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KINETICS AND MECHANISM OF SOLIDIFICATION AND HEAT TRANSFER OF EPOXY COMPOSITES

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A model is constructed of the kinetics of epoxy resin solidification of isomethyl tetraphthalate anhydride in the presence of a ternary amine. Parameters of the kinetic equation are determined from tests and a computation is performed for an epoxy resin with solidifier of amine type. The method of space—time separation permitted estimation of the influence of rheokinetics on the flow and heat transfer of the partially polymerized fluid.

Plastics are replacing metal, wood, cotton, wool, silk, etc. more and more at present, especially in thermal and electrical engineering, electronics, construction and transport, medicine and agriculture. Until recently, primarily thermal plastics synthesizable from simple organic compounds, monomers, were used. Prior to molding the thermal plastics were transformed into the flowing state for reworking into articles. Reaction plastics, obtained from oligomers of resin type with a small degree of polymerization, are slightly viscous in the initial state and expenditures on their reworking are not large while the molecular mass of the end product is practically infinite. Joining of oligomer complexes is initiated by special admixtures (solidifiers). The appearance of rapidly solidifying oligomer composites set up the beginning of a new progressive industrial technology. Obtaining both the material and the article within a very short time is combined in a single cycle during chemical molding.

Epoxy resins (ER) are evolved efficiently with good mechanical, electrical, and adhesive properties as well as insignificant shrinkage during solidification. They are applied diversely in the production of composite materials, coatings, glues, etc.

A solid substance with developed cross bonds is formed from a liquid mixture of monomers and oligomers during solidification (polymerization, polycondensation). Much heat is liberated here. The chemical reaction rates depend radically on temperature; therefore, the heat transfer governs the course of the solidification process and the quality of the end product to a decisive extent.

The spatial homogeneity of the viscosity and degree of transformation of the composite is of exceptional importance during pressure-casting of a partially solidified polymer composite. The kinetic model of the solidification and the spatial evolution of the temperature fields must be known to control the technological processes.

A kinetic model can be determined by two methods. If the chemical solidification mechanism and the change in enthalpy of the individual reactions are known, then the reagent concentration and heat liberation can be expressed by a system of differential equations. It reduces, often enough, to one kinetic equation connecting the reaction rate (the rate of

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heat liberation or the change in concentration of one of the reagents) with the degree of transformation, temperature, and other quantities. If the chemical mechanism is unknown, then a phenomenological approach is used, the kinetic equation is represented by an empirical functional dependence obtained on the basis of an analysis of existing experimental data.

The kinetics and mechanism of epoxy resin solidification are determined by the nature of their reactive groups, the kind of solidifier, and the conditions of the regime for the process. Most traditional for epoxy resins are solidifiers of amine type and anhydrides of dicarbonic acids [1-18]. The lack of a single opinion about the solidifying mechanism at this time did not prevent the development of new approaches to the examination of epoxy resin solidification by amines. A kinetic scheme [19-23] relying on the elementary reaction rates and factors governing them (reagent concentration, temperature) is used to analyze such reactions. The catalyzing influence of the hydroxyl groups being formed during epoxy complex interaction with amines is quite strong during the solidification of epoxy oligomers by metaphenylene diamine [18, 21-23]. Their interaction with the epoxy hydroxyl groups generates rapidly reacting epoxy alcohols. Therefore, solidification of epoxy oligomers by aromatic amines can be represented by the following kinetic scheme [23]:

$$\begin{gathered}
A_1 + E \xrightarrow{K_1} A_2 + A, \qquad A_2 + E \xrightarrow{K_2} A_3 + A, \\
A + E \overset{K_e}{\rightleftarrows} (EA), \qquad A_1 + (EA) \xrightarrow{K_1'} A_2 + 2A, \\
A_2 + (EA) \xrightarrow{K_2'} A_f + 2A,
\end{gathered} \tag{1}$$

where A_1, A_2, and A_3 are the concentrations of the primary, secondary, and ternary amines, E is the epoxy group, A is the alcohol group, (EA) is the epoxy–alcohol complex, K are the reaction constants, and K_e is the equilibrium constant.

