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A NEW CURING KINETIC MODEL AND ITS APPLICATION TO BPSER/DDM EPOXY SYSTEM

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Abstract

A new model has been deduced by assumed autocatalytic reactions. It includes two rate constants, k_1 and k_2, two reaction orders, m and n, and the initial concentration of [OH]. The model proposed has been applied to the curing reaction of a system of bisphenol-S epoxy resin (BPSER), with 4,4'-diaminodiphenylmethane (DDM) as a curing agent. The curing reactions were studied by means of differential scanning calorimetry (DSC). Analysis of DSC data indicated that an autocatalytic behavior showed in the curing reaction. The new model was found to fit to the experimental data exactly. Rate constants, k_1 and k_2 were observed to be greater when curing temperature increased. The activation energies for k_1 and k_2 were 95.28 and 39.69 kJ mol^{-1}, respectively. Diffusion control was incorporated to describe the cure in the latter stages.

Keywords: bisphenol-S epoxy resin, cure reaction, 4,4'-diaminodiphenylmethane, differential scanning calorimetry, kinetics model

Introduction

Epoxy resin is one of the most important polymeric materials, as polymer matrices for composite materials, and as adhesives. The kinetics of curing epoxy resins has been widely studied by using isothermal or dynamic experiments with differential scanning calorimetry (DSC); experimental data are analyzed by the homogeneous reaction model, normally using *n*th order or autocatalytic equation [1–3]. In these models, the whole reaction of curing was considered as a single kinetic process, regardless the different reactive processes and the different stages involved in the system. When the profile of the rate curves is simple, this procedure normally gives a good fit to experimental data. However, the reaction of curing epoxy resins is normally very complex, and there are other parameters that increase the complexity of the curing process, such as the change from chemical kinetic control to diffusion control in the advance of the curing [4, 5].

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Epoxy resins based on epichlorohydrin (ECH) and bisphenol-S (BPS) have better heat resistance, gel time, and mechanical properties than those of epoxy resins prepared from ECH and bisphenol-A (BPA) [6, 7]. The bisphenol-S epoxy resin (BPSER) has been synthesized and the kinetics of this epoxy resin formation has been studied before [8–10]. The results of using phenomenological approach to describe the curing kinetics of heat resin were reported in literature. The curing reactions in the kinetic control stage follow an autocatalytic kinetics and a four-parameter semiempirical equation proposed by Kamal [11].

In the work to be described here, the DSC technique was also used to study the curing kinetics of bisphenol-S epoxy resin with 4,4'-diaminodiphenylmethane (DDM). The curing process was analyzed based on a new model proposed in this paper which is quite similar to Kamal equation. And the diffusion effect was estimated to fit to the experimental data.

Theoretical analysis

All kinetic studies can start with the basic equation that relates the rate of conversion at constant temperature to some function of the concentration of reactants. For thermosets that follow *n*th-order kinetics, $\mathrm{d}\alpha/\mathrm{d}t$ is usually expressed as:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k(T)(1-\alpha)^{\mathrm{n}} \tag{1}$$

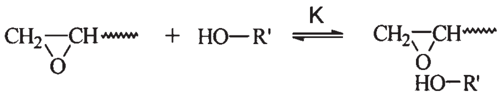
where $\mathrm{d}\alpha/\mathrm{d}t$ is the rate of conversion, α is the fractional conversion at any time t, k is the Arrhenius rate constant and n is the reaction order. Obviously, systems obeying *n*th-order kinetics will have the maximum reaction rate at zero time.

To take autocatalytic characteristics into account, Kamal proposed a generalized expression:

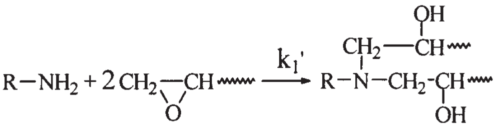
$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=(k_1+k_2\alpha^{\mathrm{m}})(1-\alpha)^{\mathrm{n}} \tag{2}$$

