Estimation of kinetic parameters for curing of epoxy-anhydride compositions by DSC

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The kinetics of the curing process of epoxy resin (ED-22) in the presence of the anhydride hardeners (*iso*-methyltetrahydrophthalic anhydride, hexahydrophthalic anhydride, and dode-cylsuccinic anhydride) and accelerators (2-methyl imidazole and *n*-butyltriphenylphosphonium bromide) has been investigated by DSC method in the dynamic mode. Processing of experimental DSC thermograms recorded at different heating rates was carried out within the frameworks of isoconvertional analysis in two versions, namely "model-free" method of Friedman and the Ozawa—Flynn—Wall method. The possibility to describe the kinetics of epoxy compositions curing in the frameworks of one-step autocatalytic reaction model has been demonstrated. Obtained kinetic parameters were used to predict the curing kinetics under isothermal conditions and for comparative analysis of the compositions.

Key words: epoxy-anhydride formulation, catalyst, curing kinetics, differential scanning calorimetry (DSC).

Polymer composite materials are widely used due to their outstanding strength-to-weight ratio. By manufacturing the products from polymer composite materials, it is necessary to take into account a number of technological factors, such as cure time, temperature, pressure, *etc*. Deviation from optimal conditions can lead to internal strains, incomplete curing of binders, increased porosity, *etc*. To minimize such defects, to obtain the final material with the best properties, and also to reduce the energy consumption, it is necessary to know the kinetic characteristics of the curing process of the binder. The DSC method is currently most convenient for studying epoxy compositions.[1—8] The curing process of epoxy compositions is usually complex, its mechanism and kinetic regularities can vary significantly depending on both the chemical structure of the components of the system and the external conditions. The effective activation energy for curing under isothermal conditions can vary due to the transition from kinetic to diffusion control. Such systems are difficult to parameterize. At present, the DSC method is widely used to obtain the kinetic parameters of the curing process. The curing of the compositions is most often carried out in a dynamic mode.[1—13]

There are two approaches to study the kinetics of curing, the first one, based on exact knowledge of mechanism and the second, the phenomenological one. The first approach is laborious and involves a detailed investigation of

all steps of the curing process, which is not always possible. The phenomenological approach is semiempirical and it is mainly used for the purpose of compositions comparison. The process of curing of epoxy-anhydride compositions with the use of new accelerators, phosphonium salts, was studied earlier.[14] The synthesis method and characteristics are also presented in Ref. 14. It has been shown using the DSC method that the use of synthesized phosphonium salts allows curing at lower temperatures than in the case of widely used accelerator, 2-methylimidazole. A new scheme of the polymerization of epoxy-anhydride system catalyzed by phosphonium salts has been proposed by studying the mechanism of the curing reaction by mass spectrometry. This scheme differs from the mechanism known in the literature for curing of epoxy-anhydride compositions in the presence of imidazoles as catalysts. It has been established[15] that the lifetime of compositions with phosphonium salts is higher than in case of tertiary amines or imidazoles used as the catalysts. It was of interest to study the influence of the accelerator on the kinetics of the compositions curing. In this paper we present the results of determination of the effective kinetics parameters of the curing process for epoxy-anhydride binders in a dynamic mode using various methods of data processing. This information is useful for comparison of the activity of different compositions and for selection of curing modes for epoxy-anhydride systems using various catalysts.

Experimental

Epoxy resin ED-22 (epoxide number 23.5%) was used. A series of carboxylic acid anhydrides, namely *iso*-methyltetrahydrophthalic anhydride (*iso*-MTHPA), hexahydrophthalic anhydride (HHFA), and dodecylsuccinic anhydride (DDSA) were used as hardeners. 2-Methylimidazol (2MI), and also synthesized by us *n*-butyltriphenylphosphonium bromide (BTPPB) were used as accelerators. The last accelerator allows to carry out the curing at temperatures lower than in case of 2MI.[14] The resin and hardener were used in stoichiometric ratio according to functional groups, while 2 wt.% of catalyst was used.

The curing process was studied using DSC method with differential scanning calorimeter Netzsch DSC 214 Polyma. The measurements were carried out in closed aluminum crucibles in the nitrogen atmosphere at different heating rates (5—20 °C min^{-1}), the weight of binder sample was 9—18 mg. Curing reaction kinetics was analyzed using Netzsch Thermokinetics 3 software.