Balance equations can be obtained from the scheme (1); in combination with the energy equation they describe the solidification process completely. Moreover, the temperature dependences of the reaction constants according to Arrhenius must be known. The computation methodology is represented in [21-24].

More widespread is the phenomenological approach of introducing an integral parameter reflecting the set of chemical transformations during solidification of the oligomer. The equation of chemical kinetics is represented in the form [25-27]:

$$\frac{d\beta}{dt} = K_0 f(\beta) \exp\left(-\frac{E}{RT}\right),$$

where K_0 is a normalizing factor, and $f(\beta)$ is a macroscopic function.

The most general form of the equation to describe the macrokinetics of the epoxy oligomer solification process is proposed in [28, 29]:

$$\frac{d\beta}{dt} = (K_1 + K_2\beta^m)(1-\beta)^n. \tag{2}$$

Here $d\beta/dt$ is the reaction rate; $\beta = (E_0 - E)/E_0$ is the degree of transformation, where E_0 and E are the initial and running concentrations of the epoxy groups; and K_1, K_2, m, and n are empirical constants. More complex methods of a calorimetric description of the process of epoxy resin cross-linking are presented in [25, 30, 31].

The macrokinetic approach (1) represents the solidification process more deeply by taking account of the multiplicity of its stages and physicochemical singularities. However, its realization demands a large volume of tedious measurements of numerous reaction constants. The phenomenological approach is attractive because of its simplicity and comparative lack of complexity for finding the model parameters. But here, however, deviations from the real dynamics of the polymerization process are possible, especially under nonisothermal conditions.

If the kinetic scheme for the description of EA solidification by amines is relatively simple, then it is considerably all the more complex for anhydrides. The EA reacts with anhydrides at noticeable rates only in the presence of accelerators, ternary amines, ammonia salts, imidazoles, etc., the so-called initiators of the solidification process. There is no unique representation at this time of the reaction kinetics and mechanism for EA interaction with anhydrides; consequently, it is expedient to use the phenomenological approach.

Solidification reactions were studied for the epoxy resin ED-20 by isomethyltetrahydrophthalate anhydride in the presence of a ternary amine in the isothermal regime on a Calvet type differential calorimeter UNIPAN 605. To assure thermal identity of the cells, the base line (zero reference) had to be written with respect to an etalon close to the specimen under investigation in specific heat. However, because the specific heat is not constant during polymer solidification, an additional contribution appears in the thermal effect during scanning. Consequently, the etalon should be different for the first scanning up to a given isothermal temperature and the second scanning up to the temperature of total solidification. Starting from this, two etalons were used: a pure EA and a completely solidified specimen of identical weight with the specimen. The data obtained on the calorimeter are the difference between the differential signal and the baseline.

A dependence of the rate of heat liberation dq/dt on the time in a 70-140°C temperature range is obtained in the tests. The values of the total heat of reaction Q for each test are independent of the temperature, and the mean value is Q = 136 ± 6 kJ/mole.

If the reaction rate is not constrained by diffusion processes, then in the general case it is determined by the concentrations of the reacting substances and the temperature. Assuming the degree of solidification related uniquely to the reagent concentrations, we obtain that the reaction rate is a function of just β and T independently of the solidification conditions.

To determine the functional dependence of $\dot{\beta}$ on β, several formulas are proposed that approximately describe the experimental data:

$$\dot{\beta} = f(\beta, A, B, m, n), \tag{3}$$

$$f = \begin{cases} (A + B\beta^m)\left(1 - \exp\left[-\dfrac{n}{(1-\beta)^2}\right]\right), & (3a) \\ (A + B\beta^m)\exp\left(-\dfrac{n\beta}{1-\beta}\right), & (3b) \\ (A + B\beta^m)(1-\beta)^n, & (3c) \end{cases}$$

where A, B, m, and n are empirical parameters whose values were determined from experimental data by least squares. To do this, a function was constructed that is the sum of the squares of the deviations

$$F(A, B, m, n) = \Sigma[\dot{\beta}_i - f(\beta_i, A, B, m, n)]^2.$$

The function was minimized with respect to all four parameters by using the Nelder–Mead method.

