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THE MECHANISM AND KINETICS OF CURING REACTION OF AG-80/SED SYSTEM BY DSC

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Abstract

The mechanism and kinetics of curing reaction of tetrafunctional epoxy resin (Ag-80)/novel diamines curing (*SED*) system were studied by non-isothermal and isothermal DSC. Different equivalent ratios of amine-epoxide give rise to different curing mechanisms. The main condensation reaction can be attributed to the reactions between the primary amine and epoxide and between the hydroxyl and epoxide when temperature is below 200°C, and to the reaction between the second-ary amine and epoxide when temperature is above 200°C. The corresponding apparent activation energies are 58.3 $kJ\cdot mol^{-1}$ and 99.3 $kJ\cdot mol^{-1}$ respectively. Apparent activation energies of condensation reactions between primary amine and epoxide and between hydroxyl and epoxide are just the same, which are 47.3 $kJ\cdot mol^{-1}$.

Keywords: cure, DSC, sulfone ether diamines (*SED*), tetrafunctional epoxy resin (Ag-80)

Introduction

Tetrafunctional epoxy resin cured by diamino diphenyl sulfone (*DDS*) possesses high tensile strength and modulus, fine heat resistance and chemical resistance as well, and it is a kind of high-quality thermosetting resin matrix of carbon fiber composite. Poor moisture resistance and toughness are drawbacks of this system. There are many ways to modify them, such as by blending with the thermoplastic PES or PEK [1, 2] or by adding novel curing agent to change the chemical structure of crosslinking networks [3, 4]. Systematic research has been carried out by author in the fields mentioned above [5–7]. In this paper, non-isothermal and isothermal DSC techniques were employed to study the mechanism and kinetics of curing reaction of tetrafunctional epoxy resin (Ag-80)/novel diamines curing (*SED*) system.

Experiment

Materials

The structure of tetrafunctional epoxy resin (Ag-80) is as follows:

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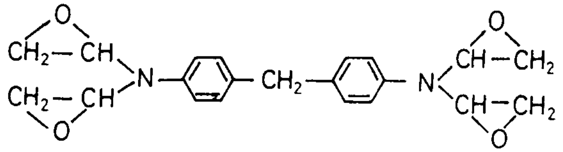
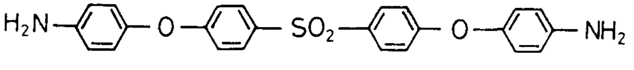


with epoxy value of 0.76, produced by Shanghai Research Institute of Synthetic Resin. The structure of curing agent, sulfone ether diamines (*SED*) is as follows:



synthesized in our laboratory.

Methods

Perkin-Elmer DSC-2C was used to investigate the mechanism and kinetics of curing reaction of Ag-80/*SED* system with different *SED* amount. The amount of sample was about 5 mg and the flow of N_2 was 20 ml·min^{-1}.

Table 1 Ratios betwen Ag-80 and *SED*

Sample No.	1	2	3	4	5	6	7	8	9	10
SED/Ag-80*	1.03	0.94	0.82	0.74	0.61	0.41	0.20	0.16	0.11	0.05
amine/epoxide**	1.25	1.15	1.00	0.90	0.75	0.50	0.25	0.20	0.13	0.06

* weight ratio(*W*), ** equivalent ratio(*R*)

In order to determine the kinetic parameters, different programmed heating rates were used for samples No. 2, No. 5 and No. 9. The programmed heating rate of 10 deg·min^{-1} was used for the other samples. The temperature range of determination was 50–350°C.

As an example, sample No. 5 was studied at temperatures 150, 155, 160, 165 and 170°C respectively.

Results and discussions

Non-isothermal curing reaction of Ag-80/SED and its kinetics

The results show that DSC curves give only one high-temperature exothermic peak with low ratio ($R \leq 0.13$), one low-temperature exothermic peak with high ratio ($R \geq 0.9$), but double curing peaks with medium ratio ($0.13 < R < 0.9$). When $0.13 < R < 0.9$, the area of high-temperature peak decrease and that of low-temperature peak increase gradually with the increment of R. At the same time, we could also see that both T_{p_1} and T_{p_2} shift to lower temperatures and ΔH reduces rapidly at the beginning and slowly afterwards with the increment of R.

