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

III. Determination of the thermokinetic parameters

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Abstract

In this paper, it is clearly demonstrated that the dependence of the rate of evolving heat on time is completely described by using Mangelsdorf's method in terms of three processes with excellent precision. The first two exothermic processes take into account the fact, that the reaction occurs by two competitive mechanisms: one is a non-catalytic mechanism and the other is catalyzed by OH-groups formed during the reaction. The third one refers to the endothermic process where the reaction is accompanied by diffusion of the reaction products.

The distinctive feature of this diffusion process is that it is the coupling of the reaction kinetics and rearrangement of the chains built to the rigid supramolecular structure. This simple model allows accurate simulation of kinetic behaviour.

Keywords: epoxy-amine, isothermal calorimetry, Mangelsdorf's method, thermokinetics

Introduction

Calorimetric measurement of cure reactions attracts our attention to the simplicity of performing kinetic experiments. Major workers in this field are surely well aware of the fact that, if the choice of the molar heat of epoxy ring opening is rather arbitrary, this kinetic analysis does not seem to be a fruitful avenue. Hence exact agreement with the experimental curve is highly improbable. Nevertheless this question, to our knowledge, received little attention in previous analyses [1].

By using Mangelsdorf's method, previous thermochemical study has led to few important and, probably, useful findings. First, it was found that amine excess over epoxide reveals the clear catalytic action. This is additional evidence for strongly structured reactive medium. Second, a consequence of the strongly structured reactive medium is equal reactivity of primary and secondary amine group on catalytic action of the amine excess.

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Since the object of deriving kinetic equations and fitting them into kinetic data is to obtain evidence about the molecular processes that control the rate of reactions, it may be noted that the aim of the presented model [2] was not to 'fit' the experimental data, but rather to provide an insight into the origin of the reaction mechanism. Little is added to our understanding of reaction mechanism by merely fitting the kinetics. Here it must be admitted that, use of a single set of reaction conditions, giving a single rate measurement, is without significance. The only sure basis of validating a possible mechanism would seem to be the kinetic studies embracing effects of reactant concentrations and temperature.

Considering reactant system such as epoxy-amine reactant mixture, it can be misleading to focus only on the properties of cross-linked molecules. There is evidence that this low-molecular liquid plays a major role in the mechanism of epoxy-amine cure reaction [3]. Then the point must be made that the epoxy-amine reactant mixture can be treated as a two-component system consisting of low-molecular mass liquid and network polymer. However, much remains to be learnt about the role of low-molecular component in the curing processes. In fact, during the reaction under consideration, the intramolecular hydrogen-bonding interactions organize the reactants to direct the process of the epoxy-ring opening.

It is important to emphasize that a vast body of information on the study of glassy systems available in literature makes it clear that interpretation of experimental data may not be as naive as formerly supposed [4]. Moreover, those data suffers from yet another problem: their kinetic treatment reviewed in some detail in [5] as has been shown in [6] is clearly wrong.

Thus, here we had the chance to repeat the cure reaction of resorcinol diglycidyl ether (RDGE) with *m*-phenylenediamine (MPDA) described in [4]. It is our belief that studies like the present one will bring the curing picture of the epoxy-amine reaction mixture into better perspective.

Experimental

Materials

The experiment is similar to the previous one [3]. In the present study resorcinol diglycidyl ether (RDGE) was also cured with *m*-phenylenediamine (MPDA).

Purification of the reagents was conducted by distillation in the argon flow. RDGE has T_{bol}=150–160°C at 0.1 Torr. The boiling point of MPDA is T_{bol}=140°C (10 Torr).

The epoxide content of the resin was determined by reacting the resin with excess hydrochloric acid in acetone/water solution and then titration 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 this method are given in [7].

Procedure

The reagents were mixed at 50°C. The sample preparations were the same as those reported previously [3]. 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 at temperatures ranging from 40 to 90°C. Attempts to follow the reaction at higher temperatures failed because of the reaction was too fast for measurement.

Cure isotherms were obtained employing 1.05 times stoichiometric quantities of diamine.

The reference consisted of fully cured sample. Reference and sample masses were matched as closely as possible.

