time is not observed.

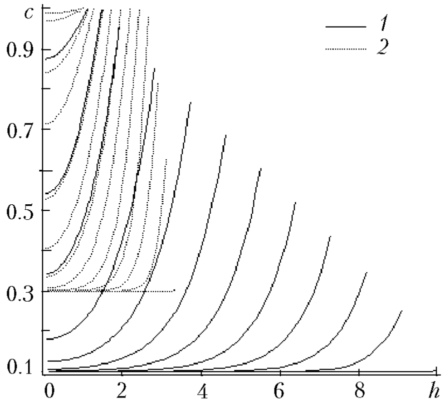

Fig. 7. Influence of the initial content of the polymer in the solution on its distribution over the layer thickness: 1) c_0 = 0.1; 2) 0.3. A = 0.1 and M = 0.001.

In the case of a low-molecular-weight polymer the dependence of the time of formation of the film on the initial thickness of the layer is observed for all the A values studied. The time itself drops with increase in A.

NOTATION

c, mass concentration; D, coefficient of mutual diffusion; H, layer thickness; N, number of grid nodes; i, node No., i = 0, ..., N; Q and q, number concentrations of the molecules (or number of nodes) of the substance and the solvent; x, z, coordinates; t, time; j, flux density; P, pressure; m, mass; w_0, rate of decrease of the thickness of the pure-solvent layer; T, characteristic time; v, total momentum of a mass unit of the solution; δ_i and δ_x, steps of the time and coordinate grids; ρ, density of the solution; β, coefficient of mass transfer from the layer surface. Subscripts and superscripts: s, solvent; v, vapor; e, evaporation; r, relative; f, film; Σ, layer surface; max, maximum value; 0, initial value.

REFERENCES

1. V. R. Gowariker, N. V. Viswanathan, and J. Sreedhar, *Polymer Science* [Russian translation], Nauka, Moscow (1990).
2. V. M. Chesunov and R. M. Vasenin, Kinetics of evaporation of a solvent in formation of films from polymer solutions, *Vysokomolek. Soed. A*, **9**, No. 10, 2067–2071 (1967).
3. V. E. Gul' and L. Z. Shenfil', *Conducting Polymer Compositions* [in Russian], Khimiya, Moscow (1984).
4. V. V. Vysotskii and V. I. Roldugin, Structure and percolation properties of conducting film compositions, *Kolloid. Zh.*, **60**, 729–745 (1998).
5. V. V. Vysotskii and V. I. Roldugin, Mechanism of formation of aggregates in metal-filled polymer compositions, *Kolloid. Zh.*, **62**, 7589–764 (2000).
6. B. É. Kashevskii, Coherent disperse structures in magnetic suspensions, *Kolloid. Zh.*, **65**, No. 3, 352–355 (2003).
7. B. É. Kashevskii and A. V. Suvorov, *Method for Obtaining Composite Materials or Products from a Magnetizable or Polarizable Liquid Disperse Composition in an Electromagnetic Field*, Patent of the Republic of Belarus No. 4396, Byull. No. 1 (2002).
8. B. É. Kashevskii, I. V. Prokhorov, V. A. Kuz'min, and A. A. Rusalovich, Effect of dissipative electromagnetic orientation of conducting particles on the electrical conductivity of filled polymer, *Dokl. Nats. Akad. Nauk Belarusi*, **46**, No. 2, 119–121 (2002).
9. B. É. Kashevskii, Theoretical prerequisites for one magnetooptical method of measurement of the viscosity of a fluid, *Inzh.-Fiz. Zh.*, **76**, No. 2, 9–11 (2003).
10. A. E. Chalykh, *Diffusion in Polymer Systems* [in Russian], Khimiya, Moscow (1987).