Curing Kinetics of *o*-Cresol Formaldehyde Epoxy Resin and Succinic Anhydride System Catalyzed by Tertiary Amine

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The kinetics of the cure reaction for system of *o*-cresol formaldehyde epoxy resin (*o*-CFER)/succinic anhydride (SA) and tertiary amine as a catalyst was investigated with a differential scanning calorimeter (DSC). Autocatalytic behavior was shown in the first stages of the cure for the system, which was well described by the model proposed by Kamal[6] 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 energy for k_1 and k_2 was 109 and 72.0 kJ/mol, respectively. In the later stages, a cross-linked network was formed and the cure reaction is mainly controlled by diffusion. Diffusion factor, $f(\alpha)$, was introduced into Kamal's equation, then the calculated values agree very well with the experimental data. The molecular mechanism of this curing reaction was discussed.

Introduction

Epoxy resins are widely used in the polymer industry as coatings, structural adhesives, insulating materials, polymer matrixes for composite materials, and so forth. However, the widespread use of epoxy resins is limited in many high-performance applications because of their thermal properties. The factors that most influence the thermal properties of epoxy resins are the cross-link density and the structure of the molecular chain. With the addition of *o*-cresol groups to the backbone of epoxy resins, the improved resins are considered worthy of further study in terms of their good thermal stability, electrical properties, chemical resistance, mechanical properties, and modification.[1,2]

Studies of the applications and physical properties of *o*-cresol formaldehyde epoxy resin (*o*-CFER) have been reported in recent years.[3−5] To provide a basis for curing process theory for applications of *o*-CFER, we must conduct research the curing kinetics of the *o*-CFER/SA system. Kamal's model,[6] arising from an autocatalytic reaction mechanism, has been applied to isothermal differential scanning calorimetry (DSC) data for the thermoset resins.[7−9] 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 deffusion-controlled. For the diffusion effect, Cole et al.[10] had discussed by a diffussion factor $f(\alpha)$.[6]

In this article, the curing kinetics of *o*-CFER with SA was studied by isothermal differential scanning calorimetry (DSC). For the consideration of the diffusion effect, the Kamal's model has been extended by introducing the diffussion factor $f(\alpha)$ and applied to the curing process of *o*-CFER /SA system. The molecular mechanism of the curing reaction for this system was discussed.

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Experimental Section

Materials. Epichlorohydrin, *o*-cresol, formaldehyde, NaOH, KOH, acetone, ethyl alcohol, hydrochloric acid, N,N′-dimethylbenzylamine, and curing agent succinic anhydride were all analytically pure and were supplied by Beijing Chemical Reagent Co. (Beijing, P. R. China).

Synthesis of *o*-CFER. An epoxy resin based on *o*-cresol formaldehyde (*o*-CFER) was synthesized according to the literature[11], the molar ratio (*o*-cresol formaldehyde:epichloro-hydrin:NaOH = 2:6:3) has been used in the synthetic experiment. The molecular structure of this resin had approximately the following form:
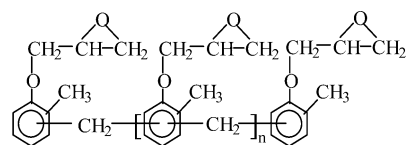
where $n = 0 − 1$. The epoxy value was determined, according to Jay's method,[12] to be 0.544 mol/100 g.

DSC method. Curing studies were carried out on a Shimadzu DT-41 differential scanning calorimeter (Shimadzu Co., Ltd., Japan). The DSC 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.[7] Under a nitrogen flow of 40 mL/min.

o-CFER and curing agent succinic anhydride were mixed homogeneously in a 1:1 equivalent ratio. The ratio of catalyst (N,N′-dimethylbenzylamine) and *o*-CFER was 1% (w/w), approximately. 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.

Samples were placed in thermostatic baths at curing temperatures (T_c's) between 110 °C and 135 °C in 5 °C increments. The reaction was considered complete when the heat curve leveled off to the baseline. The total area under the exothermal

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Figure 1. The plots of the conversion α versus time t at different temperatures.

Figure 2. The plots of the curing reaction rate $d\alpha/dt$ versus time t at different temperatures.

curve, based on the extrapolated baseline at the end of the reaction, 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.

The *n*th-order kinetics can be expressed as[13]

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

The autocatalytic kinetics can be expressed by Kamal[6] as

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

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 versus time t; k, k_1, and k_2 are the specific rate constants of these models, which are function of temperature; 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 0 initially and attains a maximum value at some intermediate conversion.