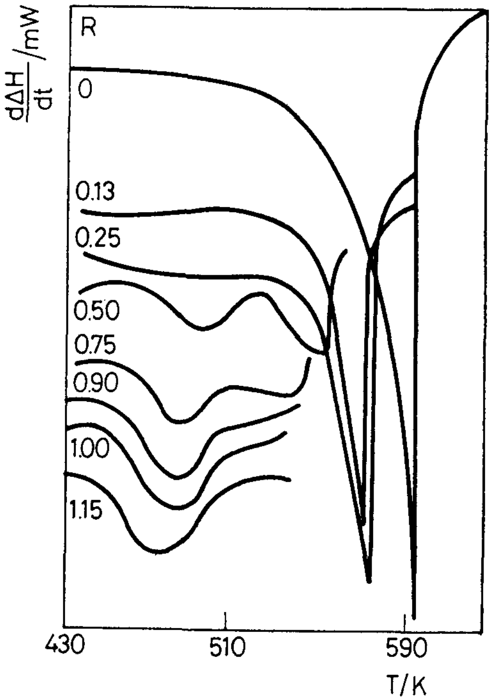


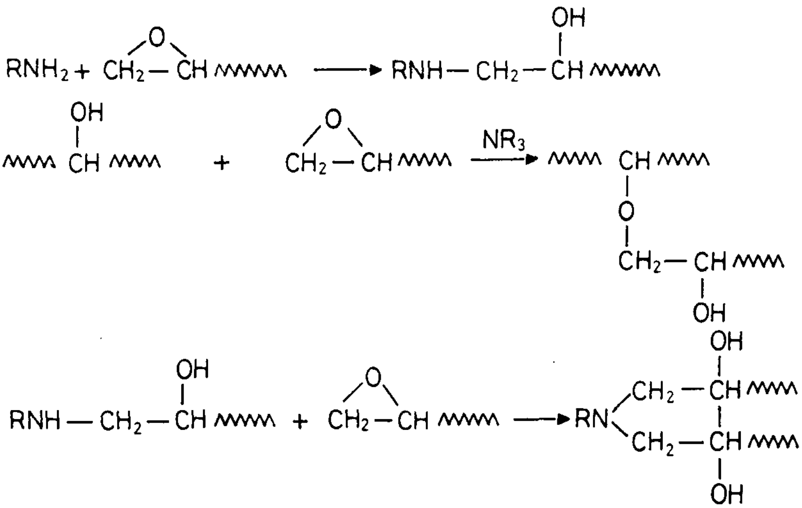
Fig. 1 Non-isothermal curing curves for Ag-80/*SED* with different *R*

Table 2 T_p and ΔH of non-isothermal curing curves for Ag-80/ *SED* with different *R*

Sample No.	1	2	3	4	5	6	7	8	9	10	Ag-80
R	1.25	1.15	1.10	0.90	0.75	0.50	0.25	0.20	0.13	0.06	0.00
T_{p1}/K	467	468	470	471	474	477	484	487			
T_{p2}/K					544	556	568	569	575	580	587
ΔH / $J \cdot g^{-1}$	380	435	446	462	549	579	818	878	1098	1309	1434

T_p is the peak temperature; ΔH is the heat of reaction.

As we have studied the system with the aid of FTIR before [7], the main reaction can be attributed to condensation reactions between the primary amine and epoxide and between hydroxyl and epoxide by the catalysis of tertiary amine when temperature is below 200°C and to the reaction between the secondary amine and epoxide when temperature is above 200°C. Comparing the results of FTIR with those of DSC, we can conclude that the low-temperature exothermic peak, ranging from 130 to 190°C ($\Phi \rightarrow 0$), corresponds to the reactions between primary amine and epoxide and between hydroxyl and epoxide, while the high-temperature one, ranging from 220 to 290°C ($\Phi \rightarrow 0$), corresponds to the reaction between secondary amine and epoxide. At much higher temperatures, it is possible for the reaction between epoxide and epoxide to be dominant. Equations for the reactions mentioned above are as follows:



Due to the smaller heat of reaction between primary amine and epoxide and between hydroxyl and epoxide, and the larger one between secondary amine and epoxide per unit mass, the total heat of reaction decreases rapidly with the increment of R. In the meantime, because the above three reactions occur easily with the increment of R, T_{p_1} and T_{p_2} shift to lower temperatures.