Results and Discussion

So-called isoconversion methods for calculation of the kinetic parameters from experimental data carried out under dynamic heating conditions are based on the idea that the rate of chemical transformation can be expressed as the product of two terms, the first of which depends on temperature and the second on the conversion (*x*) (Eq. (1)):

$$dx/dt = f(x)k(T), \tag{1}$$

where *x* is the degree of conversion, *t* is the curing time, *T* is the temperature. By substituting the expressions for the rate constant for Arrhenius law and the rate of linear heating β = d*T*/d*t* the Eq. (1) takes the form

$$\beta dx/dT = A\exp[-E_a/(RT)]f(x), \tag{2}$$

where E_a is the activation energy, *A* is the pre-exponential factor, *R* is the universal gas constant.

The calculation of the kinetic parameters is performed by analyzing the changes on DSC thermograms recorded at different heating rates.
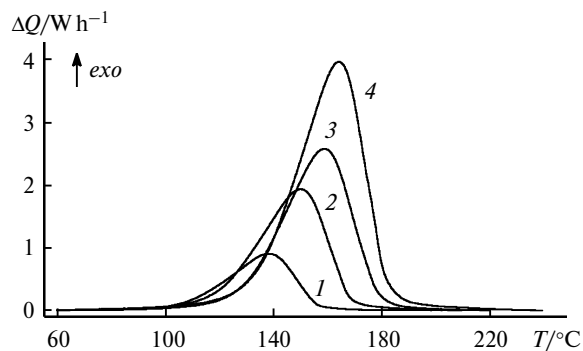
Fig. 1. DSC curves for system ED-22—*iso*-MTHPA—BTPPB, obtained at different heating rates: 5 (*1*), 10 (*2*), 15 (*3*), and 20 °C min^{-1} (*4*).

The DSC thermograms of the ED-22 binder sample, cured by *iso*-MTHPA using BTPPB as a catalyst, which were obtained at different heating rates, are shown in Fig. 1.

The calculation of activation energy in the first variant was carried out within the frameworks of Ozawa—Flynn—Wall approach.[16,17] It is based on the analysis of the integral form of Eq. (2) upon a reasonable assumption that the degree of conversion at the maximum temperature of the DSC curve is constant and does not depend on the heating rate. The integral form of Eq. (2) is reduced to the approximate equation of linear dependence:

$$\ln\beta = -(E_a R)(1/T_f), \tag{3}$$

where T_f is the temperature in the point of thermogram maximum at given heating rate.

In accordance with Eq. (3), the apparent values of curing activation energy are determined from the analysis of the dependence of the reciprocal temperature at the maximum point on the heating rate (Fig. 2). Let us note that the estimate of the activation energy within the frameworks of this approach does not require information on the order of the reaction. At the same time, the calculation of the rate constant and the pre-exponential factor is possible only for a specific process scheme, *i.e.* for the reac-
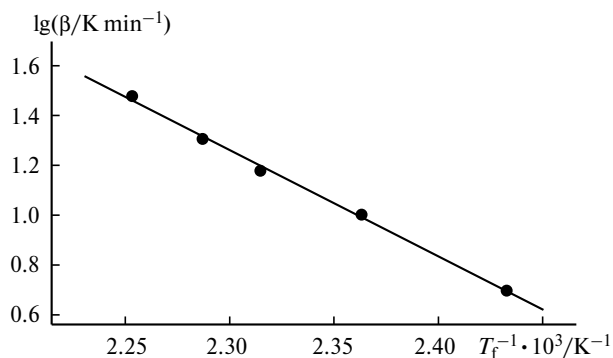
lg(β/K min⁻¹)
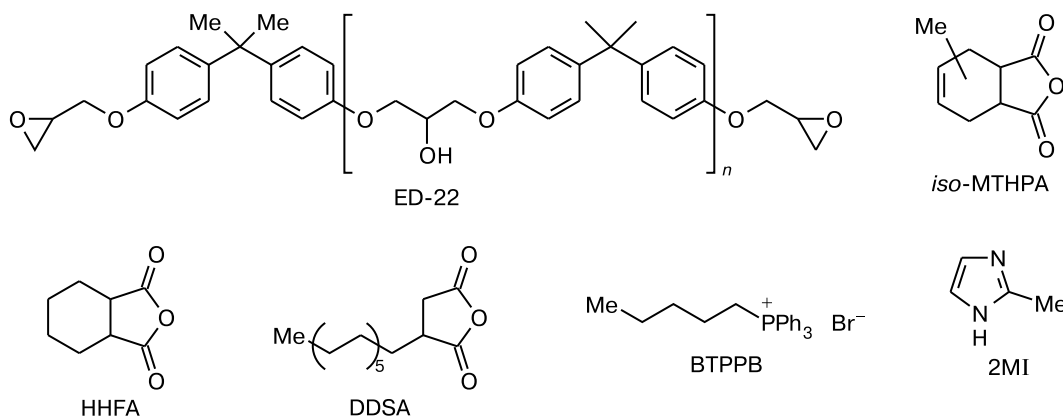
Fig. 2. Dependence of reciprocal temperature in the point of maximum of DSC curve on logarithm of heating rate for binder ED-22—*iso*-MTHPA—BTPPB.