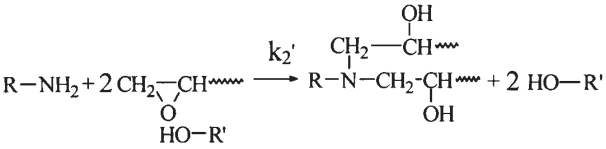
where k_1 and k_2 are the specific rate constants in this model. They are functions of temperature. m and n are the reaction orders. $m+n$ is the overall reaction order [11]. According to Kamal equation, the maximum reaction rate will be observed at some intermediate conversion. The introduction of four parameters (k_1, k_2, m, n) makes it possible to obtain a good fit to experimental data, and the equation has been successfully applied to both epoxy and polyester systems. The exponents, m and n, are often found to be temperature-dependent, so the dependency must be determined over the whole range of temperature. For epoxy-amine systems, lots of studies showed that m increases with increasing temperature by using Marquardt's regression technique [12]. But this is not easy to interpret. The increasing m indicates that the curing mechanism has changed with increasing the temperature so the results were not credible because the parameters were calculated by using an unchanged equation. After all, the Kamal equation is a semiempirical one that the parameters involved in were not easy to be related to the certain curing reaction.

Smith proposed that it is the existence of some complexes as follows that made the autocatalytic reaction of epoxy-amine curing systems [13]:



So the curing reaction contains two reactions:





Assuming that n_1 is the reaction order to amine, n_2 is the reaction order to epoxy group, a_0 is the initial concentration of [OH] group and M is the concentration of complex at any time t, so:

$$\frac{d\alpha}{dt} = k_1'(1-\alpha)^{n_1}(1-\alpha-M)^{n_2} + k_2'(1-\alpha)^{n_1} M^{n_2}$$

Because $M=K(\alpha+a_0-M)(1-\alpha-M)$, we have:

$$\frac{d\alpha}{dt} = (k_1'+k_2'[K(\alpha+a_0-M)]^{n_2})(1-\alpha)^{n_1}(1-\alpha-M)^{n_2}$$

If the concentration of the complex is very small, i.e. $M<<\alpha+a_0$, and $M<<1-\alpha$, so M can be omitted:

$$\frac{d\alpha}{dt} = (k_1'+k_2'[K(\alpha+a_0)]^{n_2})(1-\alpha)^{n_1+n_2}$$

let $k_1=k_1'$, $k_2=k_2'K^{n_2}$, $m=n_2$, $n=n_1+n_2$:

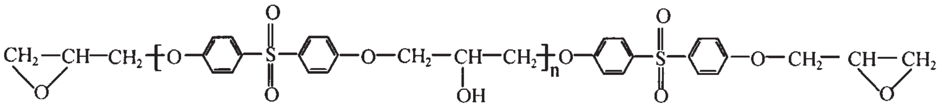
$$\frac{d\alpha}{dt} = [k_1+k_2(\alpha+a_0)^m](1-\alpha)^n \tag{3}$$

It is evident that the Kamal equation can be considered as a special form of Eq. (3), valid for $a_0 \to 0$. But the parameters involved in this equation have different but more definite meanings, than the Kamal equation except for k_1. In Eq. (3), m is the reaction order to epoxy group, $n-m$ is the reaction order to amine, and n is the overall reaction order. a_0 is the initial concentration of [OH] group. This is quite accordant to the results $m<n$ of the former researchers [12, 14].

Experimental

Bisphenol-S was recrystallized from the toluene, and a crystal with a melting point of 240°C was obtained. All agents used were analytically pure grade and were supplied by Beijing Chemical Reagent Co.

Epoxy resin based on bisphenol-S used in this work was synthesized according to [15]. The molecular structure of this resin has the following approximate form:



where n=0~1. The epoxy value was determined according to [16] to be 0.31 mol/100 g. a_0 was calculated to be 0.463.

The reactants BPSER and DDM were mixed under 5°C in a 1:1 equivalent ratio. Approximately 10 mg sample of the mixture was weighed accurately into an aluminum DSC sample pan and then covered with an aluminum lid. The entire operation was carried out in a dry chamber. DSC measurements were carried out by using a Shimadzu DT-40 thermal analyzer. The DSC was calibrated with high purity indium, α-Al_2O_3 was used as the reference material. Isothermal experiments were carried out according to [17] under a nitrogen flow of 40 mL min^{-1}.

Isothermal DSC analysis was performed at temperatures ranging from 80 to 105°C in 5°C increments. The furnace was first heated up to a desired fixed temperature and kept for a certain period of time. When the system reached the equilibrium state, the sample was quickly set on the calorimetric detector plate. The reaction was considered to be complete when the rate curve levelled off to a baseline.

The extent of reaction and the curing rate were calculated according to [17].

Results and discussion

Reaction orders and rate constants

Figure 1 shows plots of $d\alpha/dt$ *vs*. time. The reaction rate at any temperature is seen to increase with time at the initial stage of cure and then passes through a maximum. The reaction rate peak becomes higher and shifts to less time with an increase of isothermal temperature, which indicates that the curing reaction obeying an autocatalytic mechanism, not a nth-order one.

