# THERMAL METHOD OF MEASURING THE CURING MACROKINETICS OF REACTIVE OLIGOMERS

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UDC 541.64

A method of investigating the curing macrokinetics of polymer compositions with reference to the heat change using a 605 type UNIPAN scanning calorimeter is considered. By this means it is possible to improve the speed of the instrument and measure the deviation from isothermality. An illustrative example of the construction of a macrokinetic model for an epoxy composition is given.

Modeling the curing macrokinetics of reactive oligomers is a topical problem in both science and technology. The recent development of advanced polymer processing techniques (chemical molding) has generated interest in the detailed study of the heat transfer with allowance for the heat source. Accordingly, these processes can be correctly described only by using a macrokinetic model that gives an adequate account of the real process. The traditional method of constructing reactive-oligomer curing models is to investigate the heat release associated with the crosslinking of the material, by means of which a relation is established between the number of reacted functional groups and the amount of heat released during curing [1]. In this article we describe a calorimetric method of investigating curing, the choice of the kinetic equation, and the determination of its constants and their temperature dependence.

In the curing of reactive oligomers it is possible to distinguish several stages. First, the mixing of two or more reactive oligomers and/or monomers. Because of the inhomogeneity of the composition in this phase it is not possible to measure the rate of the immediately ensuing chemical reaction. The second stage is that of curing following homogenization and the reaching of the given temperature at which the kinetic measurements are made. The third stage is the stage of postcuring to equalize the conversion fields over the product. Here kinetic measurements are made difficult by the fall in the rate of heat release as thermodynamic equilibrium is approached.

The study of the thermal processes associated with the curing of reactive oligomers using calorimetric techniques involves a number of difficulties. Firstly, as a rule, the reaction begins in the liquid phase after the mixing of the components. The homogenization of the mixture takes a certain time which cannot be controlled and is the source of a certain irreproducibility of the results. With fall in temperature the curing rate of the system investigated decreases sharply. Therefore by choosing an appropriate mixing temperature it is possible to obtain satisfactory reproducibility of the measurements. Secondly, after mixing the investigated composition is placed in a measuring instrument whose cells are at another temperature. Time is needed to establish thermal balance, which also leads to some loss of information. Thirdly, curing at a given temperature proceeds only up to a certain equilibrium value of the extent of reaction and the total heat change depends on temperature. These matters were previously examined in [2]. However, the problem has not been analyzed with all the factors taken into account. In the literature the heat release process has usually been investigated on scanning calorimeters which enable the curing temperature to be varied. In accordance with Kamal's procedure [3] the composition is mixed at a certain given temperature $T_m$. A weighed amount of the composition is placed in the measuring cell of the calorimeter at the curing temperature $T_0$, $T_m < T_0$. After curing scanning is carried out up to the reduction temperature $T_r$, which is taken higher than the glass transition point of the sample. The temperature difference $T_r - T_m$ is kept constant for the entire series of experiments, which makes it possible to improve the reproducibility of the results.

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A. V. Lykov Institute of Heat and Mass Transfer, Academy of Sciences of the Belorussian SSR, Minsk. Translated from Inzhenerno-fizicheskii Zhurnal, Vol. 60, No. 6, pp. 979-986, June, 1991. Original article submitted June 28, 1990.

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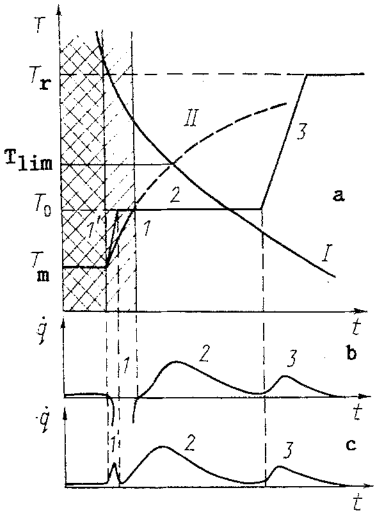

Fig. 1. Diagram of the thermal path of the sample in the calorimeter: (a) I, temperature dependence of total sample curing time; II, time taken to heat sample to given temperature; 1, 2, 3, intervals on thermal path; 1', initial heating interval; (b) variation of heat release rate in accordance with Kamal's method; (c) in accordance with the method proposed.

