MODELING NONISOTHERMAL SOLIDIFICATION OF EPOXY RESINS

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In the last ten years a new technology has come increasingly into use: the chemical molding of reactive oligomers which produces simultaneously the material and the finished product [1]. The technological cycle includes partial solidification of the mixture in the mixing chamber, pumping through channels into the mold, final solidification of the composition in the mold. The nature of the processes of heat and mass exchange at different stages has a decisive influence on the technological regimes of conversion, the quality of the material, and the operational characteristics of the product. Heat and mass exchange can be correctly described only with the use of a kinetic model that is perfectly adequate to the real process. The present article deals with the solidification of epoxy resin by an amine-type solidifier, viz., metaphenylene diamine. For this system a kinetic model was suggested in [2-4]. We investigate its mathematical correctness, the qualitative behavior of the solution, and provide experimental confirmation of the adequacy of the description of the kinetics.

The mechanisms of interaction of epoxy groups with amines include the formation of hydroxyl groups in the course of the reaction catalyzing the interaction of primary (A_1) and secondary (A_2) amine with the epoxy (E) group. Besides, a highly reactive epoxy-alcohol complex (EC) forms. Thus, the mechanism of the reactions of solidification is represented by the following kinetic scheme [2-4]:

$$\begin{gathered} A_1 + E \xrightarrow{K_1} A_2 + C;\; A_2 + E \xrightarrow{K_2} A_3 + C; \\ C + E \overset{K_e}{\rightleftarrows} (EC);\; A_1 + (EC) \xrightarrow{K_1'} A_2 + 2C; \\ A_2 + (EC) \xrightarrow{K_2'} A_3 + 2C \end{gathered} \tag{1}$$

(C are alcohol groups).

From the scheme we can obtain kinetic equations of the type of balances describing the process of solidification:

$$\begin{gathered} \frac{dA_1}{dt} = -K_1A_1E - K_1'A_1(EC); \\ \frac{dA_2}{dt} = -K_2A_2E + K_1'A_1(EC) - K_2'A_2(EC) + K_1A_1E; \\ \frac{dA_3}{dt} = K_2A_2(EC) + K_2A_2E; \\ \frac{d(EC)}{dt} = -K_1'(EC)A_1 - K_2'(EC)A_2; \\ \frac{dE}{dt} = -K_1A_1E - K_2A_2E; \end{gathered} \tag{2}$$

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$$\frac{dC}{dt} = K_1A_1\mathrm{E} + K_2A_2\mathrm{E} + 2K_1'A_1(\mathrm{EC}) + 2K_2'A_2(\mathrm{EC});$$

$$(\mathrm{EC}) = K_e\mathrm{EC}.$$

Relation (2) together with the initial conditions

$$\mathrm{E} = \mathrm{E}_0;\ C = 0;\ A_1 = A_{10};\ A_2 = 0;\ A_3 = 0 \text{ for } t = 0 \tag{3}$$

and the equation of energy

$$\rho c\frac{\partial T}{\partial t} = \operatorname{div}(\lambda\nabla T) + \left(Q\mathrm{E}_0\frac{\partial\beta}{\partial t}\right) \tag{4}$$

fully determine the problem if the temperature dependences of the constants of the reactions K_1, K_1', K_2, K_2' and of equilibrium K_e are known (where Q is the thermal effect of the reaction; β is the depth of transformation).

For the isothermal case the problem reduces to Eqs. (2) with conditions (3). This is a Cauchy problem for a dynamic system of nonlinear differential equations. Since there are singular points, a qualitative analysis of the system (2) is indispensable.

