Curing kinetics of a bisphenol-F epoxy resin and succinic anhydride system

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The kinetics of the cure reaction for the system of bisphenol-F epoxy resin (BPFER) with succinic anhydride (SA) as a curing agent was investigated with a differential scanning calorimeter (DSC). Autocatalytic behaviour was shown in the first stages of the cure for this system, which was well described by the model proposed by Kamal that includes two rate constants, k_1 and k_2, and two reaction orders, m and n. The overall reaction order, $m + n$, is in the range 2.1–2.6, and the activation energies for k_1 and k_2 are 89.1 and 68.8 kJ mol^{-1}, respectively. In the later stages, a crosslinked network is formed and the cure reaction is mainly controlled by diffusion. A diffusion factor, $f(\alpha)$, was introduced into Kamal's equation and the calculated values agree very well with the experimental data. Cure was accelerated by a tertiary amine.

Keywords: bisphenol-F epoxy resin, succinic anhydride, cure reaction kinetics

Epoxy resins are widely used as coatings, structural adhesives and advanced composite matrices in many applications. Bisphenol-F epoxy resin (BPFER) has a low viscosity and good processability. Therefore, it can be applied in the liquid state at a low viscosity.[1] Because it is not necessary to add a reactive diluent or solvent to the BPFER reaction system, the thermal stability and chemical resistance especially are not decreased.

Studies of BPFER applications[2,3] and physical properties[4] of cured BPFER have been reported extensively in recent years, for example, for use in sealing adhesives for electronic devices, for coating and for high-strength composites, but the description of the cure reaction and curing kinetics of BPFER with succinic anhydride (SA) has not previously been reported.

In order to provide a basis of curing process theory for applications of the BPFER/SA system, we must conduct research into the curing kinetics of the BPFER/SA system. Kamal's model,[5] arising from an autocatalytic reaction mechanism, has been applied to isothermal differential scanning calorimetry (DSC) data of the curing process of epoxy resins.[6-8] In general, a good fit of the experimental data has been obtained for the early stages of the cure, but deviations have been observed in the later stages, particularly near vitrification when the reaction is primarily diffusion-controlled.

In this article, the curing kinetics of BPFER/SA were studied by isothermal differential scanning calorimetry (DSC). To include consideration of the diffusion effect, the Kamal model has been extended by the addition of a diffusion factor $f(\alpha)$ and applied to the curing process of the BPFER/SA system. The acceleration of the cure by a tertiary amine is discussed.

Experimental

Materials

Bisphenol-F was recrystallised from toluene, and crystals with a melting point of 162 °C were obtained. Epichlorohydrin, NaOH, KOH, acetone, ethyl alcohol, hydrochloric acid, *N*,*N*-dimethylbenzylamine and the curing agent succinic anhydride were all analytically pure and were supplied by the Beijing Chemical Reagent Co. (Beijing, P. R. China).

Synthesis of BPFER

The epoxy resin used in this work, based on bisphenol-F, was synthesised according to Rainer *et al.*[9] The molecular structure of this resin had the form in Scheme 1.

Where n=0–1. The epoxy value was determined according to Jay[10] to be 0.554 mol/100 g.

DSC method

Curing studies were carried out on a Shimadzu DT-41 differential scanning calorimeter (Shimadzu Co., Ltd., Japan). The calorimeter was calibrated with high-purity indium; α-Al$_2$O$_3$ was used as the reference material. Isothermal and dynamic heating experiments were carried out according to Opalicki *et al.*[6] Under a nitrogen flow of 40 ml/min.

BPFER and the curing agent succinic anhydride were mixed homogeneously in a 1:1 equivalent ratio, and 0.1% *N*,*N*-dimethylbenzylamine (in weight) was added. Approximately 10 mg samples of the mixture were weighed accurately into an aluminum DSC sample pan and covered with an aluminum lid. The entire operation was carried out in a dry chamber.

The pans with samples were placed in thermostatic baths at curing temperatures (T_c's) between 110 °C and 125 °C in 5 °C increments. The reaction was considered complete when the rate curve levelled off to the baseline. The total area under the exothermal curve was used to calculate the isothermal heat of cure, ΔH_i, at a given temperature. After each isothermal run, the sample was quenched to 10 °C and then reheated at 10 °C/min to 300 °C to determine the residual heat of reaction, ΔH_r. The total heat evolved during the curing reaction was $\Delta H_0 = \Delta H_i + \Delta H_r$.