During the curing reaction of epoxy 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,[14,15] 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.[16,17] If the cure reaction is the only thermal event, then the reaction rate ($d\alpha/dt$) is proportional to the heat flow (dH/dt):

$$\frac{d\alpha}{dt} = \frac{dH/dt}{\Delta H_0} \tag{3}$$

The rate of cure can be determined with 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 Figure 2 plotted as $d\alpha/dt$ versus time t.
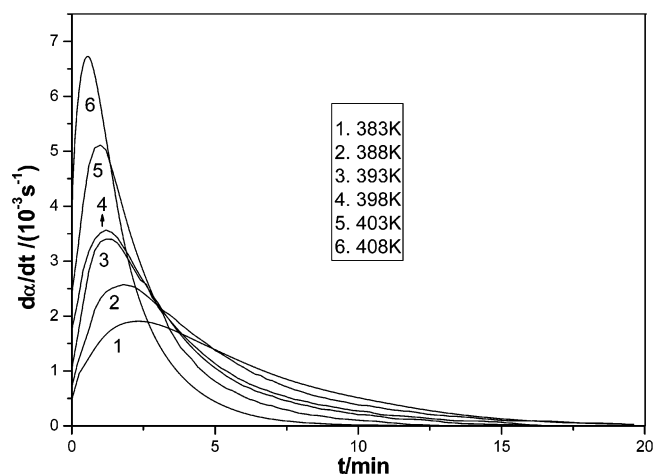
TABLE 1: Kinetic Parameters for Isothermal Curing of *o*-Cfer/Sa

T(°C)	$k_1(\times 10^{-3}\text{s}^{-1})$	$k_2(\times 10^{-2}\text{s}^{-1})$	m	n	$m + n$
110	0.479	0.507	0.50	1.62	2.12
115	0.709	0.677	0.51	1.62	2.13
120	1.04	0.952	0.53	1.82	2.35
125	1.75	1.21	0.75	1.85	2.60
130	2.40	1.57	0.68	1.79	2.47
135	3.86	2.01	0.72	1.84	2.56

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 order kinetics. The autocatalytic kinetic model of eq 2 is appropriate to describe this isothermal curing behavior. In eq 2, $m + n$ is the overall reaction order. The kinetics parameters can be obtained by fitting the isothermal data with nonlinear least-squares procedures, and they are shown in Table 1.

Table 1 shows that the k_1 values were small in comparison with k_2, which affected the reaction more, k_1 and k_2 increased with increasing temperature. The overall reaction order, $m + n$, lies in the range 2.1~2.6 and increased with ascent of the curing reaction temperature. The reaction rate constants k_1 and k_2 depend on the temperature and follow the Arrhenius relationship:

$$k = A \exp(-E/RT) \tag{4}$$

Rate constants k_1 and k_2 are shown as an Arrhenius plot in Figure 3, which yields the values of 109 and 72.0 kJ/mol for the associated activation energies E_1 and E_2, respectively. The linear correlation coefficient values is 0.998 for k_1 and 0.999 for k_2.

Typical comparisons between the experimental DSC data for 403 K and the autocatalytic model with parameters from eq 2 are shown in Figure 4.

The kinetic behavior described by the kinetic model agrees with the experimental data in the early stage. However in the later stage, as the reaction progresses, a deviation appears because of the onset of gelation and vitrification. Because of the mobility of reactive groups is hindered, and the rate of conversion is controlled by diffusion rather than by kinetic factors. Differences between the model predictions and experimental data were observed at the same conversion. This can be interpreted by free-volume considerations:[18] the free volume of materials decreased with temperature decreasing and the curing
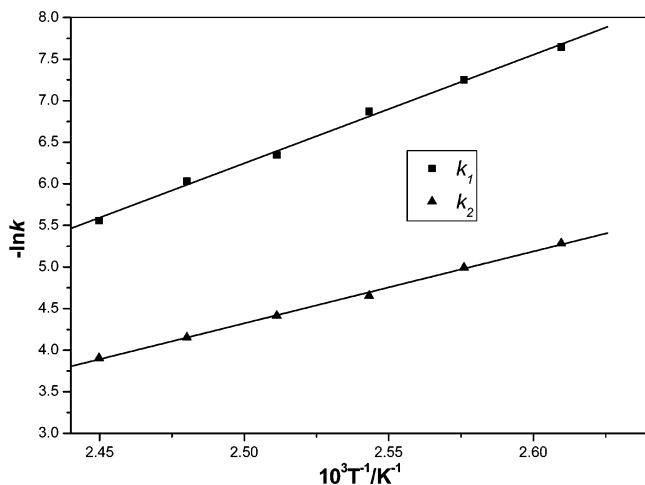
Figure 3. Arrhenious-type plots of rate constants k_1 and k_2 for *o*-CFER/SA curing system.
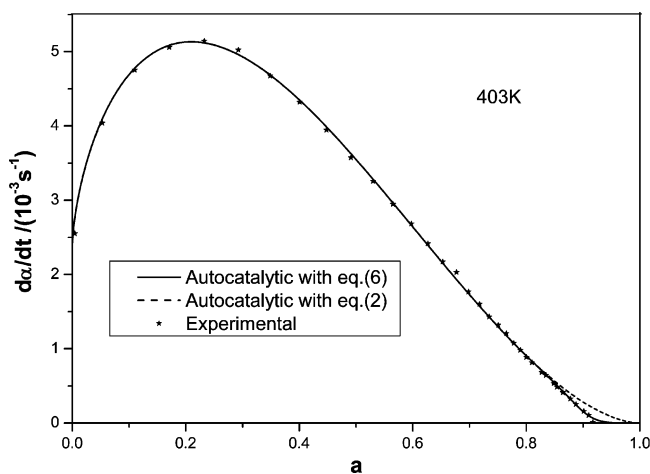