The first three integrals are

$$A_1 - A_3 + Y = \text{const};\ A_2 + 2A_3 - Y = \text{const};\ C + \mathrm{E} + 2(\mathrm{EC}) = \text{const}, \tag{5}$$

where

$$Y = \mathrm{E}_0 - \mathrm{E} - (\mathrm{EC}). \tag{6}$$

Relations (5) and the initial conditions (3) yield the equations of the material balance

$$\begin{cases} \dfrac{dA_1}{dt} = -K_1A_1\mathrm{E}(Y) - K_1'A_1K_eC(Y)\,\mathrm{E}(Y), \\ \dfrac{dY}{dt} = K_1A_1\mathrm{E}(Y) + K_1'A_1K_eC(Y)\,\mathrm{E}(Y) + K_2'A_2K_eC(Y)\,\mathrm{E}(Y) + K_2\mathrm{E}(Y)A_2, \end{cases} \tag{7}$$

where

$$\mathrm{E}(Y) = \frac{1}{2}\left[\mathrm{E}_0 - 2Y - K_e^{-1} + \sqrt{(2Y - \mathrm{E}_0 + K_e^{-1})^2 + 4(-Y + \mathrm{E}_0)K_e^{-1}}\right];$$

$$C(Y) = [\mathrm{E}_0 - \mathrm{E}(Y)]/[1 + 2K_e\mathrm{E}(Y)]. \tag{8}$$

Expressions (7), (8), (6) contain seven sought variables [A_1, A_2, A_3, E, C, (EC), Y]. Their qualitative investigation has to be carried out in a seven-dimensional phase space. The following, however, has to be borne in mind: a) the equation for A_3, which is contained in (5), is isolated; b) in accordance with (2) the complex (EC) is in local equilibrium with the epoxy groups and the alcohols, and it is therefore also determined by them; c) in accordance with the definition of Y, of the three variables Y, E, C only two are independent. Consequently, it suffices to carry out the analysis in a four-dimensional phase space, e.g., in the variables $\{A_1, Y, A_2, C\}$.

Let us consider the qualitative behavior of the autonomous system (7) with the selected initial data. The introduction of the variables $x = A_1$, $y = E_0 - Y$ transforms it to

$$\begin{cases} \dfrac{dx}{dt} = -x\,[(K_1 - K_1')\,\mathrm{E}(y) + y] \equiv P(x, y), \\ \dfrac{dy}{dt} = -P(x, y) + (\beta - 2x + y)\,\mathrm{E}(y)\,(K_2'K_eC(y) + K_2) \equiv Q(x, y), \end{cases} \tag{9}$$

where

$$\beta = 2A_{10} - E_0,$$
$$E(y) = \frac{1}{2}[2y - E_0 - K_e^{-1} + \sqrt{(-2y + E_0 + K_e^{-1})^2 + 4yK_e^{-1}}]. \tag{10}$$

In deriving these relations we took it that according to [2-4] $K_2 = 0$. Besides that it was assumed that there are no secondary amines in the initial system.

By definition of the variables under consideration, $x \geq 0$, $y \geq 0$. We will therefore investigate the phase-plane diagram in the first quadrant of the plane (x, y) where the system (9) has the following rest points: 1) the set of points of the form $M_1(\tilde{x}, 0)$, where $\tilde{x} \geq 0$ is arbitrary; 2) the point $M_2(0, -\beta)$ with $\beta \leq 0$. From the equation of the material balance (5) follows

$$A_2 = \beta - 2x + y, \tag{11}$$

which means that the first case is realized only with $\beta \geq 0$. To the case $\beta = 0$ there corresponds the singular rest point $M(0, 0)$.

We investigate the behavior of the integral curves in the vicinity of the rest points. In dependence on the value of the parameter β two fundamentally different cases occur.

With $\beta < 0$ (deficiency of primary amines) unopened epoxy groups remain after termination of the reaction because one primary amine can open two epoxy rings only. In that case the final state of the system ($x = 0$, $y = -\beta$) can be a priori determined from the equations of the reactions by the initial data.

With $\beta > 0$ (excess of primary amines), after termination of the reaction there remains, generally speaking, some number of primary ($A_1 = \tilde{x}$) and secondary ($\tilde{A}_2 = \beta - 2\tilde{x}$) amines. In that case the final state of the medium can be determined only after the system has been solved.

The case $\beta = 0$ (stoichiometry) can be classed as belonging to the first or to the second case.