The requirement of minimality of the sum of the squares of the deviations of the experimental data from a curve described by (3a)-(3c) was the selection criterion. The measurements agree best with (3c). The temperature dependence of the coefficients A and B is described by the Arrhenius equation

$$A = A_0 \exp\left(-\frac{U_a}{RT}\right), \quad B = B_0 \exp\left(-\frac{U_b}{RT}\right), \tag{4}$$

where U_a and U_b are activation energies, R is the Boltzmann constant, and T is the temperature, K.

Using (4) we obtain a six-parameter equation for the dependence of the reaction rate on the degree of solidification

$$\dot{\beta} = \left[A_0 \exp\left(-\frac{U_a}{RT}\right) + B_0 \exp\left(-\frac{U_b}{RT}\right) \beta^m \right] (1-\beta)^n. \tag{5}$$

A large array consisting of 650 points and including all the data of the isothermal sections of the solidification curves for the whole temperature range was produced to compute the values of the parameters. Obtained as a result of the computation are: $A_0 = 1.81 \cdot 10^8$ sec^{-1}, $B_0 = 6.88 \cdot 10^6$ sec^{-1}, U_a = 83.6 kJ/mole, U_b = 67.7 kJ/mole, m = 1.377, and n = 1.844. Without great loss of accuracy in describing the data, the values of the parameters m and n can be taken equal to 1.5 and 2, respectively. The the kinetic equation will be of second order in the acceleration

$$\dot{\beta} = (A + B\beta^{3/2})(1-\beta)^2.$$

The values of the activation energy equal U_a = 84 kJ/mole and U_b = 68 kJ/mole.

Utilization of integer values of the parameters n in the kinetic equation is preferable since n has a fully defined physical meaning and denotes the order of the reaction. If the reagents are present at the beginning of the reaction and are consumed in a stoichiometric relationship, then the quantity $(1 - \beta)$ is proportional to their concentration while for $(1 - \beta)$ the degree in the equation equals the quantity of the initial substances reacting with each other.

The first component A in the right side of (5) also has a physical meaning and is the concentration of the catalyst, to the accuracy of a factor, that is present even prior to the beginning of the reaction, while $B\beta^m$ is what is being formed from the initial products during its process. The power m should not certainly be an integer and, moreover, the autocatalytic term $B\beta^m$ can be described even not by a power-law dependence. However, the kinetics of an autocatalytic reaction can be described completely satisfactorily by using (5) in the majority of cases.

Qualitative estimates of the macrokinetic model (1) are obtained from an analysis of the phase portrait of the system of equations being obtained for the isothermal regime [32]. As an investigation of the integral curves showed, the system of kinetic equations has a stable solution for all values of the reaction rate constants and initial component concentrations.

Heat elimination through a wall into the environment and intensive liberation of chemical heat into the volume in real chemical reactors produce a spatial inhomogeneity of the temperature field across and along the reactor. However, for small volumes with a well-organized heat elimination the spatial temperature gradients can be neglected.

Two limit cases of thermal organization of the process are examined in an example of epoxy resin solidification by amines: 1) thermostating of the boundary surface of the volume, isothermal conditions; 2) a heat insulated surface, adiabatic conditions.

Computations were performed of the transformation kinetics for these regimes for a macrokinetic model. The numerical values of the activation energy and the reaction constants were selected according to [22, 23].

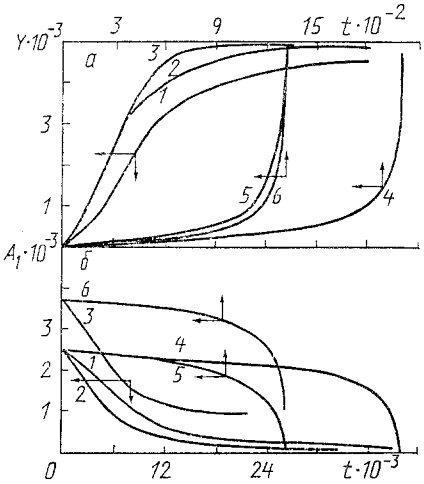

Fig. 1. Change of the degree of transformation (a) and primary amine concentration (b) with time for different solidification regimes and initial primary amine concentration. Isothermal regime: 1) T = 333.15 K, $A_{10} = 2.5 \cdot 10^3$ mole/m^3; 2) 343.15 and $2.5 \cdot 10^3$; 3) 333.15 and $3.75 \cdot 10^3$; adiabatic regime: 4) 333.15 and $2.5 \cdot 10^3$; 5) 343.15 and $2.5 \cdot 10^3$; 6) 333.15 and $2.37 \cdot 10^3$. Y, A_1, mole/m^3; t, sec.