Results and discussion

The mechanisms of the curing reaction of thermosetting resins have two general kinetic models: *n*th-order kinetics and autocatalytic kinetics.[11]

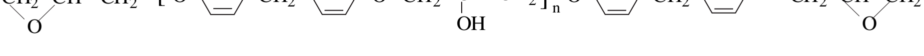
The *n*th-order kinetics can be expressed as:

$$\frac{d\alpha}{dt} = k(T)(1-\alpha)^n \quad (1)$$

The autocatalytic kinetics can be expressed by Kamal as:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n \quad (2)$$

where α is the extent of reaction, and is given by $\alpha = \Delta H_t / \Delta H_0$, ΔH_t is the partial area under a DSC trace up to time t, k, k_1 and k_2 are the specific rate constants of these models, which are



Scheme 1

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function of temperature, and *m* and *n* are the reaction orders. According to the *n*th-order kinetics model, the maximum reaction rate will be observed at *t*=0, and, according to the autocatalytic model, the reaction rate is zero initially and attains a maximum value at some intermediate conversion.

During the curing reaction of thermosetting resins, the heat evolution recorded by DSC is proportional to the extent of consumption of the epoxide groups in the epoxy resins or the reactive groups in the curing agent.[12,13] that is, the released heat is proportional to the extent of the reaction. Following this assumption, we studied the curing kinetics and determined the kinetic data.[14,15] If the cure reaction is the only thermal event, then the reaction rate (dα/d*t*) is proportional to the heat flow (d*H*/d*t*),[11] that is:

$$\frac{d\alpha}{dt}=\frac{dH/dt}{\Delta H_0} \quad (3)$$

So, the curing kinetics can be studied and the rate of cure can be determined by the curing exotherm.

Figure 1 shows plots of the curing reaction conversion α versus time *t* at different isothermal temperatures, and isothermal DSC curves are shown in Fig. 2 plotted as dα/d*t* versus time *t*.

The reaction rate at any temperature increased with time during the initial stage of cure and passed through a maximum. The peak of the reaction rate became higher and shifted to a shorter time with increasing T_c. The plots show a maximum reaction rate at time *t* >0, thereby negating simple *n*th-order kinetics. The autocatalytic kinetic model of equation (2) is appropriate to describe this isothermal curing behaviour. In eqn (2), *m*+*n* is the overall reaction order. The kinetics parameters can be obtained with non-linear regression according to eqn (2) and the resulting data obtained from this method for all isothermal experiments are shown in Table 1.

As seen from Table 1, the k_1 values were small compared with those obtained for k_2, which affected the reaction more. Furthermore, k_1 and k_2 increased with the increasing curing temperature. The overall reaction order, *m* + *n*, lies in the range 2.10–2.59. The reaction rate constants k_1 and k_2 depend on the temperature and follow the Arrhenius relationship:

$$k = A\ exp(-E/RT) \quad (4)$$

Rate constants k_1 and k_2 are shown as an Arrhenius plot in Fig. 3, which yields the values of 89.1 kJ mol^{-1} and 68.8kJ mol^{-1} for the associated activation energies E_1 and E_2. The linear correlation coefficient for E_1 values is 0.9999 and that for E_2 0.9994.

Table 1 Kinetic parameters for isothermal curing of BPFER/SA

T/°C	k_1/10^{-4}s^{-1}	k_2/10^{-3}s^{-1}	*m*	*n*	*m*+*n*
110	3.93	7.69	0.54	1.56	2.10
115	5.62	9.91	0.61	1.76	2.37
120	8.04	13.3	0.57	1.81	2.38
125	11.3	17.2	0.69	1.90	2.59

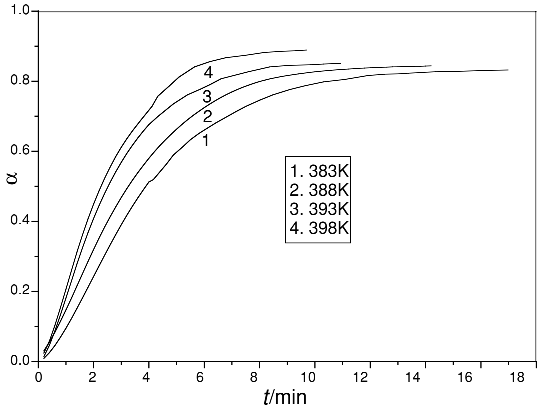


Fig. 1 α versus *t* at different temperatures.

