

Polymerization Mechanisms and Curing Kinetics of Novel Polymercaptan Curing System Containing Epoxy/Nitrogen

Changli Lü,¹ Zhanchen Cui,¹ Bai Yang,¹ Xiaoping Su,² Chengsong Huo,² Jiacong Shen¹

¹Key Lab of Supramolecular Structure & Spectroscopy, Department of Chemistry, Jilin University, Changchun 130023, People's Republic of China

²General Research Institute for Nonferrous Metals, Beijing 100088, People's Republic of China

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ABSTRACT: The bis[3-(2,3-epoxypropylthio)phenyl]-sulfone (BEPTPhS)/trimercaptothioethylamine (TMTEA) system has a self-catalytic effect and can cure without any other accelerator. The curing kinetics of the BEPTPhS/TMTEA system was studied by means of the dynamic and isothermal differential scanning calorimetry method. The dynamic kinetic parameters were calculated with the aid of the Kissinger and Ozawa methods. The kinetic reaction mechanism in the isothermal reaction of BEPTPhS/TMTEA was shown to follow autocatalytic kinetics. The isothermal kinetic parameters, including k_1 , k_2 , m , and n , from the model proposed by Kamal were determined by fitting the experimental data; a good description of the curing kinetics was ob-

tained, although deviations were observed at low conversions. The Arrhenius kinetic analysis indicated that the activation energy decreased with the increase of the reaction conversion, which indicated a change of the reaction mechanism. The isothermal kinetic analysis and Arrhenius kinetic analysis both demonstrated that the catalytic effect of the nitrogen atom in TMTEA predominated at low conversions and the autocatalytic effect predominated at high conversions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 589–595, 2002

Key words: epoxy resin; nitrogen-containing polymercaptan; differential scanning calorimetry; curing kinetics

INTRODUCTION

Because of their good chemical resistance, low shrinkage, good heat resistance, outstanding adhesion, and excellent mechanical properties, epoxy resins are widely used in the fields of microelectronics and chemical industries.^{1,2} Especially in recent years, epoxy resins were also applied to optical fields, such as optical disk matrices, lenses, and prisms.^{3–6} Studies on the curing kinetic characterization of the thermoset resins are important to understand the relationships between the structure of the cured resin and processing techniques, as well as the properties for high performance composites. It is also important to find the optimal curing conditions.

In our laboratory we recently prepared a series of new epoxy-type optical resins with high refractive index.⁷ The nitrogen-containing trimercaptothioethylamine (TMTEA) as a curing agent was used to cure the epoxy resin bis[3-(2,3-epoxypropylthio)phenyl]-sulfone (BEPTPhS) to prepare optical resins with a high

refractive index. The cured resin BEPTPhS/TMTEA has a high refractive index ($n_d = 1.67$), and it can be potentially used as a high refractive index optical coating and adhesion agent. In this work the curing process of the novel epoxy system containing a thioether glycidyl resin (BEPTPhS) and the curing agent TMTEA was studied by FTIR, and the curing kinetics of the BEPTPhS/TMTEA system was investigated in detail by means of differential scanning calorimetry (DSC). To our knowledge, no similar studies are reported on the curing kinetics modeling of the epoxy/nitrogen-containing polymercaptan system. This system can be cured without the presence of any other accelerator (such as a Lewis base) due to the catalytic effect of the tertiary nitrogen in the TMTEA molecule. The study on the curing kinetics can elucidate the mechanism of the curing reaction between the epoxy and polymercaptan, which can be used to develop a general curing model for the optimal curing process of the epoxy/polymercaptan system.

EXPERIMENTAL

Materials

The BEPTPhS synthesized in our lab according to the method of Cui et al.⁷ had an epoxy equivalent weight of 200 g/equiv. The TMTEA was obtained by means of the methods given in the literature,^{8,9} and the other reagents were analytical grade and used without fur-

Correspondence to: B. Yang (yangbai@mail.jlu.edu.cn).