This method is illustrated in Fig. 1. As the reference time we have taken the start of mixing. The interval between the beginning and end of mixing is fundamentally inaccessible for investigating the heat source (cross-hatched in Fig. 1). The continuous curve represents the process of total curing of the composition (e.g., up to the gel point). The broken curve represents the variation of the temperature of the sample as it is heated to the given temperature (i.e., the "dead time" of the calorimeter). The shaded region is also inaccessible to investigation. It is clear from the figure that there is a limiting temperature $T_{lim}$, above which the "dead time" exceeds the total curing time. This restricts the use of the method in question.

Using this method we measured the changes with time in the strength of the heat source $\dot{q}(t)$ for various curing temperatures and the total reaction energy $Q_0$ as the integral of the strength of the heat source along the path corresponding to intervals 2 and 3 (Fig. 1b). By integrating $\dot{q}(t)$ with respect to time we can obtain the enthalpy on the interval 2 (Fig. 1). The characteristics obtained determine the "calorimetric" extent of reaction during the curing of the composition $\alpha = Q(t)/Q_0$ and the rate of change of the extent of reaction $\dot{\alpha} = \dot{q}(t)/Q$. These quantities are needed to construct the macrokinetic model of the curing process:

$$\dot{\alpha} = f(\alpha, T)|_{T=T_0}, \tag{1}$$

The data obtained at various curing temperatures form a family of curves f. From them we can calculate the temperature dependence of the constants entering into the macrokinetic equation (1). The total curing reaction energy

$$Q = \int_{2,3} \dot{q}(t)\,dt = \int_{2} \dot{q}(t)\,dt + \int_{3} \dot{q}(t)\,dt = Q_2 + Q_3. \tag{2}$$

The value of $Q_2$ is an important element in the study of the curing reaction mechanism, since it is measured under isothermal conditions. The quantity $Q_3$ is of no interest in connection with the kinetics of the process, since it is obtained under nonisothermal conditions. This method does not take into account the value of $Q_1$, the integral of the strength of the heat source along the path 1 (Fig. 1b). Consequently, the extent of reaction α is in fact measured on the interval

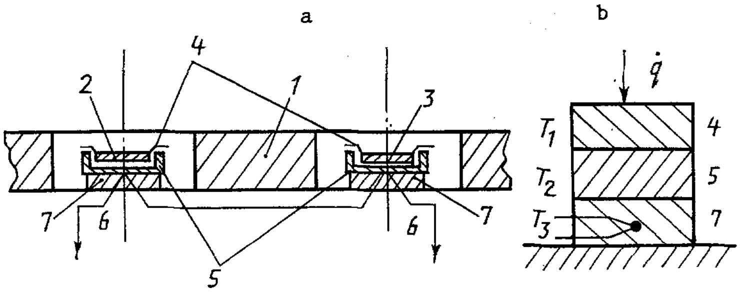

Fig. 2. Calorimeter cell: (a) diagram: 1, base; 2, composition investigated; 3, sample for comparison; 4, crucibles; 5, holders; 6, thermocouples; 7, base of cell; (b) thermal model.

$$\alpha_1 = \frac{Q_1}{Q_0} \leqslant \alpha \leqslant \frac{Q_1 + Q_2}{Q_0} = \alpha_2. \tag{3}$$

Because of the quantity $Q_1$ having been neglected, which valid only for low curing temperatures, the degree of cure lies on the interval $0 \leq \alpha \leq Q_2/Q_0$. The shortcomings of Kamal's method are as follows: the loss of information on the first interval (Fig. 1), which becomes appreciable as the limiting temperature is approached, and the low limiting temperature due to the constant temperature requirement on interval 2. Our method enables these limitations to be largely overcome.