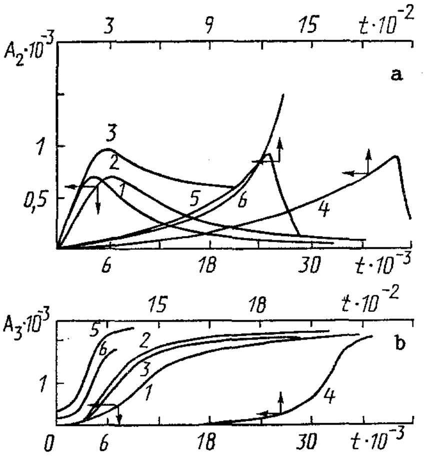

Fig. 2

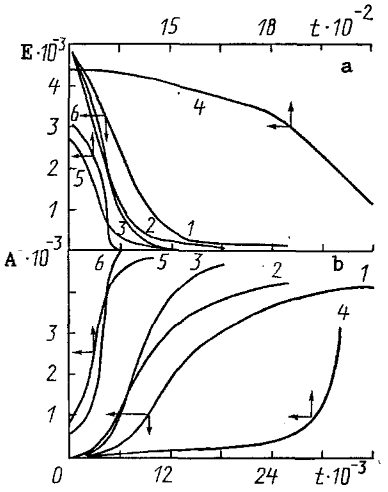

Fig. 3

Fig. 2. Change in the concentration of secondary (a) and ternary (b) amines in time (notation the same as in Fig. 1). A_2 and A_3, mole/m³.

Fig. 3. Kinetics of the change in concentration of epoxy (a) and alcohol (b) groups (notation the same as in Fig. 1). E and A, mole/m³.

Raising the temperature in the isothermal regime exerts strong influence on the degree of transformation in the initial stage of the process (curves 1 and 2 in Fig. 1a), as is explained by the strong temperature dependence of the reaction rates. An excess in primary amines as compared with the stoichiometric relationship, when $A_{10}/E_0 = 0.5$ (curve 3), where $A_{10} = A_1 - A_3 + Y$, $Y = E_0 - E - (EA)$, is similar and exerts stronger influence and for greater times.

Under adiabatic conditions, the process has the nature of a thermal explosion (curves 4-6). The time to complete a complete exposure of the epoxy rings diminishes by an order here as compared with the isothermal conditions (for the same initial data); however, the initial stage of the process (for small degrees of transformation) passes qualitatively identically (a sharp difference in the graphs is explained just by the difference in scale). In contrast to the isothermal case, the same initial excess of primary amines influences more weakly than initial overheating of the system. Under adiabatic conditions the process is apparently auto-accelerated and the role of the temperature factor grows.

The primary amines are consumed during the reaction [the concentration A_1 diminishes (Fig. 1b)]. For an excess A_{10} the final number of amines can be below the quantity $2A_{10} - E_0$ (curves 3 and 6) because of the incomplete transformation of the secondary amines (obtained because of primary amine interaction with the epoxy rings) into ternary amines. This deduction is confirmed by Fig. 2a. The rate of change of the secondary amines changes sign as a rule: there is always a point in stoichiometry where $dA_2/dt = 0$ (the results of a qualitative investigation confirm this), while the nature of the curves for an excess of amines depends on the thermal regime (curves 3 and 6), and in the adiabatic mode $dA_2/dt > 0$ prior to the end of the transformation.