Seeing Eq. (3):

$$\frac{\mathrm{d}\left(\frac{\mathrm{d}\alpha}{\mathrm{d}t}\right)}{\mathrm{d}\alpha}=mk_2(\alpha+a_0)^{\mathrm{m}-1}(1-\alpha)-nk_2(\alpha+a_0)^{\mathrm{m}}-nk_1 \tag{4}$$

Let α_p be the extent of curing at the maximum reaction rate, then we have:

$$mk_2(\alpha_p+a_0)^{m-1}(1-\alpha_p)-nk_2(\alpha_p+a_0)^m-nk_1=0 \tag{5}$$

Assuming $k_1 << k_2$, then:

$$\alpha_p=\frac{m-na_0}{m+n} \tag{6}$$

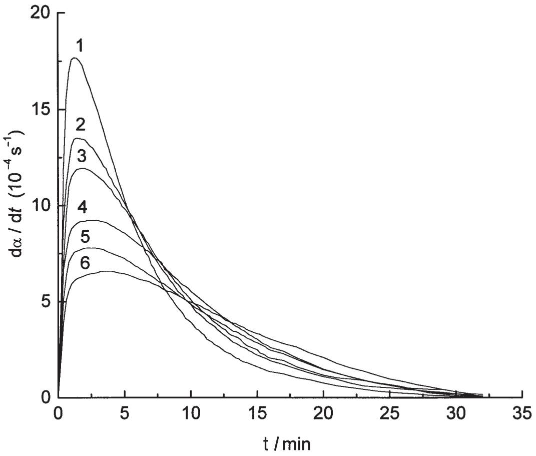


Fig. 1 Reaction rate, dα/d*t*, *vs*. time curves at different temperatures for BPSER curing with DDM. 1 – 105°C, 2 – 100°C, 3 – 95°C, 4 – 90°C, 5 – 85°C, 6 – 80°C

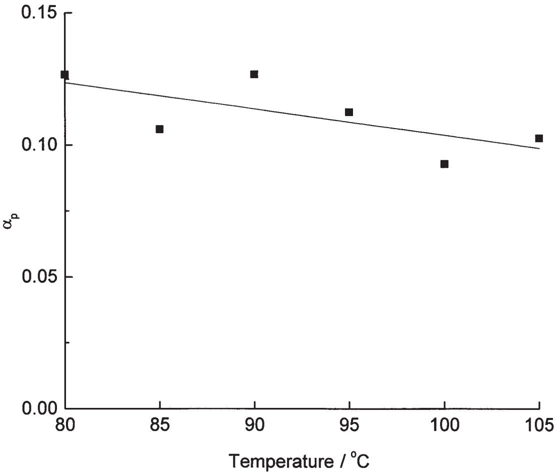


Fig. 2 Temperature dependence of α_p

Figure 2 is the α_p values at different temperatures. Using the obtained average α_p, then:

$$\frac{m}{n} = 0.646 \approx \frac{2}{3}$$

The reaction orders are always integral numbers [18]. So let n=3 and m=2, the kinetics equation of the curing reaction should be as follows:

$$\frac{d\alpha}{dt} = [k_1 + k_2(\alpha + a_0)^2](1-\alpha)^3 \tag{7}$$

This equation shows that the reaction order of the curing reaction to epoxy group is 2, to amine is 1. This is quite related to the reaction equation showed before that one amine reacts with two epoxy groups. The overall reaction order is 3.

From Eq. (7):

$$\frac{d\alpha/dt}{(1-\alpha)^3} = k_1 + k_2(\alpha + a_0)^2 \tag{8}$$

Making linear regression to this equation we will obtain k_1 and k_2. The linear relation of 80 and 100°C were plotted in Fig. 3. The good agreement shows that the assumed reaction order is correct. The experimental data were lower than the theoretical values about one minute after the curing reaction because the initial temperature was lower than the desired temperature. The deviation of experimental data from the line at the higher curing extent was because of the diffusion effect. The k_1, k_2 and k_1/k_2 values at different temperatures were tabulated in Table 1. As shown, k_1 and k_2 both increase with the increasing temperature, but k_1 was more sensitive to temperature than k_2 and k_1/k_2.