Let us consider the case $\beta < 0$. We replace the variables: $\tilde{x} = x$, $\tilde{y} = y + \beta$. In the vicinity of the singular point (with the new variables the origin of coordinates):

$$\begin{aligned} \frac{d\bar{x}}{dt} &= D_2\bar{x} + O(\bar{x}\bar{y}), \\ \frac{d\bar{y}}{dt} &= (D_2 - D_3)\bar{x} - D_4\bar{y} + O(\bar{x}, \bar{y}), \end{aligned} \tag{12}$$

where

$$D_1 = \frac{1}{2}[-(2\beta + E_0 + K_e^{-1}) + \sqrt{(2\beta + E_0 + K_e^{-1})^2 - 4\beta K_e^{-1}}];$$

$$D_2 = -K_1'\left[D_1\left(\frac{K_1}{K_1'} - 1\right) - \beta\right];$$

$$D_3 = -\frac{2K_2'K_eD_1(E_0 - D_1)}{1 + 2K_eD_1};$$

$$D_4 = \frac{K_2'K_eD_1(E_0 - D_1)}{1 + 2K_eD_1}.$$

The roots of the characteristic equation of the system are $\lambda_1 = D_2$; $\lambda_2 = -D_4$. The root λ_1 is smaller than zero because $D_2 = -K_1'(-D_1 - \beta) - K_1D_1$, but $-\beta > D_1$ ($-\beta$ is equal to the total number of epoxy groups remaining at the end of the reaction, i.e., after all the amines have been spent, and D_1 is the number of free epoxy groups at the end of the reaction;

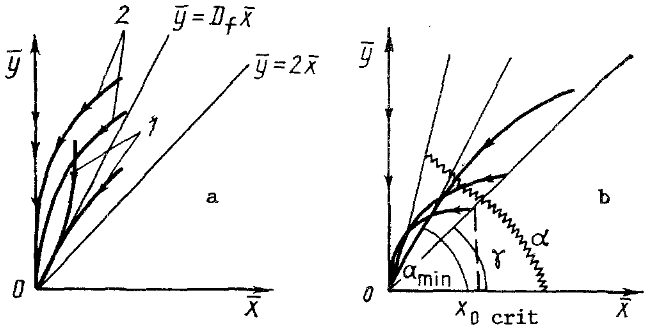

Fig. 1. Phase-plane diagram: a: 1) $D_6 > 1$; 2) $D_6 = 1$; b) of the true integral curves.

therefore $D_1 + \beta = -(EC)_f < 0$, where $(EC)_f$ is the final number of complexes (EC)). It follows from the definition of D_4 that $D_4 > 0$. Consequently, $\lambda_1 < 0$, $\lambda_2 < 0$. The singular point in the plane (x, y) is therefore a stable node. An analysis in the phase plane reduces to the study of the integral curves of the equation

$$\frac{d\bar{y}}{d\bar{x}} = D_5 + D_6\frac{\bar{y}}{\bar{x}} + O\left(\frac{\bar{y}^2}{\bar{x}}\right), \tag{13}$$

where

$$D_5 = 1 - \frac{D_3}{D_2} = 1 + \frac{2K_2'K_e D_1(E_0 - D_1)}{(1 + 2K_e D_1)\,[K_1'(D_1 + \beta) - K_1 D_1]};$$

$$D_6 = -\frac{D_4}{D_2} = \frac{K_2'K_e D_1(E_0 - D_1)}{[K_1 D_1 - K_1'(D_1 + \beta)]\,(1 + 2K_e D_1)}.$$

The form of the integral curves [of Eq. (13)] depends on the value of the coefficient D_6. With $D_6 > 1$ (Fig. 1a) the separatrix is $\bar{y} = D_7\bar{x}$, where

$$D_7 = \frac{D_5}{1 - D_6} = 2 + \frac{[K_1 D_1 - K_1'(D_1 + \beta)]\,(1 - 2K_e D_1)}{K_2'K_e D_1(E_0 - D_1) + [K_1'(D_1 + \beta) - K_1 D_1]\,(1 + 2K_e D_1)}$$

lies higher than the straight line of the initial values $\bar{y} = 2\bar{x}$ because with $D_6 > 1$ we have $D_7 > 2$. For any point of the straight line of the initial data there exists a fully determinate integral curve from the family under consideration that passes through that point. Consequently, some point on that straight line corresponds to the specified set of initial compositions (A_{10}, $E_0 < 2A_{10}$).