The secondary amine concentration is always significant for an excess of the stoichiometric state (for given reaction rates) even in the final stage of the reaction (curves 3 and 6 in Fig. 2a). But this results in a weak dependence of the final ternary amine concentration on the initial primary amine content (curves 3 and 6 in Fig. 2b). In contrast to the curves for the secondary amines (Fig. 2a), the kinetic curves for the ternary amines (Fig. 2b) have a quite definite induction period. This duration depends strongly on the thermal regime: the influence of the initial temperature is felt by the magnitude of the induction period considerably more strongly for the adiabatic regime.

Curves of the change in epoxy ring (Fig. 3a) and alcohol group (Fig. 3b) concentrations are monotonic in nature. In the isothermal regime the influence of the initial temperature and concentration is felt more strongly by the alcohols (judged by the time to reach a fixed concentration). Attention is turned to the behavior of the curves for an excess of A_{10} under adiabatic conditions (curve 6). The presence of a significant number of primary amines at the end of the reaction under conditions of an abrupt rise in the temperature results in an avalanche-like process.

The conditions of articles obtained from reactive oligomers are determined greatly by technological conditions, i.e., the heat and mass transfer and hydrodynamic molding regimes.

A method of space—time separation of the stages of kinetic solidification of a fluid in a tank and the stages of convection heat and momentum transfer for a rapid pressure flow not complicated by chemical kinetics has been developed and experimentally approved to estimate the influence of rheokinetics on these regime characteristics. Therefore, a chemical transformation in a tank is separated spatially from the subsequent convective stage in a channel. The given state and parameters of the reacting composite are shaped by the duration of its being held in the reservoir. This information is supplemented by calorimetric data about the kinetics and exothermy of the chemical transformations. Taking account of a definite kind of boundary conditions on the reservoir walls (adiabatic, isothermal, mixed) the temperature fields and degrees of transformation are computed in the reservoir as are also the average values of the velocities, temperature and degree of polymerization at the exit from the reservoir. Then the influence of solidification rheokinetics on the hydrodynamics and heat transfer are already determined for a rapid efflux of the mixture of EA and metaphenylene diamine solidifier in a stoichiometric relationship from the channel. A Newtonian behavior is noted in the 100-500 $\sec^{-1}$ range of shear velocities and a viscosity anomaly (pseudoplasticity) appears in the deep stages of solidification ($\beta > 0.3$).

In the case $\beta \leq 0.22$ the viscosity of the epoxy resin being solidified is described by the equation

$$\eta = a\left[\frac{E}{R}\left(\frac{1}{T}-\frac{1}{T_0}\right)+c\beta\right],$$

where $a = 10.78$, $c = 19.7$, and $T_0 = 298$ K. The activation energy of the viscous value $E = 84.1$ kJ/mole is determined only by the resin properties.

A relationship for the Nusselt number [33]

$$\overline{\mathrm{Nu}} = C\left(\frac{1}{\mathrm{Pe}}\frac{L}{d}\right)(\eta_w/\eta_f)^{-0.14}$$

is obtained in an investigation of the convective heat transfer in the thermal entrance section of a channel at Peclet numbers $\mathrm{Pe} = (0.7\text{-}5)\cdot 10^3$ for the nonisothermal flow of a partially solidified fluid, where $C = 1.55\text{-}1.86$; $(\eta_w/\eta_f) = \exp\,[E/R(1/T_w - 1/T_f)]$; η_w is the viscosity at the channel wall temperature; L and d are the channel length and diameter; η_f is the viscosity at the fluid temperature, and T_f is the effective temperature:

$$T_f = T_w - \frac{0.5\,(T_e - T_{en})}{\ln\,[(T_f - T_{en})/(T_w - T_e)]}$$

(T_{en} and T_{ex} are the temperatures at the channel entrance and exit).

Processing the data on the hydraulic drag of the channel showed the competency of the computation of the pressure drop by the Poiseuille formula

$$\Delta P = \frac{32\eta_{ef} L \bar{v}}{d^2},$$

where $\bar{v}$ is the average-consumption flow rate. The effective viscosity

$$\eta_{ef} = \eta_{en}\exp\left[\frac{E}{R}\left(\frac{1}{T_f}-\frac{1}{T_{en}}\right)\right]$$

is used here.

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