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KINETIC METHOD BY USING CALORIMETRY TO MECHANISM OF EPOXY–AMINE CURE REACTION

Part II. On catalytic action of the amine excess

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Abstract

The results of using the calorimetric method to the mechanism of epoxy–amine cure reaction are presented. Under isothermal conditions, the cure kinetics was analysed by the Mangelsdorf approach. The kinetics of epoxy–amine cure reaction has clearly shown that interaction between epoxy and amine-groups follow the second-order rate law. This finding is important evidence in favour of conception of structured reactive medium during epoxy–amine cure reaction.

It is found that amine excess over epoxide reveals the clear catalytic action. Possible mechanism involving the complex formation between initial reagents is considered.

Keywords: amine, cure reaction, epoxy ring opening, isothermal calorimetry, kinetic study, Mangelsdorf`s approach, mechanism

Introduction

Today calorimetric method is a conventional one in the kinetic study of the epoxy–amine reaction. As is well known, this method has the advantage of being simple but somewhat crafty.

Under isothermal conditions, the cure kinetics can be analysed by using the Mangelsdorf approach. This method is especially helpful in the case in question, since it makes possible to use the calorimetry in the kinetic studies of the complicated reactive systems [1].

The Mangelsdorf approach to the reaction kinetics lets us to determine the effective reaction rate constant as well as the heat of epoxy ring opening for every epoxy–amine cure kinetics. The preceding analysis shown that observed kinetics is seldom as simple as this. The kinetics of epoxy–amine cure reaction has consistently shown that interaction between epoxy and amine-groups follow the first order rate law with respect to concentration of the deficient reagent. This finding is important evidence in favour of forming relatively weak or ‘labile’ bonds between the functional groups of the reagents.

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Until now, there is not any information in the literature regarding the nature of epoxy–amine reactive medium. The latter comprises the mixture of reactants and low molecular products, playing the role of solvent for reactive system. An ability of the functional groups of amine- and epoxy-molecules to form complexes may provide a common basis for understanding of the cure reaction mechanism.

The results of kinetic analyses could only be explained on the supposition that curing reaction proceeds in strongly structured reaction medium [2]. This in effect is a valid interpretation of the properties of the reaction medium (acting as a solvent) in facilitating curing reaction.

A detailed understanding of the rate controlling mechanisms of cure processes restricted to so-called models [3], is slight evidence. Meanwhile 'kinetic investigation' approach to curing mechanism is a much less developed area. Little is known of the actual mechanism of epoxy ring opening during the cure reaction in a solvent-free reacting medium, since the adherence to Beer's law is not observed among cure reactions [4]. Thus, this report is an attempt to fill this gap.

The present paper that is concerned with our previous study [2] is intended to test the set of differential equations as observed by isothermal calorimetric method thoroughly by extending the kinetic study to various reagent ratios.

Experimental

Materials

In the present study resorcinol diglycidyl ether (RDGE) was cured with *m*-phenylenediamine (MPDA). Purification of the reagents was conducted by distillation in the argon flow. RDGE has T_{bol}=150–160ºC at 0.1 Torr. The boiling point of MPDA is T_{bol}=140ºC (10 Torr).

The epoxide content of the resin was determined by reacting the resin with excess hydrochloric acid in acetone/water solution and then titrating the excess acid with $AgNO_3$. The values for the epoxy number (equiv./100 g) were obtained in seven parallel experiments: arithmetic mean 37.9, deviation from the mean 0.42 with 0.95 probability, epoxide number 37.9±0.4. Experimental details of the method are given in [5].

Procedure

A beaker of capacity 2–2.5 mL is supplied with 0.7–0.9 g of the epoxide and the calculated amount of amine. This beaker containing the mixture was placed in a thermostat at 50ºC for 16 min. The melted mixture was stirred at room temperature. This procedure for mixing the reactants was chosen in order to avoid chemical reaction during mixing.

Samples of approximately 0.25 g were encapsulated in standard DSC aluminium pans and cured isothermally in DSC. The samples were studied in crimpseeled conditions. Differential scanning calorimeter DSC-111 ('Setaram', France) was used to obtain the extent of reaction during the isothermal reactions of epoxy–amine systems. Samples of approximately 0.25 g were sealed in aluminium pans and subjected to isothermal curing at different reagent ratios. Cure isotherms were obtained at temperatures 50 and 60ºC. At temperature 60ºC, kinetic studies were performed using isothermal calorimeter DAC-1-1 (Institute of Chemical Physics, Russian Academy of Sciences, Chernogolovka). Samples of approximately 0.3 g were sealed in glass ampoules and subjected to isothermal curing. The reference consisted of fully cured sample. Reference and sample masses were matched as closely as possible. A baseline recorded previously with reference for the same heating rate was subtracted from the calorimetric signal.