As already noted, the initial nonisothermality of the sample can be neglected, since its thickness is much less than the dimensions of the calorimeter measuring cell. It may therefore be assumed that the thermal trajectory of the sample repeats the path of the measuring cell, although the instrument may record a temperature different from that of the sample. In order to reduce the heat losses on interval 1 it is proposed to maintain in the calorimeter not the temperature $T_0$ but the temperature $T_m$, and then bring the sample to the predetermined curing temperature as quickly as possible (Fig. 1, interval 1'). In this case $\dot{q}(t)$ is recorded and the heat release $q_1(t)$ on this interval is calculated and taken into account in the total reaction energy (Fig. 1c). This improves the reproducibility of the experiments at temperatures close to the limit. Moreover, the thermal trajectory of the sample will be determinate, which makes it possible to propose another method of finding the temperature dependence of the constants of the macrokinetic model. As distinct from Kamal's method, in calculating the constants it is possible not to remain confined to a family of curves obtained at constant temperature (interval 2, Fig. 1). Since the thermal trajectory is known, for finding the parameters of the macrokinetic model we can use the methods of nonlinear programming with constraints [4]. The parameters of the macrokinetic model (1) are determined from the experimental data by minimizing the sum of the squares of the deviations of the calculation results from the measured values for the family of curves recorded for various thermal trajectories of the sample. On the interval of temperatures much less than the limiting temperature $T_{lim}$ there is no difference between our method and Kamal's. Accordingly, it makes sense to start measuring and analyzing the results on the low-temperature interval using the traditional approach and then, as the limiting temperature is neared, go over to the method proposed, using the macrokinetic model obtained as the initial approximation. An important feature of the method proposed is the measurement of the thermal trajectory of the sample. It has already been noted that the calorimeter reading may differ from the temperature of the sample. This is because the temperature transducer is usually located some distance from the sample, which leads to a sharp deterioration in its dynamic characteristics and may introduce distortions into the thermal trajectory.

For the purpose of a detailed analysis of the dynamic distortions we will consider the measuring system of the 605 type UNIPAN calorimeter (Fig. 2a). In design it corresponds to a Tian—Calvet differential calorimeter with variable base temperature [5]. The cell of this instrument is a complex thermal system. It consists of a cell base 7, with which the holder 5 for the crucible 4 containing the sample for investigation 3 is rigidly connected. Between the cell base and the holder thermocouples 6 are introduced. All these components are made of materials with different thermophysical characteristics: aluminum crucible, ceramic cell

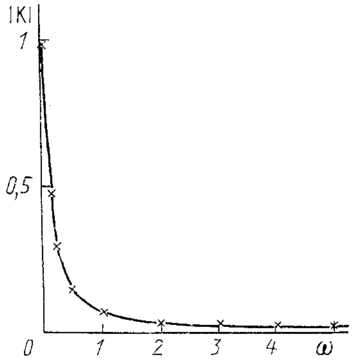

Fig. 3. Modulus of the transient response of the cell. ω, 1/sec.

base, and nickel–nichrome thermocouples. The dynamic characteristics of the system must be found experimentally. For example, by investigating the response of the cell to a short heat pulse supplied by a pulse microheater, it is possible to show that for small times the dynamic distortions cannot be neglected. In order to establish the true value of the signal we will consider the propagation of the heat pulse from the microheater to the cell. In the case in question the rate of temperature equalization is much greater than the scanning and heat-release rates. It is therefore possible to neglect the dynamic effects associated with temperature equalization in the sample and the standard. The thermal model of the cell is equivalent to a stack of thin disks with different thermophysical properties (Fig. 2b). The heat $Q_1$ released in the sample passes through the disks into the massive base of the calorimeter, which is at the constant temperature $T_0$, across the thermal resistance formed by the thermocouple leads. In the quasi-static approximation (neglecting the temperature nonuniformity of the disks) the process can be described by the system of equations

$$m_i c_i \dot{T} = q_{i+1} - q_i + Q_0, \quad q_{i+1} = \frac{\lambda_1}{h_1}(T_{i+1} - T_i) S. \tag{4}$$