tions of the first, second, and higher orders. As it is noted above, the actual curing mechanism for epoxy resins is very complex and sometimes involves several sequential-parallel reactions. There is no detailed kinetic information required for a complete description of the process. However, to solve some practical problems, for example, for the purpose of comparing the activity of the same type of compositions, a simplified scheme for calculating the first-order reaction model is applied. Such a calculation is carried out automatically using the calorimeter software. The values of the reaction rate constant of the first order, the apparent activation energy, and the apparent pre-exponential factor for each system are presented in Table 1.

It can be concluded from obtained data that the rate of system curing with phosphonium accelerator is also higher than in the case of the corresponding systems with 2MI. At the same time, *iso*-MTHPA-based compositions are most active, and the curing reactions of system ED-22—DDSA—catalyst proceed more slowly than others. In addition, the values of the apparent activation energy at implied constant conversion and the same catalyst content, reached at the point of the exothermic maximum for epoxy-anhydride compositions using 2MI, are slightly higher than that obtained with phosphonium salt as an accel-

erator. This indicates a slightly higher activity of BTPPB as an accelerator compared to 2MI.

To determine the activation energy in the course of the reaction, we also carried out a calculation using the so-called "model-free" Friedman method.[13] This method is assigned to the second group of computational methods based on the analysis of the differential form of the Eq. (1). In this case, unlike the first method, the initial data for the calculation are two characteristics, namely the temperature and the reaction rate at the point of achieving a certain conversion.

By substituting the Eq. (2) into the Eq. (1), and also by replacing $Af(x)$ for $F(x)$, then taking a logarithm of the Eq. (1) we obtain a relationship linking the reaction rate with conversion:

$$\ln(dx/dt) = -[-E_a/(RT)] + \ln F(x). \tag{4}$$

The DSC thermograms of composition, cured in the dynamic mode, rearranged in the coordinates of the reaction rate—the inverse temperature, are presented in Fig. 3, *a*. Each curve corresponds to corresponding heating rate. As the heating rate increases, the curves shift to the left and up.

The isoconversion lines obtained by processing the experimental thermograms using Friedman method are the dependencies of the reaction rate dx/dt on the reciprocal temperature at which a given conversion is achieved in

Table 1. Obtained in the frameworks of Ozawa—Flynn—Wall approach the value of apparent activation energy E_a^*, apparent pre-exponential factor A, rate constant k at temperature 100 °C for different compositions of binder

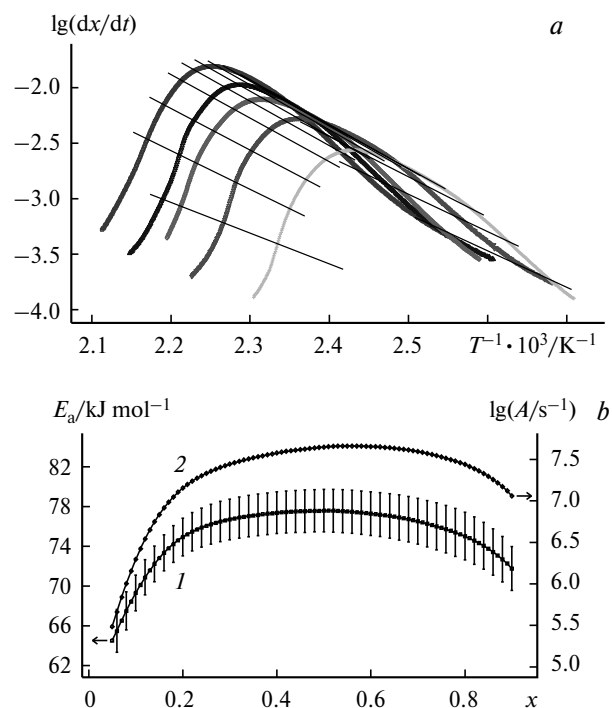| Binder composition	E_a^* /kJ mol⁻¹	lg(A/s⁻¹)	$k \cdot 10^4$ /s⁻¹
ED-22—*iso*-MTHPA—2MI	76.2±4.3	7.26	3.8
ED-22—*iso*-MTHPA—BTPPB	72.2±2.0	6.80	4.8
ED-22—HHFA—2MI	85.4±3.9	8.54	3.7
ED-22—HHFA—BTPPB	65.5±2.2	5.82	4.3
ED-22—DDSA—2MI	69.7±3.4	6.05	1.9
ED-22—DDSA—BTPPB	69.1±2.7	6.14	2.8