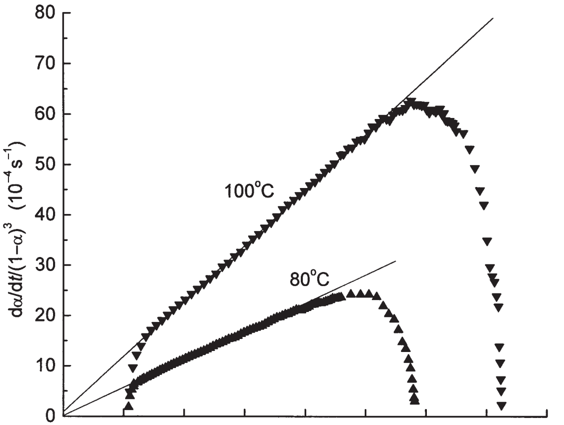


Fig. 3 Plot of $(d\alpha/dt)/(1-\alpha)^3$ as a function of $(\alpha+a_0)^2$ for curing reaction at 80 and 100°C

Table 1 Kinetic parameters for isothermal curing of BPSER/DDM

Temp./°C	80	85	90	95	100	105
$k_1/10^{-4}$ s^{-1}	0.1625	0.5291	–	0.7071	0.9122	2.220
$k_2/10^{-4}$ s^{-1}	27.79	31.94	41.97	49.18	55.91	68.17
$\frac{k_1}{k_2}/10^{-3}$	5.85	16.57	–	14.38	16.32	32.57

Introduce m=2 and n=3 to Eq. (5), we have:

$$5\alpha_p^2+1.704\alpha_p+3\left(\frac{k_1}{k_2}\right)-0.2828=0$$

Obviously, when k_1/k_2 increases, α_p will decrease. This is quite accordant to the plot shown in Fig. 2.

The reaction rate constants k_1 and k_2 depend on the temperature following the Arrhenius relationship:

$$k=A\exp\left(-\frac{E}{RT}\right)$$

Rate constants k_1 and k_2 are shown as Arrhenius plots in Fig. 4, –ln$k$ *vs.*1/T, which yield the values of 95.28 and 39.69 kJ mol^{-1} for the associated activation energies E_1 and E_2. E_2 is much lower than E_1 because that K will decrease with increasing temperature. Since k_1 value is very small, the calculated k_1 has a relatively larger deviation. So does the linear relatively of the line of lnk_1 *vs.* 1/T.

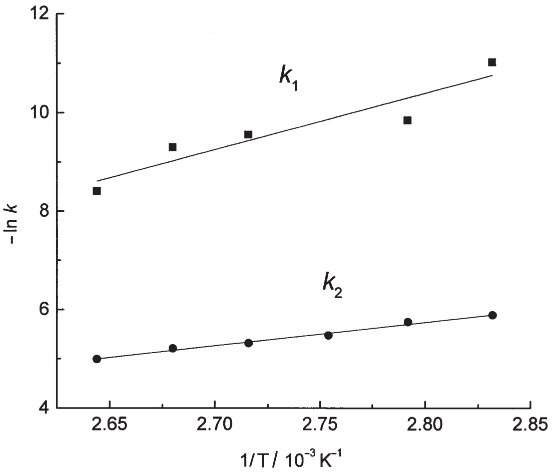


Fig. 4 Rate constants of curing reaction, k_1 and k_2 *vs.* temperature

Diffusion-controlled reaction

As shown, good agreements are obtained for the middle stage of reaction; whereas, deviations are observed when the curing extent is some larger. This is due to the onset of gelation and the reaction becomes the diffusion control. High curing extent leads to the difficulties of the chain to move to and react with each other.

As the cure progresses and the resin crosslinks, the glass transition temperature, T_g, of the system raises. When it approaches the curing temperature, the resin passes from a rubbery state to a glassy state. At this stage, the mobility of the reacting groups is hindered and the rate of conversion is controlled by diffusion rather than by chemical factors. The actual reactive rate decreases with increasing the conversion and approaches to zero when the glass transition temperature T_g raises.

To consider diffusion effect we introduce a diffusion factor $f(\alpha)$ according to [17] and defined as the ratio k_e/k_c, k_c being the rate constant for chemical kinetics and k_e the overall effective rate constant. This diffusion factor is given by:

$$f(\alpha)=\frac{k_e}{k_c}=\frac{1}{1+\exp[C(\alpha-\alpha_c)]} \tag{9}$$

where α_c is the critical conversion and C is the diffusion coefficient. When α is much smaller than the critical value, $\alpha<<\alpha_c$, then $f(\alpha)$ approximates unity, $k_e\approx k_c$, the reaction is kinetically controlled, and the effect of diffusion is negligible. As α approaches α_c, $f(\alpha)$ begins to decrease, reaching a value of 0.5 at $\alpha=\alpha_c$ and beyond this point approaches to zero as the reaction effectively stops. It shows that with conversion increasing the effect of diffusion develops gradually. The effective reaction rate k_e at any conversion is equal to the chemical reaction rate k_c multiplied by $f(\alpha)$.