The case $D_6 = 1$ corresponds to a dicritical node. In this case the separatrices are $\bar{x} = 0$. The existence and uniqueness of the solution of the Cauchy problem are proved analogously to the one described above.

For $D_6 < 1$ we also have a dicritical node.

The asymptotics of the solution of Eq. (13) for $t \to \infty$ is:

$$\bar{x} = \bar{x}_0 \exp D_2(t - t_0),$$

$$\bar{y} = \begin{cases} \bar{y}_0 \exp[D_2(t - t_0)] & \text{for } D_6 > 1, \\ \bar{x}_0 \exp\left[D_2(t - t_0)\left[\dfrac{\bar{y}_0}{\bar{x}_0} - D_2(t - t_0)\right]\right] & \text{for } D_6 = 1, \\ \bar{y}_0 \exp[D_2 D_6(t - t_0)] & \text{for } D_6 < 1, \end{cases} \tag{14}$$

where $\bar{x}_0$ and $\bar{y}_0$ are the corresponding values of the primary amines and of the degree of transformation at the instant $t = t_0$, respectively. Formula (14) makes it possible to shorten considerably the time of calculating actual variants.

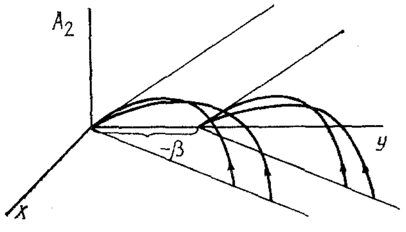

Fig. 2. Three-dimensional representation (x, y, A_2) of the four-dimensional phase-plane diagram (x, y, c, A_2).

Let us analyze the case $\beta = 0$. In this variant the linear terms vanish, and the subsequent terms of the expansion have to be used. In the phase plane, system (9) reduces to

$$\frac{dy}{dx} = B_1 + B_2\frac{y}{x} + O(y) + O\left(\frac{y^2}{x}\right). \tag{15}$$

Here

$$B_1 = \frac{K_1 - K_e E_0 (2K_2' - K_1')}{K_1 + K_e E_0 K_1'};$$

$$B_2 = \frac{K_2' K_e E_0}{K_1 + K_e E_0 K_1'}.$$

It can be shown that the passage to the limit $\beta \to 0$ entails the change of the coefficients D_5 and D_6 in Eq. (13) into B_1 and B_2 of Eq. (15), respectively. Thus, the perturbation of the problem with respect to the parameter β is regular at least in the region $\beta \leq 0$, and qualitatively the phase-plane diagram in this region looks alike in both cases: $\beta < 0$ and $\beta = 0$.

For a clearer understanding it is more expedient to analyze the phase-plane diagram in the case of stoichiometry ($\beta = 0$). In the plane (x, y) it has the same form as the phase-plane diagram for $\beta < 0$ in the plane ($\bar{x}$, $\bar{y}$).

The reduction of the initial Cauchy problem (2), (3) to system (7) with relations (6), (8) modifies in fact the problem because the initial conditions become part of the initial equations. As a result only one integral curve is realized out of the entire family of integral curves plotted for certain values of B_1 and B_2 (fixed E_0); we will call it the true curve. The change of initial concentration of epoxy groups and correspondingly of primary amines (for maintaining the stoichiometric relation) shifts the initial mapped point along the straight line of the initial values $y = 2x$.

Let us investigate the phase-plane diagram of the true integral curves (Fig. 1b). Each true integral curve with $B_6 > 1$ reaches the origin of coordinates (the rest point) at its own slope α, equal to:

$$\alpha = \operatorname{arctg}\left(2 + \frac{1}{B_1 - 1}\right).$$

For $x_0 \to \infty$ $\alpha \to \alpha_{\min} = \operatorname{arctg}\left(2 + \frac{K_1'}{K_2' - K_1'}\right)$. Since with $B_2 > 1$, according to (15), $K_2' > K_1'$, we have $\alpha_{\min} > \gamma = \operatorname{arctg} 2$ (γ is the slope of the straight line of initial values). As x_0 decreases, the angle α increases, and with $x = x_{0\,\mathrm{crit}} = K_1/2K_e(K_2' - K_1')$ it becomes equal to $\pi/2$ (here $B_2 = 1$). To this corresponds the initial concentration of the epoxy groups, the parameter of the problem is

$$E_{0\,\mathrm{crit}} = \frac{K_1}{K_e(K_2' - K_1')}.$$

The analysis presented above is correct for $K_2' > K_1'$, i.e., when the speed of the catalytic transformation of secondary amines into tertiary ones is higher than the speed of the catalytic transformation of primary into secondary ones. In case $K_2' \leq K_1'$, the parameter