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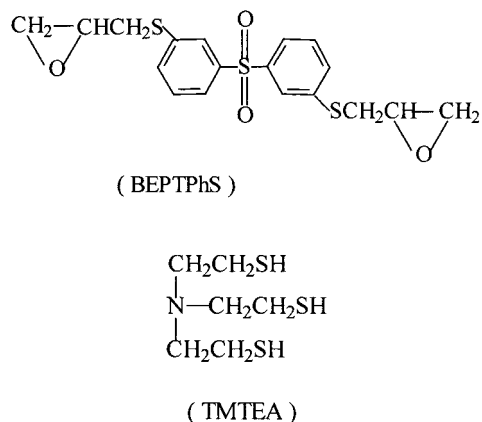


Figure 1 The chemical structures of BEPTPhS and TMTEA.

ther purification. The components were mixed in a molar ratio of 3:2 BEPTPhS/TMTEA. The mixtures were prepared at room temperature and stored at -20°C for no longer than 3 h.

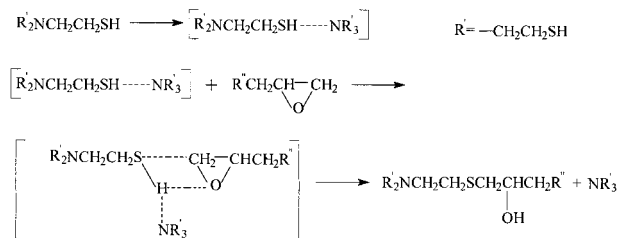
Characterization and measurement

The FTIR spectra were measured by a Nicolet AVATAR360 FTIR spectrometer in an air atmosphere. The DSC measurements were performed on a Perkin-Elmer DSC 7. The DSC apparatus was calibrated with high-purity indium, and $\alpha\text{-Al}_2\text{O}_3$ was used as the reference material. The dynamic DSC analysis was carried out at heating rates of 2.5, 5, 7.5, and $10^{\circ}\text{C}/\text{min}$ from 10 to 250°C . The isothermal curing reaction was conducted at 100, 120, 140, and 160°C . The reaction was considered to be complete when the isothermal DSC thermogram leveled off to the baseline. The total area under the exothermic curve, based on the extrapolated baseline at the end of the reaction, was used to calculate the isothermal heat of cure (ΔH_1) at a given temperature. After each isothermal run the sample was cooled to 10°C and then reheated at $10^{\circ}\text{C}/\text{min}$ to 250°C to determine the residual heat of the reaction (ΔH_r). The total heat evolved during the curing reaction was $\Delta H_0 = \Delta H_1 + \Delta H_r$. The isothermal conversion at time t was defined as $\alpha(t) = \Delta H_t / \Delta H_0$, where ΔH_t is the heat evolved during the isothermal cure for a particular period of time.

RESULTS AND DISCUSSION

Curing process of beptphs/tmtea system

The chemical structures of BEPTPhS and TMTEA are shown in Figure 1. Compared with the epoxide-amine reaction, the reaction of an epoxy resin with a mercaptan is not vigorous and requires another curing agent (such as an accelerator). However, the epoxide-mercaptan reaction can be carried out at a low temperature in the presence of a proper catalyst such as a



Scheme 1 A schematic representation of the curing mechanism for the BEPTPhS/TMTEA system.

Lewis base, although it needs a number of hours to complete the curing reaction. The TMTEA used in this work can react with the epoxy group at room temperature in the absence of an accelerator because the TMTEA itself contains a tertiary nitrogen atom, which possesses a catalytic effect. Analogous with alcohol and acid, the generally accepted scheme of the mercaptan-epoxide cure involves a complex intermediate stabilized by the formation of a hydrogen-bonded species.^{10,11} The hydrogen bonding causes the electron deficient epoxy complex to be more susceptible to nucleophilic attack by the incoming mercapto group. According to this mechanism, the catalytic reaction mechanism between TMTEA and the epoxy group can be drawn as shown in Scheme 1.