Here, $m_i$, $c_i$, $\lambda_i$, and $h_i$ are the mass, specific heat, thermal conductivity, and thickness of the i-th disk, respectively; $q_i$ is the heat accumulated in the disk; $T_i$ is its temperature; and S is the area of the disk. In the instrument in question there are two identical cells differentially connected. This makes it possible to measure the thermophysical characteristics of the system formed by the cell base, the holder, and the thermal resistance of the thermocouple leads. Knowing the coefficient relating the thermal power released in the cell and the e.m.f. generated by the thermocouples we can calculate the thermal resistance between the cell base and the calorimeter block. The sensitivity of the instrument was 70 μW/μV. The number of thermocouples was 6. The sensitivity of the individual thermocouple was 40 μV/deg. The thermal resistance was equal to 0.29 μW/deg, which is considerably higher than the thermal resistance of the holder. We may therefore assume that for the unit in question the thermal resistance is concentrated in the connection between the holder and the calorimeter block. Consequently, the heat capacity of the unit as a whole is concentrated in the holder and the cell base. For measuring the specific heat the following method was employed. By means of a copper plate the holder of one cell was connected with the block and the temperature of the block was scanned. Thus the thermocouple output signal corresponded to the specific heat of the unit. The time constant of the unit was 16 sec.

The time constant of the cup in which the investigated sample was placed can be estimated as $\tau \approx h^2/a$, where a is the thermal diffusivity of aluminum. The substitution of numerical values gives $\tau \approx 2$ sec. Thus, the system of equations (4) can be decomposed into two first-order differential equations:

$$\begin{gathered} m_1 c_1 \frac{dT_1}{dt} = \dot{q}(t) - \beta_1 \lambda_1 (T_1 - T_2), \\ m_2 c_2 \frac{dT_2}{dt} = \beta_1 \lambda_1 (T_1 - T_2) - \beta_2 \lambda_2 (T_2 - T_3), \\ T_1 = T_2 + T_3. \end{gathered} \tag{5}$$

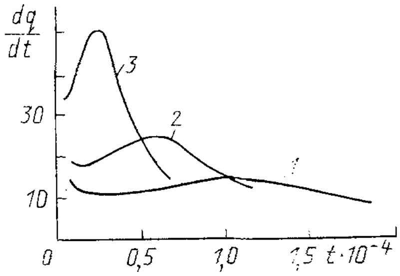

Fig. 4. Heat release rate as a function of time: 1) T = 70°C, 2) 80°C, 3) 90°C. dg/dt, W/kg; t, sec.

Here, $m_1$ and $c_1$ are mass and specific heat of the cup; $\lambda_1$ is the thermal conductivity of the cup; $\beta_1$ is a coefficient that takes into account the geometry of the holder and the thermal contact between the cup and the holder; $m_2$, $c_2$, and $\lambda_2$ are the mass, specific heat, and thermal conductivity of the holder respectively; $\beta_2$ is a coefficient that takes into account the thermal contact between the cell base and the holder; $T_1$ is the temperature of the cup; $T_2$ is the temperature of the holder; and $T_3$ is the temperature of the thermocouple (Fig. 2b). The system of equations (5) is equivalent to the second-order equation in the sample temperature

$$\tau_1\tau_2\ddot{T}_3 + (\tau_1 + \tau_2 + \tau_3)\dot{T}_3 + T_3 = \frac{1}{m_1c_1}\dot{q}(t). \tag{6}$$

Here, $\tau_1 = m_1c_1/\beta_1\lambda_1$, $\tau_2 = m_2c_2/\beta_2\lambda_2$, $\tau_3 = m_2c_2/\beta_1\lambda_1$. Solving equation (6) for the known constants and measured $T_1$, we can calculate the function $\dot{q}(t)$ and, knowing the thermal resistance between the sample investigated and the instrument transducer, the temperature of the sample $T_1$. Using a short heat pulse as the input makes it possible to refine the accuracy of the thermophysical constants of the cell. For such a pulse the transition stage is described by the solution for the homogeneous part of system (5). The solution is compared to the measured response of the calorimeter to a short heat pulse. It is convenient to make this comparison in the domain of Fourier transforms of the measured system response. In Fig. 3 the measured and transformed values are represented by crosses. The transient response of system (5) can be written as follows:

$$H(i\omega) = \frac{1}{1 - \omega^2\tau_1\tau_2 + i\omega(\tau_1 + \tau_2 + \tau_3)}. \tag{7}$$