Since the kinetic model has been given and discussed in [2, 3] it is not repeated here again, but the resulting equation of the net rate of heat evolution is written as:

$$\begin{aligned} W=W_1+W_2+W_3=Q_{\mathrm{mol1}}k_{\mathrm{ef1}}(C_{\mathrm{A}}-C_{\mathrm{x}})(C_{\mathrm{E}}-C_{\mathrm{x}})+Q_{\mathrm{mol2}}k_{\mathrm{ef2}}(C_0-C_{\mathrm{x}})(C_{\mathrm{x}}-C_{\mathrm{x3}})+ \\ +Q_{\mathrm{mol3}}k_{\mathrm{ef3}}[(C_{\mathrm{x}}-C_{\mathrm{x}}^{\mathrm{sat}})-C_{\mathrm{x3}}](C_{\mathrm{x}}-C_{\mathrm{x}}^{\mathrm{sat}}) \end{aligned} \tag{1}$$

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 process in a saturated with OH groups reacting medium.

The computer program used for fitting Eq. (1) was the same as that used before [2, 3]. A measure of the goodness of fit of the above equations was obtained by the residual mean-square deviations, which did not exceed 1.5%.

Results

The above kinetic analysis is ground on the assumption that the interaction between an epoxy- and an amine- molecules consist mainly of epoxy ring opening. This assumption does not ensure the possibility of other reactions that can occur. It appears to be well established that the etherification reaction is significant and cannot be ignored [6]. We use the term etherification to refer to both the epoxide–hydroxyl reaction and the homopolymerisation reaction. In both cases, the net results are the same: an epoxide ring is transformed into an ether linkage. However, no etherification reaction was observed in the case of excess amine. Therefore, the relevant calculations were carried out only for excess amine mixtures.

Figure 1 summarizes the results of computer treatment of experimental kinetic curve of the reaction between resorcinol diglycidyl ether and *m*-phenylenediamine (55°C). The curve W is decomposed to show the contribution from the three different processes involved, namely, W_1, W_2 and W_3. The curve obtained by the calculation clearly demonstrates that the dependence of the rate of evolving of the heat W on time, shown in Fig. 1, is completely described in terms of these three processes with excellent precision.

The ‘uncatalyzed’ reaction evolving heat at a rate W_1, plays an important part in early stage of curing. A given reaction yields up to 6% OH groups at the end of curing.

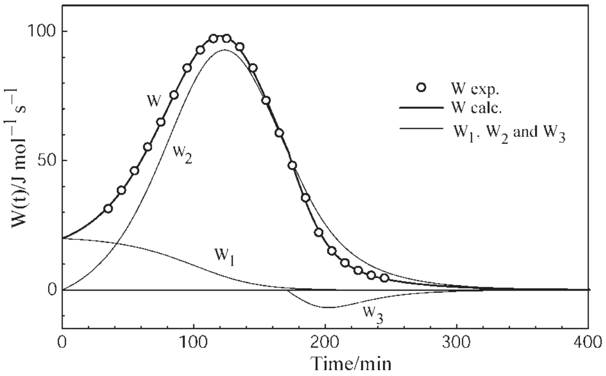

Fig. 1 The result of computer treatment of the kinetic curve of the heat release rate *vs*. time for the isothermal reaction between resorcinol diglycidyl ether and *m*-phenylenediamine. The curing temperature is 55°C and the ratio of functional groups amine/epoxy resin equals 1.05

Curve W_2 takes into account the autocatalytic nature of the epoxy-amine reaction and clearly shows the maximum typical of an autocatalytic reaction.

The third process included in the model, which makes its appearance only at high degree of conversion ($C_x > C_x^{sat}$), is described by the curves W_3. This curve represents the endothermic process. The corresponding plot of W_3 as a function of time is shown at the bottom of Fig. 1. When the degree of conversion approaches C_x^{sat} the drop-off in the rate of evolving of the heat due to the onset of endothermic process is obvious. The onset of endothermic process C^{sat} is indicated by an arrow. For experimental kinetic curve represented in Fig. 1, this point corresponds to 73% of the epoxy groups have reacted.