The structure changes of the BEPTPhS/TMTEA system during the curing process were detected by an IR instrument. The IR spectra of the BEPTPhS/TMTEA system during the curing reaction are shown in Figure 2. The characteristic absorption of the mercapto group at 2544 cm^{-1} disappeared after curing at 80°C for 1 h, and the absorption peak of the epoxide group at 921 cm^{-1} gradually decreased. There was also an absorption peak of the hydroxyl at 3500 cm^{-1} , which indicated that the mercaptan and the epoxy group had reacted. The epoxide group decreased continually

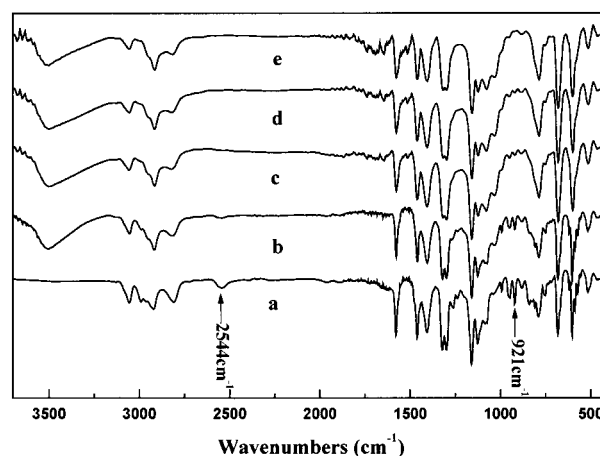


Figure 2 FTIR spectra of BEPTPhS/TMTEA curing reactions at (a) 0 and (b) 0.5 h at 80°C , (c) 1 h at 80°C , (d) 2 h at 80°C , and (e) 2 h at 80°C and 0.5 h at 120°C .

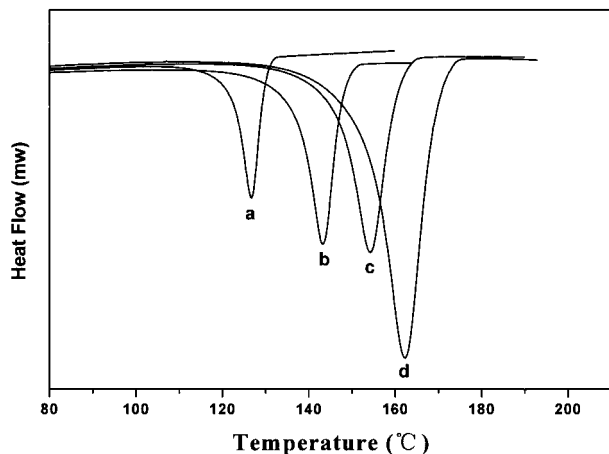


Figure 3 Dynamic DSC curves of the BEPTPhS/TMTEA system (stoichiometric amounts) at four different heating rates: (a) 2.5, (b) 5, (c) 7.5, and (d) 10°C/min.

with the increase of the curing time at 80°C; and the absorption peak of the epoxide group finally disappeared completely after curing at 80°C for 2 h and 120°C for 0.5 h, which demonstrated that the curing reaction was complete.

Dynamic scanning kinetics

The dynamic DSC scans of the BEPTPhS/TMTEA curing system (stoichiometric amounts) at four different heating rates are given in Figure 3. The temperature of the curing onset (T_i), the exothermic peak position (T_p), and the temperature of completion of the exotherm (T_f) shifted to higher temperatures while there was a decrease in the curing heat (ΔH) with the increasing scan rate. This is probably because the reaction takes place very rapidly at higher curing temperatures. The curing heat evolved is not fully recorded in the DSC curves within the time required for temperature equilibration, which leads to a decrease in the value of ΔH_{miso} . The total enthalpies of the curing reaction (ΔH_{miso}) evaluated from the DSC curves are listed in Table I.