A comparison with the measured values of the real transient response of the instrument enabled us to improve the accuracy of the characteristic times $\tau_1$, $\tau_2$, and $\tau_3$, which were found to be equal to: $\tau_1$ = 2.2 sec, $\tau_2$ = 14.7 sec, and $\tau_3$ = 15.2 sec. Figure 3 shows the modulus of the transient response (continuous curve) calculated using the above characteristic times. It is clear from the figure that there is satisfactory agreement between the measured transient response and that calculated from expression (5).

Knowing these parameters, we can calculate the true function $\dot{q}(t)$ of the source of the heat generated during the curing process and the true temperature of this process or the thermal trajectory of the sample investigated $T_1(t)$. This can be achieved fairly simply by carrying out a convolution operation in the space of transforms of the measured values with the reciprocal of the transient response by means of standard application programs used for analyzing time series, and then mapping into the space of the inverse transforms.

This procedure made it possible to resolve times to 2 sec rather than 27 sec and to establish the true thermal trajectory of the sample, which is important in connection with the method described above.

For carrying out the experiment we designed an automated system based on the IVK-6 set incorporating peripheral computers of the SM-1300 type and a set of KAMAK apparatus. The calorimeter generated heat flux power signals in the form of binary-decimal values, which were fed to an input—output register; in addition, the calorimeter programmer signals, which

TABLE 1. Parameters of the Kinetic Model

| $m$ | $n$ | $A_1$, $10^{-3}$ 1/sec | $A_T$, 1/K | $A_0$, $10^{-7}$ 1/sec | $U_a$, kJ/mole | $B_1$, $10^{-3}$ 1/sec | $B_T$, 1/K | $B_0$, $10^{-7}$ 1/sec | $U_b$, kJ/mole |
|---|---|---|---|---|---|---|---|---|---|
| 1,45 | 1,89 | 0,114 | 0,0748 | 7,06 | 82,3 | 1,213 | 0,0622 | 0,776 | 68,5 |
| 1,50 | 2,0 | 0,112 | 0,0745 | 6,22 | 81,9 | 1,398 | 0,0629 | 1,151 | 69,4 |
| 1,38 | 1,84 | — | — | 18,1 | 83,6 | — | — | 0,888 | 67,7 |

induce the scan—stop—scan operating regime, causing changes in program execution, were supplied to the interruption register. An ADC analog—digital converter was used to check the deviation of the calorimeter temperature from the given value and then correct it. The program selection time was set by a timer.

The programming included an algorithm for restoring the true form of the output signal by calculating the convolution of that signal with the reciporocal of the transfer function in transform space and converting the data obtained to the space of the inverse transforms with filtration of the high-frequency noise.

Using the method described we experimentally investigated the kinetic characteristics of the curing of ÉD-20 epoxy resin with iso-methyltetrahydrophthalic anhydride (IMTHPA) in the presence of tertiary amine (2,4,6-tris-1-dimethylamino/methyl/phenol). We obtained the dependence of the heat release rate dq/dt in the isothermally cured resin on time t in the temperature interval from 70 to 140°C. Some typical curves are shown in Fig. 4. As the temperature rises, the heat release maximum is reached more quickly and its value increases. The fall in the heat release rate beyond the maximum is due to the decrease in the epoxide group and anhydride concentration. The values of the heat released in the cured sample $\dot{q}(t)$ and the total heat of reaction Q were determined by numerical integration of the heat release rate with respect to time using Simpson's rule. The quantity Q does not depend on temperature and its average value is equal to 137±6 kJ/mole.

If the reaction rate is not limited by diffusion processes, then in general it is determined by the reactant concentrations and temperature. Assuming that the degree of cure is uniquely related to the reactant concentrations, we find that the reaction rate is a function of α and T only, irrespective of the curing conditions.