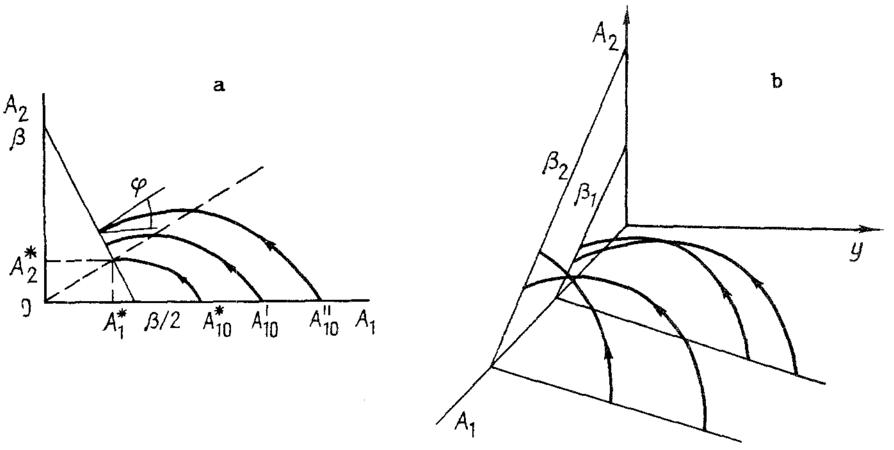

Fig. 3. Phase-plane diagram: a) in the plane (A_1, A_2) with $\beta < 0$ (mapped with fixed value of the parameter β), b) in the three-dimensional space (A_1, y, A_2) with variable parameter.

$B_2 < 1$, and with any initial concentration E_0 the integral curves form a dicritical node. The physical cause of the fundamentally different nature of the curves is obvious. When $K_1' \geq K_2'$, then the primary amines vanish at first, and the opening of the remaining epoxy rings proceeds on account of the secondary amines (here $x \to 0$), for $K_2' > K_1'$ the speeds of transformation of primary and secondary amines are comparable, and x is nonzero up to the end of the process.

It can be seen from the presented dependences and from their graphic illustration (Fig. 1b) that with $B_2 \geq 1$ the integral curves in the phase-plane diagram intersect. This ambiguity is a consequence of the transition from the seven-dimensional phase space of system (2) to the plane space of problem (7). The initial concentration as parameter changed over to the right-hand side of system (7), and this also is the reason why the curves intersect. In the three-dimensional phase space ($x = A_1$, Y, C) there is no intersection. In fact, let the points $E_{0,1}$ and $E_{0,2}$ be points of the line of initial values. For them $B_2 > 1$, and in the phase plane (x, y) the integral curves intersect. However, it follows from (8) that

$$\frac{\partial C}{\partial E_0} = \left.\frac{\partial C}{\partial E_0}\right|_{E=\mathrm{const}} + \frac{\partial C}{\partial E}\,\frac{\partial E}{\partial E_0} > 0,$$

since

$$\left.\frac{\partial C}{\partial E_0}\right|_{E=\mathrm{const}} > 0, \quad \frac{\partial C}{\partial E} < 0, \quad \frac{\partial E}{\partial E_0} < 0.$$

Therefore in the three-dimensional phase space (x, y, C) the integral curves, to which higher initial concentration of the epoxy groups corresponds, always have higher concentration of alcohols, too, i.e., there is no intersection of the integral curves.