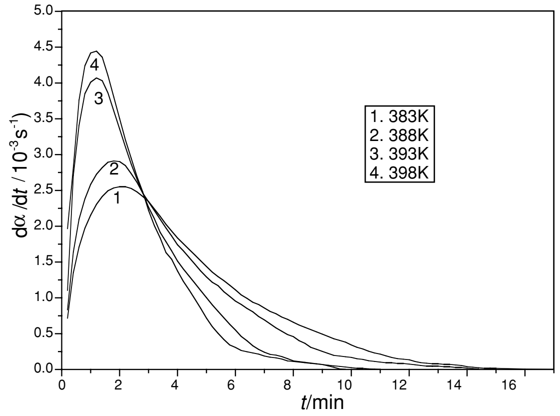


Fig. 2 dα/d*t* versus *t* at different temperatures.

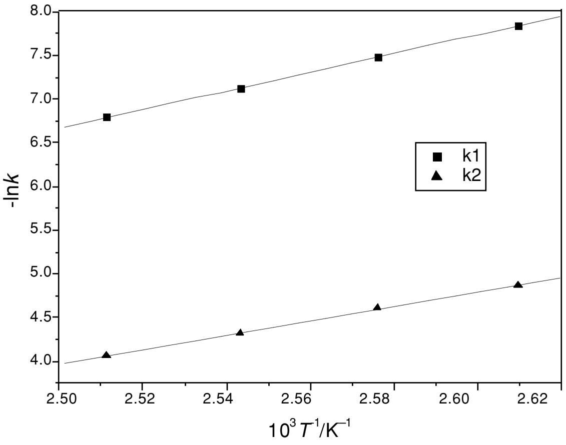


Fig. 3 lnk_1 and lnk_2 versus 1/*T*.

Typical comparisons between the experimental DSC data for 388 K and parametres obtained from the autocatalytic model with eqn (2) are shown in Fig. 4. As seen from Fig. 4, the kinetic behaviour described by the Kamal kinetic model coincides with the experimental data at the early stage of the curing reaction. At early stages of cure, before gelation and vitrification, the reaction takes place in the liquid phase and is controlled by chemical kinetics. However, in the later stage, as the reaction progresses, a deviation appears because of the onset of gelation and vitrification. At this stage,

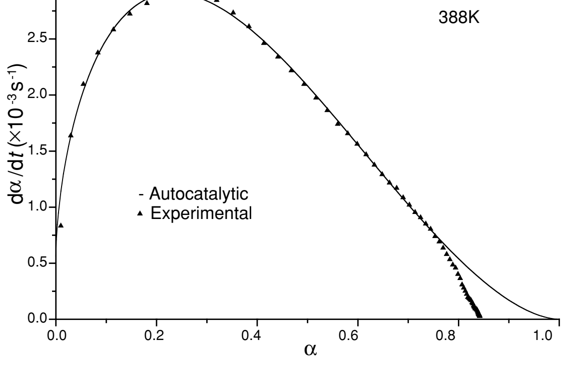


Fig. 4 Comparison of the experimental data and theoretical values calculated with eqn (2): dα/d*t* versus α at 388K.

the mobility of reactive groups is hindered, and the rate of conversion is controlled by diffusion rather than by kinetic factors.[16] Differences between the model predictions and experimentaldata were observed at the same conversion. This can be interpreted by free-volume considerations:[17] the free volume of materials decreased with decrease of temperature and increase of curing reaction conversion. Then the rate of diffusion of reactive groups was reduced, leading to a decreasing reaction rate.

To consider the diffusion effect more precisely, Cole *et al.*[16] proposed a semiempirical relationship based on free-volume considerations and earlier work by Chern and Poehlein.[17] In this relationship, the diffusion factor, $f(\alpha)$ is defined with two empirical parameters as follows:

$$f(\alpha) = \frac{1}{1 + \exp[C(\alpha - \alpha_c)]} \qquad (5)$$

Where C is the diffusion coefficient and α_c is the critical conversion depending on T_c. Plots of $f(\alpha)$ versus α at different T_c's are shown in Fig. 5. For $\alpha = \alpha_c$, $f(\alpha)$ approximately equals unity, and the effect of diffusion is negligible, so that the reaction is kinetically controlled. As α approaches α_c, $f(\alpha)$ begins to decrease, reaching a value of 0.5 at $\alpha = \alpha_c$. Beyond that point, it continues to decrease and approaches zero, which means that the reaction becomes very slow and effectively stops.