In the dynamic model the temperature scan of the catalyzed epoxy monomer sample produced an exo-

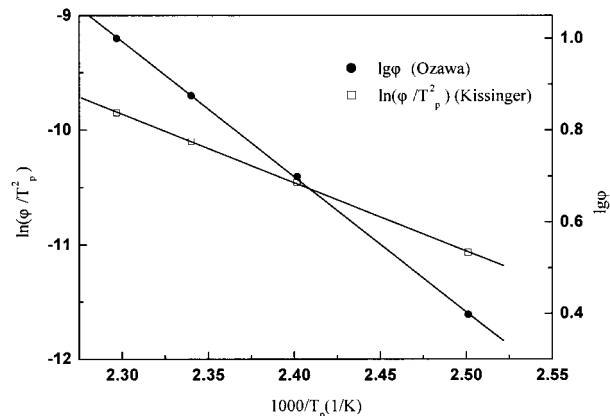


Figure 4 A Kissinger plot of $\ln(\phi/T_p^2)$ versus $1/T_p$ and an Ozawa plot of $\log \phi$ versus $1/T_p$.

thermic curing peak in the DSC trace. Based on the fact that the exotherm peak temperature (T_p) varies with the heating rate, the apparent activation energy (E_a) and preexponential constant (frequency factor A) can be determined by the Kissinger equation¹²:

$$-\ln(\phi/T_p^2) = E_a/RT_p - \ln(AR/E_a) \quad (1)$$

where ϕ is the heating rate, R is the ideal gas constant, and the other parameters have the same meanings as described earlier. Kissinger's method assumes that the maximum reaction rate occurs at peak temperatures, where $d^2\alpha/dt^2 = 0$. Therefore, by plotting $\ln(\phi/T_p^2)$ versus $1/T_p$ on the basis of eq. (1), the E_a can be obtained from the slope of the corresponding straight line. The plot of $\ln(\phi/T_p^2)$ versus $1/T_p$ for the BEPTPhS/TMTEA curing system is shown in Figure 4. The activation energies calculated from Figure 4 are listed in Table I.

Another theoretical treatment, the Ozawa method,¹³ can also be applied to the thermal data. At the same conversion there is a relationship among the E_a , ϕ , and T_p :

$$\log \phi = -0.4567 \frac{E_a}{RT} + \left(\log \left(\frac{AE_a}{R} \right) - \log F(\alpha) - 2.315 \right) \quad (2)$$

where $F(\alpha)$ is the conversion-dependent term.

The activation energies of the curing reaction of the BEPTPhS/TMTEA system determined from the slope of the plot of $\log \phi$ versus $1/T_p$ (Fig. 4) are listed in Table I. Its value (53.6 kJ/mol) is slightly higher than the activation energy (49.4 kJ/mol) obtained from the Kissinger method.

Unfortunately, the dynamic DSC method can only analyze the overall process and the complex reaction exotherm may actually conceal several competing reactions. For example, the epoxy-amine curing system

TABLE I
Results of DSC Scans of BEPTPhS/TMTEA System (Stoichiometric Amounts) at Different Heating Rates

ϕ (°C/min)	T_i (°C)	T_p (°C)	T_f (°C)	ΔH (J/g)
2.5	91	126	135	371.1
5	113	143	154	368.8
7.5	117	154	168	365.6
10	121	162	177	361.4
E_a (kJ/mol)	49.4 ^a		53.6 ^b	

^a Via the Kissinger method.

^b Via the Ozawa method.

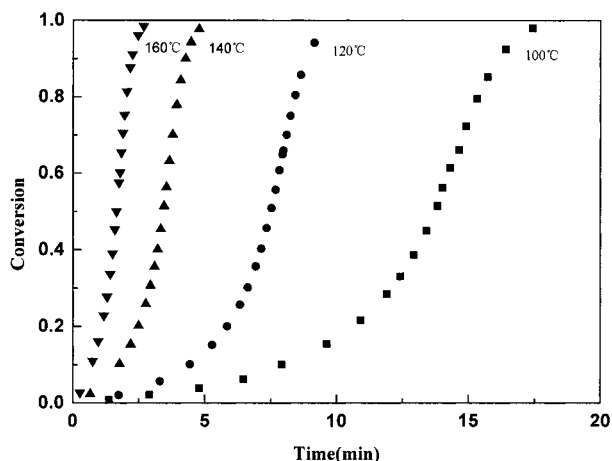


Figure 5 Conversion versus time curves for the BEPTPhS/TMTEA system at different cure temperatures.

includes primary and secondary amine attacks on the epoxy group, homopolymerization, etherification, and degradation. This makes the analysis of the E_a and polymerization kinetics from the temperature scanning DSC experiments fraught with difficulty.