Let us analyze the nature of the change of concentrations of all the chemical components: A_1, A_2, C, E, Y. It follows from system (7) that $dA_1/dt < 0$, $dY/dt > 0$. Therefore $dx/dt < 0$, $dy/dt < 0$, and the mapping point in the phase-plane diagram, starting on the straight line of initial data, moves from right to left (as was proved earlier on, $\alpha > \gamma$). In accordance with relations (7), (8), the concentrations of the epoxy groups and alcohols also change monotonically: $dC/dt > 0$, $dE/dt < 0$. The change of the secondary amines is of a more complex nature. At the initial period of the reaction they increase, and from some instant onward they decrease (with $t \to 0$ and $t \to \infty$ $A_2 = 0$). From dependences (6) and (8) we can obtain the equation of line $dA_2/dt = 0$ in the three-dimensional phase space:

$$x_* = \frac{K_2' K_e y_* C_*}{K_1 + K_e C_* (2K_2' + K_1')}.$$

The entrance angle of the curve $dA_2/dt = 0$ to the rest point is $\beta = \mathrm{arctg}(2 + 1/B_1)$, i.e., $\gamma < \beta < \alpha$, which means that there is always intersection of the curve $dA_2/dt = 0$ with the path of the system. In the case $\beta < 0$ all the qualitative traits of the phase-plane diagram, revealed with $\beta = 0$, are retained. However, now there can be intersection of the integral curves even in the three-dimensional space ($x \equiv A$, y, C) since one point in such a space can correspond to different values of β. In that case transition to the four-dimensional space (x, y, C, A_2) is indispensable. In the three-dimensional space (x, y, A_2), on account of the existence of the bond $A_2 - y + 2x = \beta$, different planes correspond to different values of β (Fig. 2).

The integral curves for each fixed β intersect each other, but they are "led apart" in the four-dimensional space (x, y, C, A_2). The planes in which the curves lie intersect the coordinate planes on the lines $y = 2x - \beta$ in the plane (xy) and $A_2 = y - \beta$ in the plane (yA_2).

For the case $\beta < 0$ (excess of amines) it is expedient to carry out the analysis of the phase-plane diagram in the plane (A_1, A_2). At the rest point

$$2A_1 + A_2 = \beta. \tag{16}$$

The integral curves start from the axis $0A_1$ at the angle $\pi/4$ [this follows from system (2)] and end on the straight line (16) (Fig. 3a).

Let us determine the entrance angle of the integral curves to the straight line of the state of rest (the angle φ). From the system (2) we find ($K_2 = 0$):

$$\frac{dA_2}{dA_1} = -\frac{K_1A_1\mathrm{E} + K_1'A_1(\mathrm{EC}) - K_2'A_2(\mathrm{EC})}{K_1A_1\mathrm{E} + K_1'A_1(\mathrm{EC})}.$$

Expanding the right-hand sides in the vicinity of the singular straight line and retaining the first terms of the expansion, we obtain

$$\varphi = \mathrm{arctg}(-1 + B_2\tilde{A}_2/\tilde{A}_1),$$

where the sign ~ relates to the final state of the system.

With $\tilde{A}_1 > A_1^* = \beta/(2 + B_2^{-1})$ the angle $\varphi < 0$, with $\tilde{A}_1 < A_1^*$ $\varphi > 0$. Since the integral curves start at a negative angle, the ones intersecting the line of final state with $\tilde{A}_1 = A_1^*$ have an extremum. With $\tilde{A}_1 = A_1^*$ the extremum is attained at the rest point (then $A_2^* = B_2^{-1}\beta/(2 + B_2^{-1})$. The value of B_2 can be expressed through the initial concentration A_{10}:

$$B_2 = \frac{K_2'}{K_1' + K_1/[K_e(2A_{10} - \beta)]}.$$

As A_{10} increases from $A_{10\,\min} = \beta/2$, B_2 and correspondingly A_1^* increase, and A_2^* decreases.

The integral curves in the plane (A_1, A_2) may intersect each other. The intersection of curves relating to different β is reduced by the transition to the three-dimensional phase space (A_1, y, A_2) (Fig. 3b). In such a space each family of integral curves plotted according to the parameter lies in its own plane.