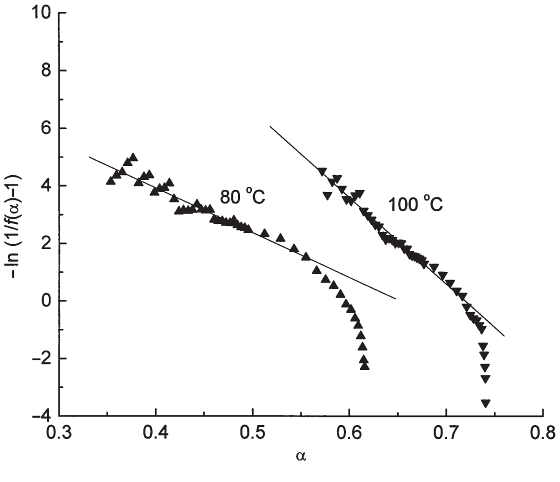


Fig. 5 Plot of –ln(1/*f*(α)–1) *vs*. α

From Eq. (9):

$$-\ln\left(\frac{1}{f(\alpha)}-1\right)=C\alpha_{c}-C\alpha \qquad (10)$$

C and α_c will be obtained from the slope and the intercept of the plot of $-\ln(1/f(\alpha)-1)$ *vs.* α. Figure 5 is the $-\ln(1/f(\alpha)-1)$ *vs.* α plot at temperature 80 and 100°C. As shown, the linear correlation is good in the relatively lower curing extent, but it has an obvious deviation in the final curing reaction. This indicates that even using the equation described upon it is difficult to calibrate the diffusion effect throughout the whole curing reaction. The calculated C and α_c at different temperatures were tabulated in Table 2.

As shown in Table 2, the diffusion coefficient C and critical curing extent α_c increase with the increasing temperature.

Table 2 C and α_c at different temperatures

Temp./°C	80	85	90	95	100	105
C	15.58	21.44	24.92	25.48	30.28	33.88
α_c	0.653	0.660	0.684	0.692	0.717	0.726

Figure 6 shows the results of the curing system at 80 and 100°C, where the experimental values of dα/dt are compared with those calculated by the new autocatalytic model (dot line) and coupled with the diffusion factor (solid line) according to Eq. (9). Although there is some larger deviation between the experimental data and the non-diffusion-calibrated, the agreement of the experimental data with the diffusion calibrated predicting data is excellent. Differences between model predictions and experimental data are observed to be smaller when the curing temperature increases.

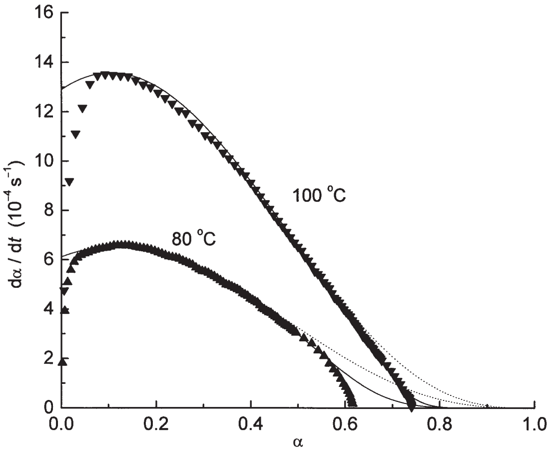


Fig. 6 Comparison of experimental data with autocatalytic model: reaction rate, dα/dt, *vs*. conversion, α at 80 and 100°C dot line: new autocatalytic model, solid line: new autocatalytic coupled with the diffusion factor

Conclusions

The new model proposed here which includes two rate constants, k_1 and k_2, two reaction orders, m and n, and an initial concentration of [OH] is suitable to interpret the curing kinetics of the BPSER/DDM curing system. The cure reaction for the system of BPSER/DDM is shown as an autocatalytic behavior. The overall reaction order n is 3.

In the first stage of the cure the reaction is chemical kinetically controlled. In the latter stage the reaction is controlled by diffusion.

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