In light of the diffusion effect, a diffusion factor, $f(\alpha)$, was introduced into Kamal's equation, and the reaction rate equation of cure can be expressed in the following form:

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1-\alpha)^n f(\alpha) \qquad (6)$$

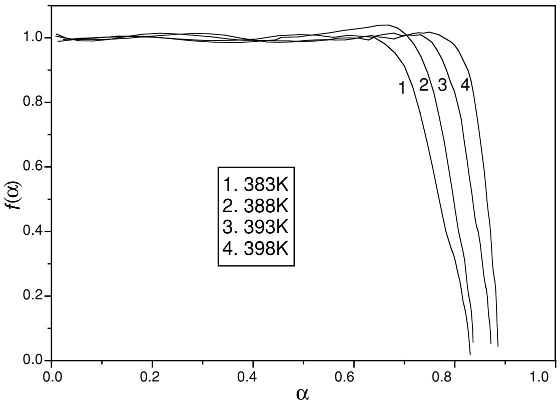


Fig. 5 *f*(α) versus α at different T_c's.

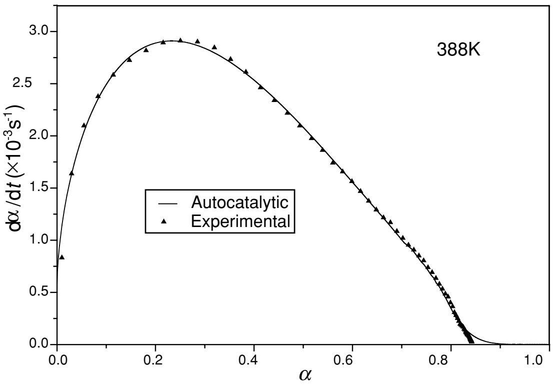
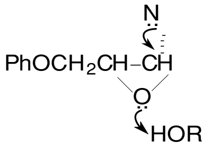


Fig. 6 Comparison of the experimental data and theoretical values calculated with Eqn.(6): d*α*/d*t* versus α at 388K.

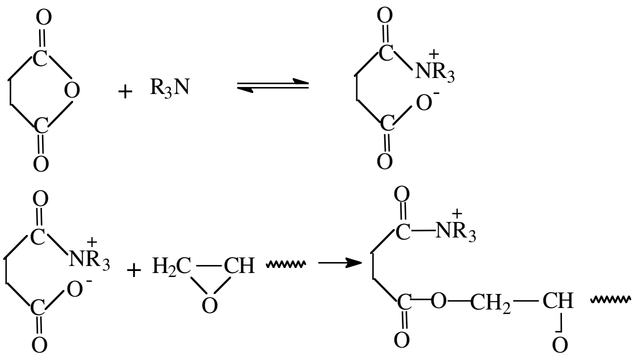
Figure 6 shows a comparison between experimental values and those obtained form eqn (6) at 388K.

The calculated values agree very well with the experimental data. Therefore, we employ the proposed generalised kinetic model to predict and describe the advance of this epoxy resin systems as a function of T_c.

It is known[12,15] that the addition of hydroxyl-containing compounds (water, alcohols, phenols, *etc.*) considerably promotes the interaction of epoxy compounds with anhydrides, amines and other nucleophilic species. The reaction proceeds through a trimolecular transition state initially suggested by Smith[18] for the reaction of epoxy compounds with amines.



As reported,[19] the maximum curing reaction rate was observed at $t = 0$ in the presence of a hydroxyl-containing solvent and obeyed *n*th order kinetics. This is due to the participation of a proton. The curing reaction is as follows when the pure epoxy resin/anhydride system is accelerated by a tertiary amine:



Then the negatively charged oxygen reacts with the epoxy group. The tertiary amine is not reformed in the reaction and this is also not the typical tertiary amine catalytic reaction mechanism. Because of the participation of hydroxyl group in the epoxy resins molecular chain, the k_1 is not zero, but this curing reaction is not a standard nth order reaction. It is favourable for the –OH in the epoxy resin molecular chain to become a proton donor and participate in reaction with the increasing curing temperature. The reaction mechanism ought to become the trimolecular mechanism with the participation of the proton. This is the reason that the $m + n$ values increase with increase of the curing reaction temperature as seen in Table 1.

Conclusions

1. The cure reaction for the BPFER/SA system was shown to have autocatalytic behaviour in the kinetically controlled stage and was well described by the model proposed by Kamal, which includes two rate constants, k_1 and k_2, and two reaction orders, m and n. The overall reaction order, $m + n$, is in the range 2.1–2.6, and the activation energy of k_1 and k_2 was 89.1 and 68.8 kJ mol^{-1}, respectively.
2. In the later stages of cure reaction, a crosslinked network is formed and the reaction is mainly controlled by diffusion; Kamal's equation cannot describe the curing reaction at this stage. The extended Kamal equation (Equation 6) which includes a diffusion factor $f(\alpha)$ is able to describe and predict the cure reaction at these stages, and the theoretical values agree very well with the experimental data.

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