Fig. 3. Isoconversion lines, obtained by "model-free" analysis according to Friedman (*a*), and also effective activation energy (*1*) and effective pre-exponential factor (*2*) on degree of conversion (*x*) (*b*) for system ED-22—*iso*-MTHPA—BTPPB.
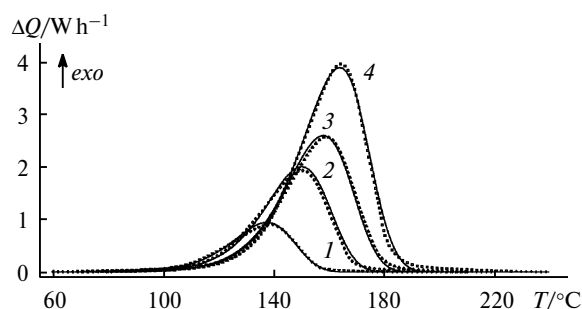
Fig. 4. Comparison of calculation results (curves) with experimental data (dots), obtained for system ED-22—*iso*-MTHPA—BTPPB at different heating rates: 5 (*1*), 10 (*2*), 15 (*3*), and 20 °C min⁻¹ (*4*).

experiments with different heating rates (see Fig. 3, *a*). The effective activation energy is calculated on the basis of the slope of the isoconversion curve and corresponds to a certain conversion of the process. The dependence of the change in the calculated activation energy and the effective value of the pre-exponential factor (calculated in the approximation of the first-order reaction) on the degree of conversion is presented in Fig. 3, *b*.

As it can be seen from Fig. 3, *b*, upon change of the conversion, the effective activation energy varies from 64 to 76 kJ mol⁻¹. In absolute terms, it does not differ much from the values calculated using the Ozawa—Flynn—Wall method (see Table 1) at the conversion at the maximum point of the DSC thermogram. However, the fact that the activation energy depends on the conversion, especially at the beginning of the process, indicates that the real mechanism of the process is more complex than the representation by a one-step reaction. Nevertheless, the obtained effective kinetic parameters are useful for comparing the same type of systems, for example, containing different catalysts or characterized by different content of catalyst.

To describe the kinetics of the curing reaction in the dynamic mode, we also used in this study the model of an autocatalytic reaction of the *n*th order. The model is also often used to describe the curing of epoxy resins (Fig. 4). The autocatalytic effect is usually associated with the contribution of formed in the process of carboxyl and hydroxyl groups into the reaction.[18,19]
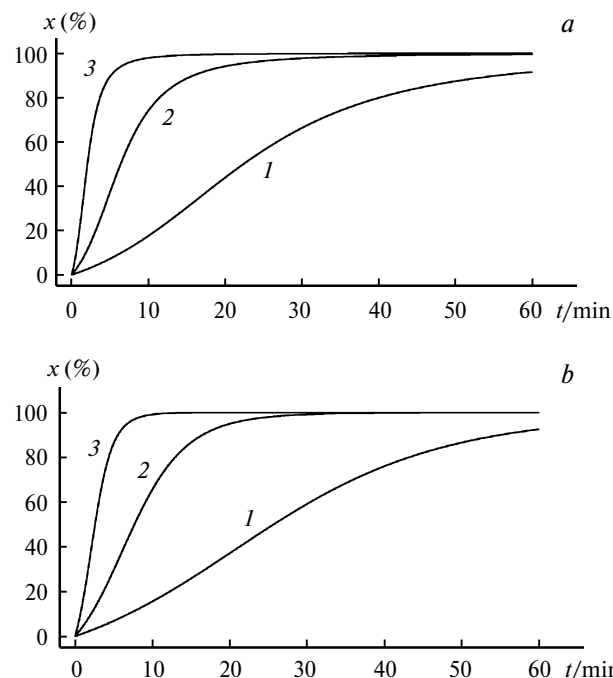

Fig. 5. Calculated curves for curing process of compositions ED-22—*iso*-MTHPA—BTPPB (*a*) and ED-22—*iso*-MTHPA—2MI (*b*) in isothermic mode at temperatures 100 (*1*), 120 (*2*), and 140 °C (*3*).