The experimental data are best described by the equation, widely used in epoxy resin curing kinetics calculations [1]:

$$\dot{\alpha} = (A + B\alpha^m)(1 - \alpha)^n, \tag{8}$$

$$A = A_0 \exp\left(\frac{U_a}{RT}\right), \quad B = B_0 \exp\left(-\frac{U_b}{RT}\right). \tag{9}$$

The value of the model parameters was determined from a file of experimental data corresponding to 650 points including measurements of the isothermal curing curves for various temperatures. The calculations were carried out by least squares using the Nölder—Mead numerical algorithm. Since the minimization method is sensitive to the choice of initial approximation, we first calculated the parameters for the Reynolds temperature dependence model, which is more economical from the computation standpoint:

$$A = A_1 \exp\left[-A_T(T - T_0)\right], \quad B = B_1 \exp\left[-B_T(T - T_0)\right]. \tag{10}$$

Here

$$A_T = \frac{U_a}{RT_0}, \quad A_0 = A_1 \exp(A_T T_0), \quad B_T = \frac{U_b}{RT_0}, \quad B_0 = B_1 \exp(B_T T_0).$$

As $T_0$ we took 90°C. The results of the calculations for the six-parameter model are presented in the first row of Table 1. The second row of the table gives the data obtained for the four-parameter model at the fixed values m = 1.5, n = 2. In both cases the values

TABLE 2. Effect of the Parameters m and n on the Value of $r^2$

| $n$ | $m$ | | | |
|---|---|---|---|---|
| | 0,9 | 1,2 | 1,5 | 1,8 |
| 1,5 | 0,950 | 0,950 | 0,937 | 0,913 |
| 2,0 | 0,928 | 0,947 | 0,956 | 0,951 |
| 2,5 | 0,872 | 0,909 | 0,936 | 0,951 |

of the correlation coefficient $r^2$ were 0.96. In order to estimate the effect of m and n on the correlation coefficient, we made calculations with different fixed values of these parameters. The data are presented in Table 2. The values obtained with model (10) were used as the initial approximation for calculating the parameters with the Arrhenius temperature dependence (9). The results are presented in the third row of Table 1. The correlation parameter increased to $r^2 = 0.971$. This shows that the Arrhenius model gives a better description of the experimental data.

As may be seen from Table 2, without serious loss of accuracy we can take m = 1.5, n = 2. This value of n shows that the curing reaction is second-order. The reactants are consumed in stoichiometric proportions and the reaction rate is proportional to their concentration. The autocatalytic term $B\alpha^m$ in (8) characterizes the acceleration of the reactions as a result of product formation. Representing the experimental data for various temperatures in the form of the dependence of $\dot{\alpha}/(1-\alpha)^2$ on $\alpha$ shows that up to $\alpha \approx 0.8$ the effective rate increases almost linearly. Therefore the fractional value m = 1.5 is associated with the average description of the two stages $\alpha \lesssim 0.8$ and $\alpha \gtrsim 0.8$.

Near 140°C it is not possible to study the macroscopic properties of the system using the traditional Kamal method. This is because it takes the calorimeter about 10 minutes to reach the specified temperature, which corresponds to 50% reaction of the sample at these temperatures. Even when the sample is heated to the specified temperature at 10°C/min, the proposed method makes it possible not to lose the heat generated and to trace the thermal trajectory of the sample correct to 1°C.

Thus, as distinct from the traditional methods, the method developed makes it possible to improve the speed of the instrument and considerably expand the range of investigation of the kinetic processes in reacting media. It enables the thermal trajectory of the sample investigated to be established and thereby makes it possible to improve the estimation of the kinetic parameters of the initial reaction rate.

## NOTATION

$T_0$, $T_m$, $T_r$, $T_{lim}$ are the curing, mixing, reduction, and limiting temperatures respectively; $\dot{q}$ is the strength of the heat source; $Q_0$ and $Q_i$ are the total reaction energy and the reaction energies on the various curing intervals (i = 1, 2, 3); $\alpha$ is the calorimetric degree of cure; $\lambda$ is the thermal conductivity coefficient; c is the specific heat; R is the universal gas constant; $A_0$, $B_0$, $U_a$, $U_b$, m, and n are model parameters; and a is the thermal diffusivity.

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