Isothermal curing kinetics

It is widely accepted that isothermal experiments generate more reliable kinetic parameters.¹⁴ The isothermal cure was investigated to establish an accurate kinetic model for the curing reaction of the BEPTPhS/TMTEA system. The isothermal experiments were conducted at a series of curing temperatures ranging from 100 to 160°C. Theoretically, if the cure reaction is only a thermal event, then the reaction rate $d\alpha/dt$ is equal to the heat flow. According to this assumption, the extent of the reaction and the reaction rate at any time during an experiment can be described by

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

where dH/dt is the flow rate of heat and ΔH_0 is the total heat of the reaction.

The degree of conversion curves as a function of time at different temperatures are shown in Figure 5. At a given temperature the conversion rapidly increases with the curing time, as shown in the figure. Figure 6 shows the plots of the reaction rates ($d\alpha/dt$) versus time at different isothermal curing temperatures. The reaction rate increases with the time at every given temperature at the initial stage of the curing reaction and passes through a maximum. The reaction rate also increases with the temperature increase and reaches a maximum sooner.

The mechanisms of the curing reaction of thermo-setting resins follow the general kinetic models,

namely, n th order and autocatalytic mechanisms.¹⁵ According to the n th order kinetic model, the maximum reaction rate will be observed at time $t = 0$; according to the autocatalytic model, the reaction rate is zero or very small initially and reaches a maximum value at an intermediate conversion. Figure 6 shows a maximum reaction rate at $t > 0$, which reveals that the autocatalytic kinetic model is appropriate to describe this isothermal curing behavior. The autocatalytic kinetics was expressed by Kamal¹⁶ as

$$d\alpha/dt = (k_1 + k_2\alpha^m)(1 - \alpha)^n \quad (4)$$

where α is the cure conversion, k_1 and k_2 are the apparent rate constants with two different activation energies and preexponential factors, and m and n are the reaction orders.

Figure 7 shows the plots of $d\alpha/dt$ versus the conversion (α) at different temperatures. The reaction rate is affected by two factors: the isothermal curing temperature and conversion. As expected, at a given temperature we observed that the reaction rate initially increased with the increase of conversion and then gradually slowed down, finally tending to zero at a certain degree of conversion, although the conversion did not necessarily reach 100% before the reaction ceased. Moreover, at a given conversion the reaction rate increased with the increase of the isothermal curing temperature. The DSC results (Figs. 6, 7) show a nonzero initial rate, indicating that the initial catalysis by the nitrogen of TMTEA occurred at a very early stage of the reaction in the epoxy-polymercaptan system. In addition, the maximum values of the reaction rates appeared between 60 and 70% of the conversion, which are somewhat different from those of the amine-epoxy curing system with a typical maximum between 20 and 40% conversion.¹⁶ The kinetic parameters can be obtained by the Kamal autocatalytic model by fitting the isothermal experimental data

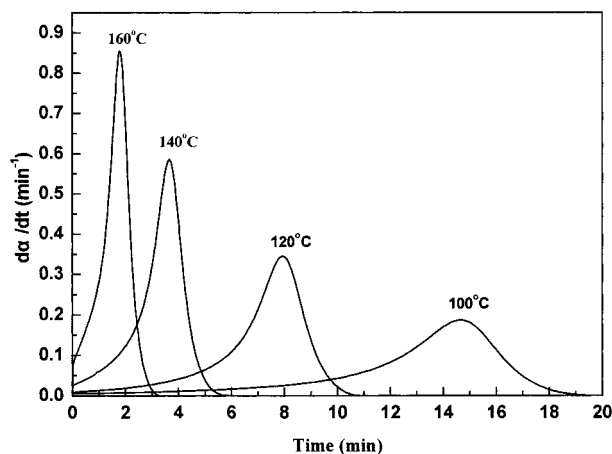


Figure 6 A plot of $d\alpha/dt$ versus time for the BEPTPhS/TMTEA system at different cure temperatures.