The values of the molar heat of epoxy ring opening for 'uncatalyzed' and autocatalyzed reactions denoted by Q_{mol1} and Q_{mol2}, respectively as well as the molar heat Q_{mol3} of the endothermic process at different cure temperatures are given in Fig. 2. These data were obtained from cure isotherms represented in Fig. 3. There is clearly

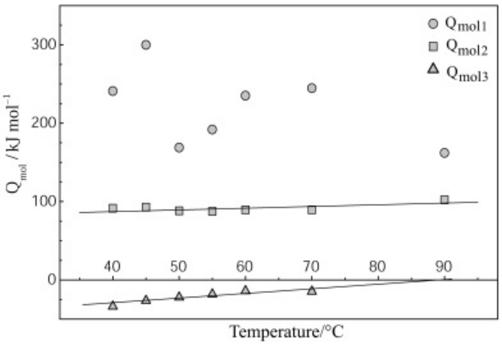

Fig. 2 Dependence of Q_{mol1}, Q_{mol2} and Q_{mol3} on curing temperature; the ratio of functional groups amine/epoxy resin equals 1.05

considerably more scatter in the dependence of Q_{mol1} than for Q_{mol2} and Q_{mol3}. This is believed to be because at the conditions of the kinetic measurements there is a brief period of temperature equilibration after the sample is introduced into the instrument. Hence the first points of the kinetic curves are subject to some error.

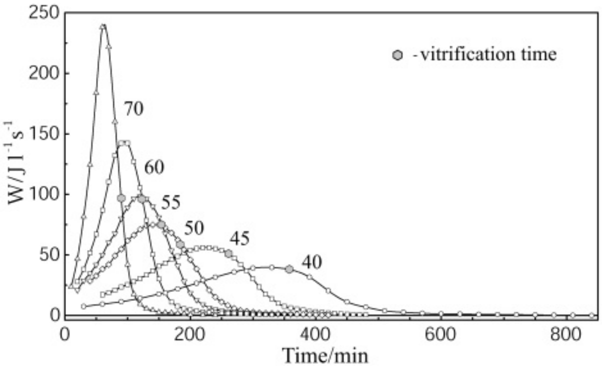

Fig. 3 Isothermal cure rate curves at various reaction temperatures; a ratio of functional groups amine/epoxy resin equal to 1.05. The onset of the endothermic process marked off

The values of the molar heat of epoxy ring opening for autocatalyzed reaction Q_{mol2} for various temperatures are the same and equal 92 kJ mol^{-1}.

The values of Q_{mol1} are higher in comparison with the molar heat of epoxy ring opening for autocatalyzed reaction Q_{mol2}. It can be seen that the values of Q_{mol1} lie between 163 and 276 kJ mol^{-1}, which are close to the value of ~247 kJ mol^{-1} obtained for 'uncatalyzed' reaction in [8].

Under the conditions of the kinetic measurement, this endothermic process was examined as the appearance of the new formed OH groups, which cannot bring about catalysis of reaction. We explained it as the transfer of the new formed OH groups to solid matrix. Leaving of the newly formed OH groups (C_{x3}) the reaction medium is accompanied by the endothermic effect. Q_{mol3} is the molar heat of this endothermic process. The character, which has attracted our attention, is Q_{mol3} may be temperature dependent (Fig. 2). From Fig. 2 it is apparent that molar endothermic heat Q_{mol3} decreases with increasing the cure temperature. The detailed analysis of this result is beyond the scope of this paper and will be present in a separate paper [9] where, for the reaction system under investigation, the calorimetric data during the late stages will be considered.

Values of the rate constants for 'uncatalyzed' and autocatalyzed reaction mechanisms, which provide the best fit to the experimental data, are listed in Table 1. The 'non-catalytic' rate constant is very low compared to the autocatalytic one. However, as shown in Fig. 4, the activation energies of the cure reaction, both 'uncatalysed' and catalysed with forming OH groups, are virtually the same. Figure 4 shows Arrhenius plots for the rate constants determined from the kinetics analysis. The activation energies for 'uncatalyzed' and autocatalyzed epoxy ring opening reactions are 52 and 51 kJ mol^{-1}, respectively. It will be noted that activation energy means the apparent activation energy.