Results and discussion

Model narrative

In previous work [1], it has been shown that, if it is assumed equal reactivity of primary and secondary amine hydrogens, epoxy–amine cure kinetics in terms of the observed concentration may be expressed by the set of differential equations:

$$\frac{dC_{x1}}{dt}=k_{ef1}(C_A-C_x)(C_E-C_x) \tag{1}$$

$$\frac{dC_{x2}}{dt}=k_{ef2}(C_0-C_x)C_x \tag{2}$$

$$\frac{dC_{x3}}{dt}=k_{ef3}[(C_x-C_x^{sat})-C_{x3}](C_x-C_x^{sat}) \tag{3}$$

where dC_{x1}/dt and dC_{x2}/dt are the reaction rates in bimolecular uncatalyzed and autocatalyzed reactions, respectively; C_E is the initial concentration of functional groups of epoxy resin in mol L^{-1}; C_A is the initial concentration of amine groups in mol L^{-1}, for both reactions; k_{ef1} is a rate constant for uncatalyzed reaction, k_{ef2} is a rate constant for the same reaction catalyzed by OH groups formed in the reaction; C_x (mol L^{-1}) is the total concentration of OH groups formed (C_x=C_{x1}+C_{x2}). C_0 is the initial concentration of the deficient reagent. (C_0-C_x) is the concentration of the complex consisted of the molecules amine and epoxide in mol L^{-1}.

The first two equations describe the reaction of epoxy ring opening taking into account the reaction occurs by two competitive mechanisms: one is noncatalytic mechanism and the other is catalysed by OH-groups formed during the reaction as well as equal reactivity of primary and secondary amine hydrogens. In contrast to the Eq. (1), the Eq. (2) is based on the assumption that the reaction medium comprises the reagents bounded into a complex, here ($C-C_x$) is the concentration of the complexes consisted of the molecules amine and epoxide in mol L^{-1}; C_0 is the initial concentration of the deficient reagent.

The results reported in [2] revealed the endothermic process during the later stages of the cure reaction. The third Eq. (3) refers to the diffusion process. One important consequence of this is that the product concentration, from now on denoted by C_x^{sat}, remains constant. By this is meant that the newly formed OH groups leave the reaction medium. To describe this diffusion process we introduced Eq. (3).

Taking into consideration the saturation with OH groups the Eq. (2) may be written in the form:

$$\frac{\mathrm{d}C_{\mathrm{x2}}}{\mathrm{d}t}=k_{\mathrm{ef2}}(C_0-C_{\mathrm{x}})(C_{\mathrm{x}}-C_{\mathrm{x3}}) \tag{4}$$

with initial condition $C_{\mathrm{x3}}=0$ at $C_{\mathrm{x}}<C_{\mathrm{x}}^{\mathrm{sat}}$.

Consider kinetic system as observed by isothermal calorimetric method. Rewriting Eqs (1), (3) and (4) in terms of the molar heat of epoxy ring opening we obtain:

$$\begin{aligned}\frac{\mathrm{d}Q}{\mathrm{d}t}=&Q_{\mathrm{mol1}}k_{\mathrm{ef1}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}})+Q_{\mathrm{mol2}}k_{\mathrm{ef2}}(C_0-C_{\mathrm{x}})(C_{\mathrm{x}}-C_{\mathrm{x3}})+\\&+Q_{\mathrm{mol3}}k_{\mathrm{ef3}}[(C_{\mathrm{x}}-C_{\mathrm{x}}^{\mathrm{sat}})-C_{\mathrm{x3}}](C_{\mathrm{x}}-C_{\mathrm{x}}^{\mathrm{sat}})\end{aligned} \tag{5}$$

where Q_{mol1} and Q_{mol2} are the molar heat of epoxy ring opening for uncatalyzed and autocatalyzed reactions; Q_{mol3} is the molar heat of the endothermic process.

Kinetic computations were carried out by nonlinear regression analysis [6]. The cure rate constants, the molar heat of epoxy ring opening and the molar heat of diffusion process may be considered adjustable parameters that are modified to achieve the best possible fit.

The uncatalyzed reaction has a negligible effect on the curing process. As shown by the data in previous paper [2], the magnitude of the uncatalyzed reaction does not exceed 6–8%. If uncatalyzed reaction is not taken into account in defining the degree of conversion, then one believes that the reaction rate will be determined fundamentally by the autocatalyzed reaction. The existence of a maximum in the isothermal kinetic curve of the heat release rate is indicative of catalytic action of the hydroxyl groups formed during the epoxy–amine reaction.

The computer program used for fitting Eqs (1)–(5) was the same as that used before [2].