Figure 4. Comparison of the experimental data, theoretical values calculated with eq 2 and with eq 6:$d\alpha/dt$ versus α at 403K.

TABLE 2: Values of Critical Conversion, α_c and the Constant C at Different Temperatures

T (°C)	110	115	120	125	130	135
α_c	0.86	0.87	0.88	0.89	0.90	0.91
C	30	55	48	36	53	35

reaction conversion increasing, and 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.[10] proposed a semiempirical relationship based on free-volume considerations and earlier work by Chern and Poehlein.[18] In this relationship, $f(\alpha)$ defined with two empirical parameters is as follows:

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

Where k_c is the rate constant for chemical kinetics, k_e is the overall effective rate constant, C is constant, and α_c is the critical conversion depending on T_c. Values of C and α_c were obtained by fitting $f(\alpha)$ vs α data to eq 5, and they are listed in Table 2. For $\alpha \ll \alpha_c$, $f(\alpha)$ 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, the reaction rate equation of cure can be expressed in the following form to account for the effects of diffusion:

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

Figure 4 shows a comparison between experimental values and those obtained from eq 6 at 403 K.

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

It is known that the addition of hydroxyl-containing compounds (water, alcohols, phenols, etc.) considerably promotes the interaction of epoxy compounds with anhydrides, amines, and other nucleophilic attack. The reaction proceeds through a trimolecular transition state initially suggested by Smith[19] for the reaction of epoxy compounds with amines. As reported,[20]
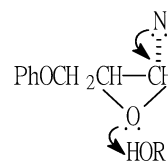
the maximum curing reaction rate was observed at $t = 0$ in the presence of hydroxyl-containing solvent, and obeyed nth order kinetics. This is due to the participation of proton. As to the pure epoxy resin/anhydride system, the curing reaction is as follow formula:
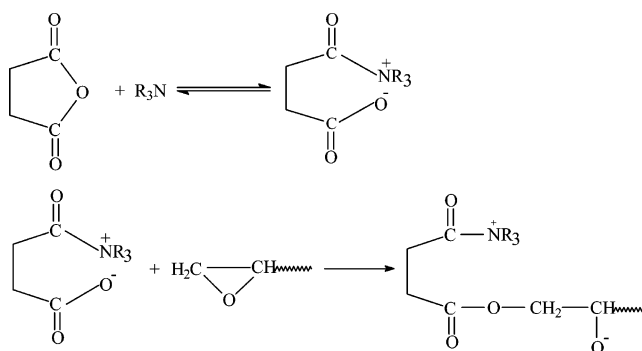
Then the oxygen negative ion reacts with epoxy group. Tertiary amine is not reformed in the reaction and is not the typical tertiary amine catalytic reaction mechanism. But the k_1 is not zero, this is because of the participation of the little hydroxyl group in the epoxy resins molecular chain, but this curing reaction is not a standard nth order reaction. It is favorable for the −OH in the epoxy resin molecular chain to become proton donor and participate reaction with the increasing curing temperature. The reaction mechanism ought to become trimolecular mechanism with the participation of the proton. This is the reason that the m + n value increase with the temperature.

Conclusions

(1) The cure reaction for the *o*-CFER/SA system was shown to have autocatalytic behavior in the kinetically controlled stage and was well described with 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 109kJ/mol and 72.0 kJ/mol, respectively.

(2) In the later stages of cure reaction, a cross-linked 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 (eq 6) which introduced diffusion factor $f(\alpha)$ is possible to describe and predict the cure reaction of epoxy resins, and the theoretical values agree very well with the experimental data.

(3) The reaction mechanism of epoxy resinswith anhydrides is a trimolecular mechanism with the participation of the proton.

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