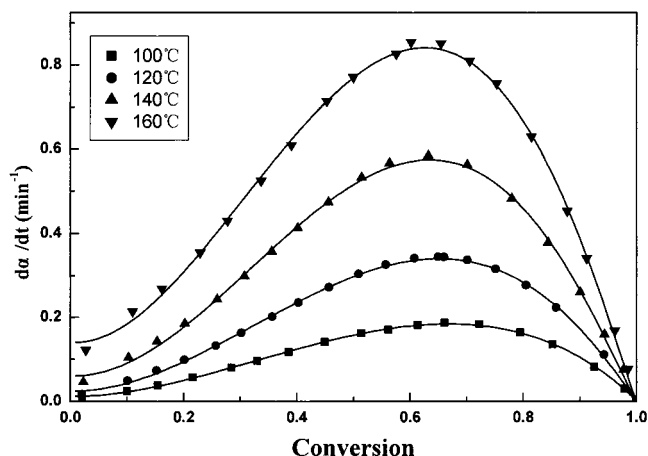


Figure 7 A plot of da/dt versus conversions at different temperatures from (—) eq. (4) compared to the data points for the experimental results for the BEPTPhS/TMTEA system determined by isothermal DSC.

with the aid of a least squares regression method, and these are shown in Figure 7. Good agreement was obtained for the curing process whereas deviations due to the effect of diffusion were not observed in the later stage. The reason for this phenomenon may be that the glass-transition temperature of the curing system is very low. After the torsion braid analysis (TBA) sample was cured at 80°C for 4 h, 100°C for 2 h, and 120°C for 0.5 h, its curves show that the glass-transition temperature of the BEPTPhS/TMTEA curing resin is about 41°C (see Fig. 8). The low glass-transition temperature is due to the low crosslink density of the curing system. The BEPTPhS/TMTEA system does not vitrify at higher temperatures (100–160°C) and the vitrification effects can be neglected here. Thus, our curing system is kinetically controlled over the whole curing process. However, the poor fits at low conversions could suggest a more complex mechanism. This is discussed below. The kinetic parameters

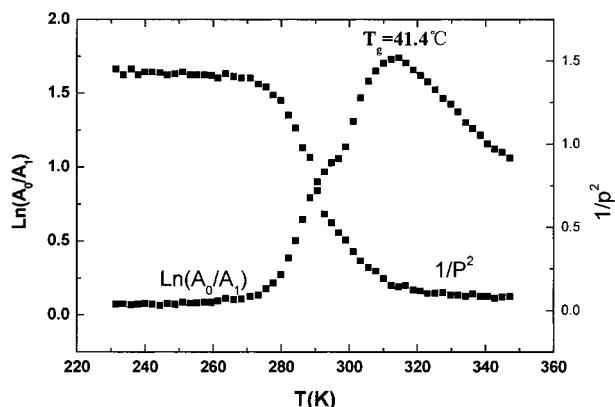


Figure 8 TBA curves of the BEPTPhS/TMTEA curing resin sample after curing at 80°C for 4 h, 100°C for 2 h, and 120°C for 0.5 h.

TABLE II
Kinetic Parameters for Isothermal Cure of BEPTPhS/TMTEA System by Kamal Model

	100°C	120°C	140°C	160°C
k_1	0.0122	0.0248	0.0617	0.1416
k_2	1.1093	2.3671	4.3578	5.8358
k_2/k_1	91	95	71	41
m	1.93	2.0	2.03	1.95
n	0.94	1.05	1.13	1.10
$m + n$	2.87	3.05	3.16	3.05
A_1 (min ⁻¹)	12.37			
A_2 (min ⁻¹)	13.36			
E_{a1} (kJ/mol)	55.4			
E_{a2} (kJ/mol)	37.8			

obtained by fitting the experimental data are summarized in Table II.

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

$$k = A \exp(-E_a/RT) \quad (5)$$

The k_1 and k_2 values are shown as the Arrhenius plots in Figure 9, which yield the associated activation energies. The activation energies E_{a1} and E_{a2} and pre-exponential factors A_1 and A_2 are listed in Table II.