Curing kinetics

The results of computer treatment of experimental kinetic curves of the reaction between resorcinol diglycidyl ether and *m*-phenylenediamine are shown in Figs 1a and b. Figure 1a concerns isothermal curves at 50ºC and Fig. 1b illustrates cure reaction data at 60ºC. The cure time corresponding to the appearance of endothermic effect is marked off by the arrows. It can be seen that the excellent agreement found in this work between the calculated curves of heat release and the experimental data. The experimental points follow closely the calculated curve. In all cases, the error of fit not exceeding 1.5% is estimated by the *R*-factor. Hence, it may be concluded that the data are consistent with the assumed cure rate Eq. (5).

It is of interest that the reaction rate of epoxide with an excess of amine (in solution of the latter) increases with respect to the stoichiometric composition. In mixtures, where an excess of epoxide over amine was used, the reaction rate, as one would expect, is maximal at the stoichiometric composition.

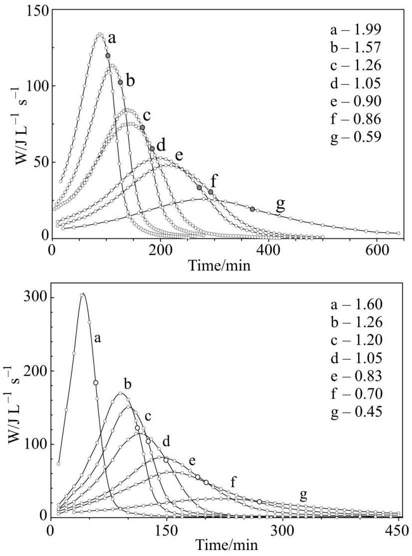


Fig. 1 Isothermal cure rate curves for RDGE/MPDA system with different reagent ratios: a – at 50°C; b – at 60°C. The onset of the diffusion process marked off by the circles

The simplest explanation of kinetic data presented in Figs 1a and b is that amine excess over epoxide reveals the clear catalytic action. In Fig. 2 the rate constant for catalyzed reaction k_2 is plotted as a function of excess amine for different ratio of the reagents. As indicated in Fig. 2, the linearity of plot of k_{ef2} *vs*. (C_{A}–C_{E}) tends to occur at excess of amine over epoxide. While in the case of excess epoxide the rate constant k_2 is virtually independent of composition.

When the amine is taken in excess over epoxide, the k_2 values increase linearly with the increase in the amine concentration indicating the catalytic activity of the latter. It should be noted that the occurrence of the catalytic activity only on using excess amine provides evidence in favour of complete binding of amine and epoxide in a complex with a ratio 1:1 with respect to the reacting functional groups.

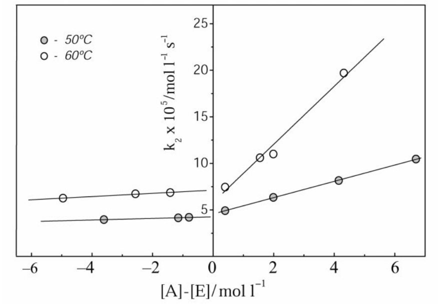


Fig. 2 Dependence of effective rate constant k_{eff2} on the excess amine for RDGE/MPDA system at 50 and 60°C

When an excess of amine over epoxide is used, the rate constant can be written as:

$$k_{\mathrm{ef2}} = k_{\mathrm{amine}}(C_{\mathrm{A_0}} - C_{\mathrm{E_0}}) + k_{\mathrm{ef2(A=E)}} \tag{6}$$

The k_{amine} term describes catalytic activity of excess amine; $k_{\mathrm{ef2(A=E)}}$ is the apparent rate constant of the stoichiometric composition; $(C_{\mathrm{A_0}} - C_{\mathrm{E_0}})$ is excess of amine over epoxide, mol L^{-1}. Thus, in the case of amine excess the value $(C_{\mathrm{A_0}} - C_{\mathrm{E_0}})$ appears in the apparent rate constant.

Figure 3 illustrates the specific heat of epoxy ring opening for autocatalyzed reaction, Q_{mol2}, as a function of molar ratios of functional groups. It is apparent that the molar heat of epoxy ring opening for autocatalyzed reaction is independent of epoxy–amine composition and equals 92 kJ mol^{-1}. As shown by the data in paper [7], the molar heat of epoxy ring opening for autocatalyzed reaction is almost temperature independent.

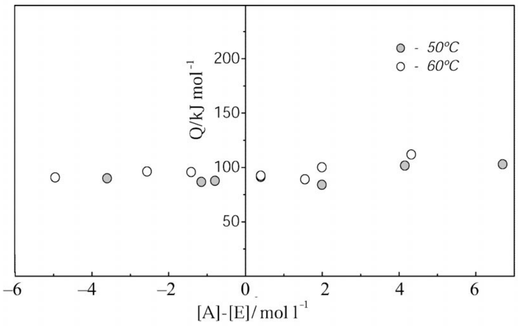


Fig. 3 Variation of the molar heat of epoxy ring opening for autocatalyzed reactions Q_{mol2} as a function of the excess amine for RDGE/MPDA system at 50 and 60°C

The ‘uncatalyzed’ reaction plays an important part in early stage of curing. However, it is common observation that the first points of the kinetic curves are subject to some error because of the scatter in the data is most evident at the beginning of the calorimetric measurements.