Table 1 The rate constants corresponding to ‘uncatalyzed’ and autocatalyzed reaction mechanisms for different cure temperatures

T / °C	k_1 / l mol^{-1} s^{-1}	k_2 / l mol^{-1} s^{-1}
40	$4.27 \cdot 10^{-7}$	$2.49 \cdot 10^{-5}$
45	$6.08 \cdot 10^{-7}$	$3.66 \cdot 10^{-5}$
50	$1.52 \cdot 10^{-6}$	$4.76 \cdot 10^{-5}$
55	$1.22 \cdot 10^{-6}$	$6.60 \cdot 10^{-5}$
60	$1.02 \cdot 10^{-6}$	$7.55 \cdot 10^{-5}$
70	$1.19 \cdot 10^{-6}$	$1.56 \cdot 10^{-4}$
90	$1.02 \cdot 10^{-5}$	$3.56 \cdot 10^{-4}$

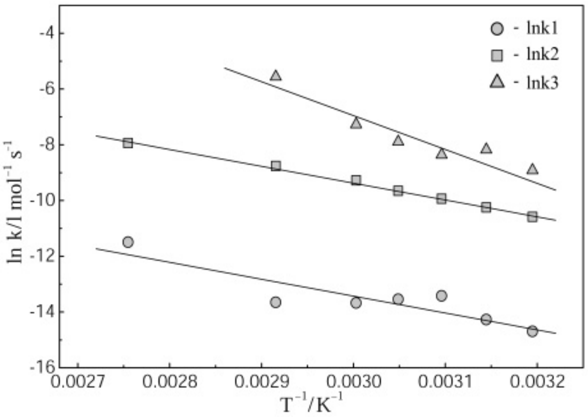

Fig. 4 Arrhenius plot of the reaction rate constants for reaction system with the ratio of functional groups amine/epoxy resin equals to 1.05

The results obtained from the method described above are in reasonable agreement with value of 52 kJ mol^{-1} obtained by titrimetric analysis in [10].

The corresponding Arrhenius plot of lnk_3 *vs.* 1/T is shown in Fig. 4 together with the rate constants for ‘uncatalyzed’ and autocatalyzed reaction mechanisms. The activation energy of endothermic process is defined to be 103 kJ mol^{-1}. It is clearly seen that the activation energy for this new kinetic process is much more than the values of the activation energies for the reaction of epoxy ring opening.

We may assume that a new kinetic (diffusion) process accompanied by the endothermic effect occurs in combination with the rearrangement of the chains crosslinked into the rigid supramolecular structure. This implies that the rate limiting step of the third process must be the collective motion of the polymer chains in the rigid supramolecular structure.

Based on kinetic analysis, the interaction between diepoxy and diamine- molecules is able to proceed in the kinetic region from start to finish, since the cure reaction progresses in structured reaction medium generated by the functional groups of amine and epoxy molecule almost completely bound into a complex by means of H-bonds.

Leaving of the new formed OH groups the reaction medium implies the appearance the new phase where the cooperative chain displacement is accompanied by the endothermic effect. This new phase is the solid whereas reaction medium the low-molecular liquid makes up the liquid phase that is entrapped in the solid phase. At that time, the reaction proceeds exclusively in the liquid phase.

Due to the superposition of endothermic and exothermic processes the completion of the rate of heat evolving occurs much earlier than the completion of the chemical reaction. Thus, the combination of the exothermic reaction together with the endothermic process must have been responsible for leveling off the degree of conversion in the late stage of curing. According to the proposed model, the endothermic process is indicative of the glass transition. Previously the vitrification during the same isothermal reaction was studied by using torsional braid analysis [11]. It was shown that the onset of endothermic (diffusion) process in the isothermal kinetic curve corresponds to the vitrification time of the reaction system.

In fact, further investigation will be necessary to elucidate the process responsible for this observed experimental behavior. The endothermic effect was discovered in examining the kinetic curves. However, as early as in [12] this effect was noted as ‘break’ in the curve of the rate of heat evolving. However, this feature of the epoxy-amine reaction, to our knowledge, received little attention. The detailed analysis of this result is beyond the scope of this paper and will be present in [9].

Conclusions

As mentioned above, this study is intended to describe by equation the epoxy-amine cure kinetics with the purpose of finding the molar heat of epoxy ring opening for ‘uncatalyzed’ and autocatalyzed reactions as well as the rate constants for ‘uncatalyzed’ and autocatalyzed reaction mechanisms. The kinetic curve obtained by calculation clearly demonstrates that the dependence of the rate of heat evolving on time is completely described in terms of these three processes with excellent precision.

The present work has shown that the new (endothermic) process can be found from ‘kinetic investigation’ approach. The rate limiting step of this endothermic process must be the collective motion of the polymer chains in the rigid supramolecular structure. Thus, this endothermic process is indicative of vitrification time.

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