Table II shows that the overall reaction order ($m + n$) is a constant and approximates to 3 with $m \approx 2$ and $n \approx 1$. The cure system of BEPTPhS/TMTEA with reaction orders $m \approx 2$ and $n \approx 1$ is different from other cure systems such as the epoxy-amine system^{17,18} and the epoxy-anhydride system,^{19,20} where the reaction order n is greater than m . Although it is generally not possible to infer a mechanism from the reaction order alone, it is usually possible to evaluate the order of the reaction if the mechanism is known. For the BEPTPhS/TMTEA system it is possible that the competitive catalysis effect between the nitrogen atom of TMTEA and the hydroxyl group produced during the cure reaction exists at the same time throughout the

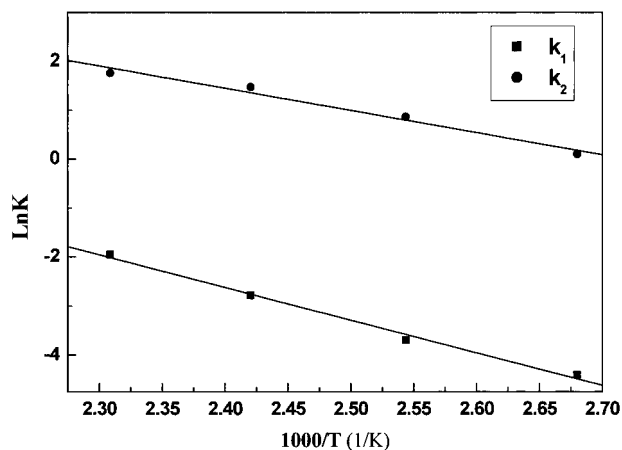


Figure 9 The relationship of $\ln K$ versus $1/T$.

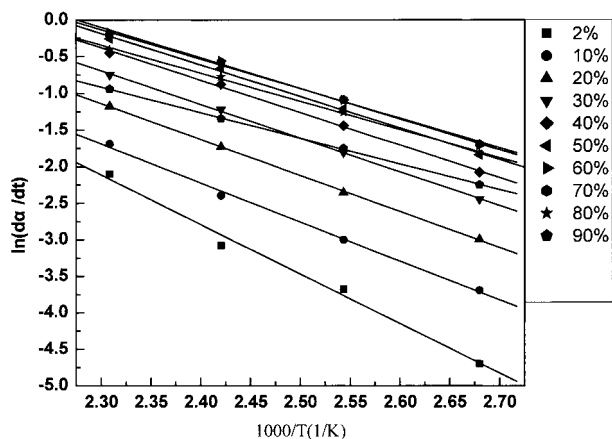


Figure 10 A plot of $\ln(d\alpha/dt)$ versus $1/T$ at different conversions to calculate the activation energy.

curing process. It is seen from Figure 9 that the k_1 values (the apparent rate coefficient for the reaction catalyzed by the nitrogen atom of TMTEA) are small compared with k_2 (the apparent rate coefficient for the reaction catalyzed by hydroxyl groups formed in the curing reaction), which mainly determine the reaction rate. This indicates that the hydroxyl autocatalysis effect is greater than that of the nitrogen atom of TMTEA, but the catalysis effect of the nitrogen atom is vital for the occurrence of the epoxy–mercaptan reaction at a lower temperature. In addition, as can be seen from Table II, the ratio of k_2/k_1 varies from 91 to 41 as the temperature increases from 100 to 160°C. It seems that the catalytic effect of the nitrogen atom of TMTEA increases faster with the increase of temperature than the autocatalytic effect of the hydroxyl groups. Hence, both of the competitive catalysis effects indicate a rather more complex mechanism for autocatalysis than the complex intermediate proposed in Scheme 1.

Arrhenius kinetics

The $d\alpha/dt$ can be described by the following equation:

$$d\alpha/dt = k(T)f(\alpha) \quad (6)$$

where $k(T)$ is the apparent reaction rate coefficient and $f(\alpha)$ is the type of reaction. Assuming that k takes the form of an Arrhenius rate, then

$$\ln(d\alpha/dt) = \ln A - E_a/RT + \ln f(\alpha) \quad (7)$$

By plotting $\ln(d\alpha/dt)$ versus $1/T$, eq. (7) can be used to calculate the activation energy of an isothermal curing reaction at any conversion without having accurately known the function $f(\alpha)$.