The kinetic equation of the model with the autocatalysis has the following form:

$$\mathrm{d}x/\mathrm{d}t = A\exp[-E_a/(RT)](1 + k_{cat}\alpha)(1 - \alpha)^n, \qquad (5)$$

where k_{cat} is the autocatalysis constant, n is the reaction order.

The calculation was carried out by the method of multivariant nonlinear regression using the Netzsch Thermokinetics 3 software. The values of the effective activation energy (E_a), the pre-exponential factor, the autocatalysis constant, the order of the reaction, and the correlation coefficient (*r*) for binders of different compositions, which ensured the best agreement between the calculated and experimental data, are represented in Table 2.

For all compositions, the values of the effective activation energy calculated by this method are close to those obtained by the isoconversion methods (see Table 1). The

Table 2. Kinetic parameters for curing of different epoxy-anhydride systems

Composition of system	lg(*A*/s⁻¹)	E_a/kJ mol⁻¹	lgk_{cat}	*n*	*r*
ED-22—*iso*-MTHPA—2MI	6.99	77.48±0.14	0.99	1.44	0.997
ED-22—*iso*-MTHPA—BTPPB	6.60	73.56±0.12	0.78	1.11	0.998
ED-22—HHFA—2MI	7.51	79.87±0.15	0.92	1.37	0.996
ED-22—HHFA—BTPPB	5.23	67.96±0.19	1.46	1.26	0.995
ED-22—DDSA—2MI	6.02	78.35±0.27	0.87	0.90	0.997
ED-22—DDSA—BTPPB	6.45	72.70±0.13	0.72	0.77	0.994

Table 3. Time (min) to achieve a certain conversion (25, 75, and 95%) at 70 and 120 °C

Composition of system	70 °C			120 °C		
	25%	75%	95%	25%	75%	95%
ED-22—*iso*-MTHPA—2MI	119.92	357.93	617.86	5.07	12.18	20.63
ED-22—*iso*-MTHPA—BTPPB	110.06	312.19	532.23	4.17	9.96	20.15
ED-22—HHFA—2MI	127.52	393.22	650.83	6.31	13.19	21.40
ED-22—HHFA—BTPPB	118.67	359.90	605.28	3.69	9.43	20.87
ED-22—DDSA—2MI	121.54	373.17	630.02	5.96	12.31	21.08
ED-22—DDSA—BTPPB	111.36	334.41	581.40	4.49	10.18	20.29

effective order of the reaction and the effective constant of the autocatalysis, which allows predicting the course of curing process, was also determined by this method.

The calculation of the change in the degree of conversion depending on the duration of the system kept under isothermal conditions was performed using automatic software based on obtained kinetic parameters (Fig. 5). The time for achieving certain degree of conversion (25, 75, 95%) at temperatures of 70 and 120 °C (Table 3) was also calculated.

Therefore, the study of the kinetic features of the binder curing in the dynamic mode makes it possible to compare different formulations, to select hardeners, catalysts, and the optimal temperature mode of curing.

Thus, in present work, the kinetics of curing of a number of epoxy-anhydride compositions in the dynamic mode in the presence of the new accelerator of *n*-butyltriphenylphosphonium bromide was investigated by the DSC method in comparison with experiments in the presence of 2-methylimidazole. Using the methods of the isoconversion analysis of the experimental data in Friedman and Ozawa—Flin—Wall variants, as well as the model of the autocatalytic reaction, it has been demonstrated that the effective activation energy for curing of epoxy-anhydride compositions catalyzed by *n*-butyltriphenylphosphonium bromide is somewhat lower, and the rate of the curing reaction is higher than for the systems, containing 2-methylimidazole as an accelerator. The kinetic parameters obtained by the processing experimental data were used to calculate the kinetic curves of the curing process of reaction systems under isothermal conditions at different temperatures. It is established that the methodology used for carrying out the experiment in the dynamic mode makes it possible to conduct a comparative analysis of epoxy compositions quickly and efficiently and to select the optimum mode of their curing.

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