The intersection of the integral curves with fixed β is eliminated if the concentration of the alcohols is also brought into consideration. The projection of the integral curves onto the plane (y, C) is found from the equation

$$C = (\mathrm{E}_0 - y)/[1 + K_e\mathrm{E}(y)],$$

where $E(y)$ is determined by relation (10). The shape of the integral curves in this plane depends on the value of E_0, not on β. With $\beta \geq 0$ the integral curves end on the axis $y = 0$ at the points $C_i = E_{0i}$. When there is a deficiency of amines, the abscissa of the rest points is equal to $-\beta$.

It follows from our analysis of the phase-plane diagram of the initial system (2) that for all values of the constants of the speed of the reactions and initial concentration of the components, the problem has a stable solution.

Verification of the kinetic model from the point of view of adequacy of describing the process of solidification of epoxy compositions was carried out by comparing the results of

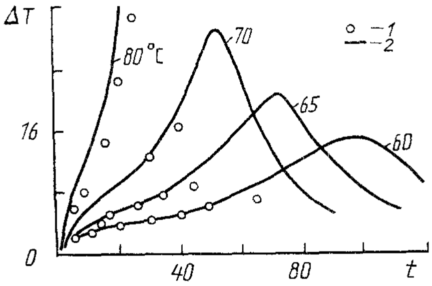

Fig. 4. Overheating of the solidified composition at different initial temperatures of the process of polymerization: 1) experiment; 2) theory. ΔT, °C; t, min.

the calculated magnitude of overheating of the reacting mixture with the experimental data obtained on a specially devised experimental installation. This is a cylindrical tank with thick walls. On the outer boundaries of the tank thermostating was specified for the lateral surface, and adiabatic conditions at the end faces.

The kinetics and heat exchange with a view to the spatial inhomogeneity of the temperature fields and depths of transformation, due to heat removal through the walls to the environment, to the final dimensions of the volume, and to intense chemical heat liberation, were calculated by numerically solving the equations of heat conduction (4) with heat liberation in the region occupied by the composition, and of the kinetics of solidification (7). We used the finite difference method with splitting into physical and chemical factors and into directions [5]. With the splitting procedure used, the chemical reactions were calculated at the first half-step, conductive redistribution of heat in accordance with the external conditions at the second half-step. The values of the kinetic, thermodynamic, and thermophysical parameters were taken from [2, 3], the geometric parameters and the thermophysical properties of the material of the walls correspond to the conditions of the experiment [5]. The results of the calculations for the center of the volume are presented in Fig. 4. It can be seen from the figure that the calculation by the macrokinetic scheme is in good agreement with the measurements, especially at lower initial temperatures of the process of solidification (T_0 = 60, 65°C). That the theoretical values are somewhat higher than the experimental ones for higher temperatures of thermostating the lateral surface can be ascribed to a possible small shift of the thermocouple from the center of the volume. Numerical modeling shows that with increasing T_0 the nonuniformity of temperature distribution over the volume greatly increases. The error of the indications of the thermocouple due to a possible shift therefore increases substantially.

Thus, on the basis of the qualitative investigation of the system of equations of the kinetics (2) it was shown that the macrokinetic model under consideration expresses the regularities of the kinetics of solidification: the final composition of the compound corresponds to the stable rest point. We studied the structure of the phase-plane diagram of the system in dependence on the parameter characterizing the deviation of the composition of the compound from stoichiometry. We analyzed the different regimes realized in dependence on the ratio of the speeds of catalytic reactions. We obtained confirmation of the adequacy of the chosen kinetic model which can be used for modeling processes of flow and heat exchange accompanying the chemical molding of reactive oligomers.

NOTATION

A_1, A_2, A_3, primary, secondary, tertiary amines, respectively; C, alcohol groups; E, epoxy groups; K_1, K_2, K_1', K_2', reaction constants; K_e, constants of equilibrium; (EC), epoxy alcohol complex; Q, thermal effect of a reaction; β, depth of transformation; Y, number of open epoxy groups; ρ, density; c, specific heat; λ, thermal conductivity; T, temperature; t, time; x, y, variables; M_i, rest points; λ_1, λ_2, roots of the characteristic equation; D_i, B_i, coefficients; α, slope of the integral curve.

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