Figure 10 illustrates the isothermal DSC results for the BEPTPhS/TMTEA sample plotted according to eq. (7). Linear least squares fits to the data in the conver-

sion range from 2% to 90% are shown in Figure 10, and the activation energies calculated from them are shown in Figure 11. As can be seen, the activation energy decreases rapidly at the initial stage of the curing process and then the decreasing rate of activation energy slows down. This is in accordance with the results of the isothermal cure process, where the isothermal curing curves exhibit deviations at low conversions. The change of the activation energy indicates a change in the mechanism with the increasing extent of the reaction. For the BEPTPhS/TMTEA system the higher activation energy in the initial stage is reasonable because the catalytic effect of the tertiary nitrogen of the TMTEA molecules (as seen in Scheme 1) is predominant. At higher conversions the hydroxyl groups formed during the curing reaction partly protonate the oxygen atom of the epoxy group, facilitating the ring-opening reactions; this may lower the energy barrier of the reaction between mercaptan and the epoxy groups. Thus, the reason that the autocatalytic model cannot provide a good description of the curing reaction of BEPTPhS/TMTEA at the initial stage may be that the catalytic effect of the nitrogen atom of TMTEA predominates at low conversions, where the autocatalytic effect is not apparent. Like the epoxy–polymercaptan system we studied, Vyazovikin and Sbirrazzuoli²¹ also found that in the epoxy–amine system the autocatalytic model eq. (4) leads to the dependence of E_a on α , and $E_{a1} > E_{a2}$ (the E_a values determined from the Kamal model). In addition, the low activation energy possibly represents some average values between the activation energies of the reaction catalyzed by the nitrogen atom of TMTEA and those of the reactions autocatalyzed by hydroxyl groups formed in the curing reaction, and it is closer to the latter value. This is also supported by the autocatalytic model in which the E_{a1} (55.4 kJ/mol) and E_{a2}

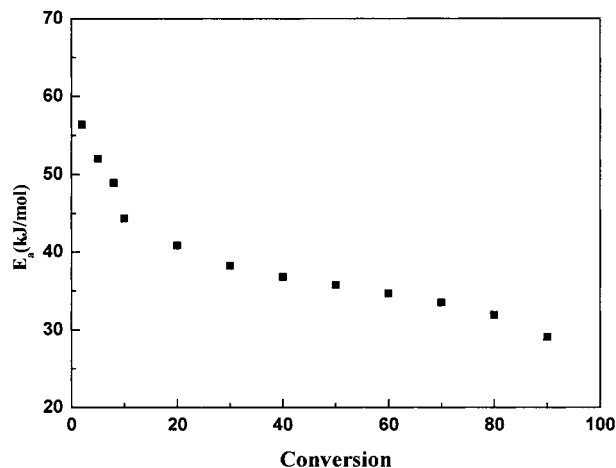


Figure 11 A plot of the activation energy versus the conversion for the cure process of the BEPTPhS/TMTEA system according to eq. (7).

(37.8 kJ/mol) are the activation energies of the reaction catalyzed by the nitrogen atom of TMTEA and the autocatalyzed reaction, respectively.

CONCLUSIONS

The curing behavior of the BEPTPhS/TMTEA system was investigated using the nonisothermal and isothermal DSC methods. The results indicate that the Kissinger and Ozawa methods for calculating the apparent activation energies gave fairly close results of 49.4 and 53.6 kJ/mol. The Kamal autocatalytic model with a total order of the reaction of about 3 was successfully applied to describe the curing kinetics of the BEPTPhS/TMTEA system with the exception of the initial stages. Diffusion control was not observed in the later stages of the cure process, but deviations were observed in the initial stages. The reason for this may be that the autocatalytic effect of the hydroxyl is not obvious and the catalytic effect of the tertiary nitrogen atom of the TMTEA molecules plays an important role at low conversions. The Arrhenius kinetics analysis shows that the activation energies change with the extent of reaction, indicating a change in the reaction mechanism.

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