Within the frame of the proposed model, the epoxy–amine cure reaction displays simple second-order kinetics. In the light of this proposal, it is suggested that the interaction between an epoxy group and an amine progresses in strongly structured melts. By this is meant that reactants are almost completely hydrogen bonded into a complex. At later stages of the cure reaction, when endothermic process makes its appearance, we note a sudden decrease in the rate curve of evolving of the heat during isothermal calorimetric measurement.

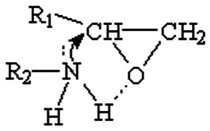
The proposal model is supported by the following observations. First, there is reasonable agreement between the values of rate constants (k_{ef1}, k_{ef2} and k_{ef3}) as well as the values of the molar reaction heat (Q_{mol1}, Q_{mol2} and Q_{mol3}) at various reagent ratios. Second, the occurrence of the catalytic activity only on using excess amine provides additional evidence in favour of complete binding of amine and epoxide in a complex with the ratio 1:1 with respect to the reacting functional groups. This finding is of particular interest for kinetic analysis, since they provide additional evidence in favour of our kinetic model.

The mechanism of the reaction between amine and epoxide molecules in solvent-free medium

In solvent medium, the mechanism of the epoxy–amine reaction has been widely studied [8–11]. To obtain a clearer picture of the mechanism of epoxy ring opening in solvent-free medium, the reaction kinetics was considered. The molecular interpretation of the cure reaction kinetics was suggested as being in accord with the kinetic results.

The mechanism of the epoxy–amine reaction appears to involve the following steps. The epoxide ring opening is started by hydrogen bonding of amine atom with epoxide ring making the alpha carbon atom electrophilic and facilitating nucleophilic attack.

In the light of the proposed model [2], it is suggested that such arrangement (**I**) cannot be reactive. In a reactive complex, the nitrogen attacks by the lone pair electrons an epoxide ring and opens its. The structure of a reactive complex can therefore be expressed as (**II**).



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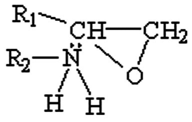

II

According to the kinetic data, the reactive complexes initiate the uncatalyzed reaction. Epoxide group of the reactive complex has a partial polarisation in the direction of oxygen atom. The curved arrows represent a process of polarisation. According to the kinetic data, the reactive complexes initiate the uncatalyzed reaction. However, such complexes are not much. In general, the reagents are hydrogen bound into the unreactive complexes. In order to form N–C covalent bond between nitrogen and carbon atoms it is necessary to weaken C–O bond by means of hydrogen bonding. The function of hydrogen bonding between the reagents is to hold a nucleophile within the critical distance of an electrophile for a sufficient length of time [12]. Nevertheless, by itself hydrogen bonding cannot assure the epoxide ring opening. Therefore, epoxy–amine reaction occurs over the catalyst which is commonly ascribed to formation of OH groups [13].

The proposed mechanism allows us to explain the way the lone pair electrons on nitrogen atom of NH_2–group attacks and opens an epoxide ring in the course of the reaction both of the primary amine hydrogen and of the secondary amine hydrogen. The latter, however, is possible on conditions that epoxy–amine cure reaction is aided by hydrogen bonding of the reagents.

Here the clear catalytic action exhibited by excess of amine comes from the kinetic data, suggesting the presence of the initial association between reagents during the cure reaction. The existence of association between epoxy and amine groups is prerequisite for reaction in these systems. This is good evidence that steric hindrance can not be a crucial factor in the reaction between the epoxy- and amine-groups.

The proposal for the initial association between reagents is in agreement with the concept of Semenov stated in [14]. In the Semenov's opinion, the formation of regularly oriented groups of monomer molecules must permit us to explain the peculiarities of the polymerization at low temperatures. In the modern form of materials science, the idea of the spontaneous organization of the reagents are well understood [15].

Conclusions

Under isothermal conditions both the cure kinetics of the mixture resorcinol diglycidyl ether with high *m*-phenylenediamine contents was analysed and possible mechanism involving the complex formation between initial reagents is considered.

Additional support for the interpretation involving the complex formation between initial reagents was derived from epoxy–amine cure kinetics being measured by the calorimetric method. The approach reported here expands significantly the scope of calorimetric method as applied to the epoxy–amine cure reaction. The experimental evidence, from the kinetic study of epoxy–amine cure reaction, suggest that such consideration based on the conception of strongly structured reactive medium, may provide a common basis for understanding of the cure reaction mechanism.

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