According to the Kissinger equation [8]:

$$d(\ln\Phi/T_p^2)/d(1/T_p) = -E_a/R$$

where E_a is the apparent activation energy, R is the gas constant, one can compute the apparent activation energy of the curing reaction, as shown in Fig. 2. Results indicate that, sample No. 2 has only one low-temperature exothermic peak with E_a of 58 kJ·mol^{-1}; sample No. 9 has only one high-temperature exothermic peak with E_a of 104.3 kJ·mol^{-1}; sample No. 5 has double curing peaks with E_a of low-temperature peak which is 58.3 kJ·mol^{-1}, same as that of No. 2, and that of high-temperature peak which is 99.3 kJ·mol^{-1}, close to that of No. 9. These results further indicate that the mechanisms of curing reaction are different with the changing of R.

Isothermal curing reaction of Ag-80/SED system and its kinetics

Sample No. 5 was selected to study the isothermal curing reaction of Ag-80/*SED* system at medium temperatures. The isothermal curing exothermic peak in Fig. 3 corresponds to the low-temperature peak mentioned above.

Table 3 Peak temperature of curing curve with different programmed heating rates for three samples.

	Heating rate(Φ / deg·min^{-1})							
	2.5		5		10		20	
Sample No.	T_{p1}	T_{p2}	T_{p1}	T_{p2}	T_{p1}	T_{p2}	T_{p1}	T_{p2}
2	436		453		470		491	
5	437	514	453	528	474	544	494	560
9		543		557		575		590

Peak temperature(T_p/K)

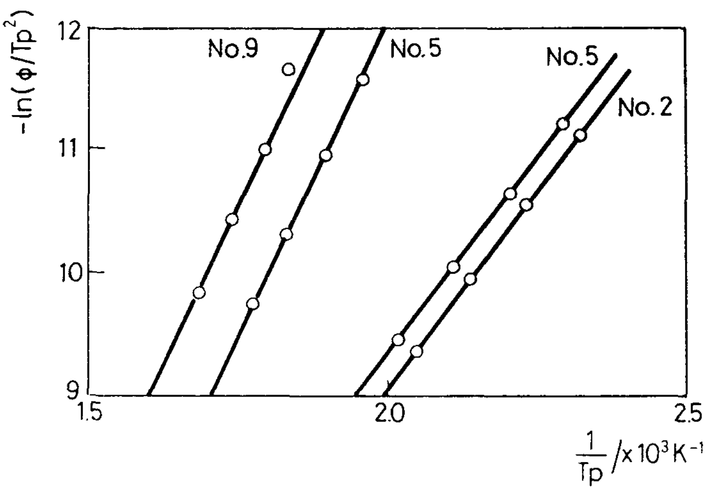


Fig. 2 Plots of $\ln(\Phi/T_p^2)$ *vs.* $1/T_p$ for three samples

It can be seen from Fig. 3 that the time corresponding to the minimum of curve decreases as the curing temperature rises. That is to say, the higher the curing temperature, the faster the rate of the curing reaction.

According to:

$$d\alpha / dt = kf(\alpha) \tag{1}$$

where α is the extent of the curing reaction, k is the rate constant of the reaction, whereas

$$k = A\exp(-E_a / RT) \tag{2}$$

where A is the frequency factor, E_a is the apparent activation energy, R is the gas constant, T is the absolute temperature.

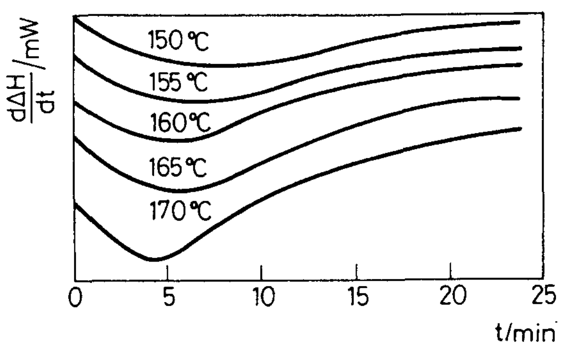


Fig. 3 Isothermal curing curve of sample No. 5

Combination of Eqs (1) and (2) gives

$$d\alpha\ /f(\alpha) = k\mathrm{d}t = A\exp(-\ E_a\ /\ RT)\mathrm{d}t \tag{3}$$

when α is given a fixed value, f(α) is a constant, integration leads to

$$\ln t = E_a\ /\ RT + \text{constant} \tag{4}$$

By the Eq. (4), apparent activation energy can be obtained, known as the Arrhenius method [9].

Applying the Arrhenius method to the system, one can see the result in Fig. 4.

Five almost parallel lines in Fig. 4 suggest that within the temperature range studied, apparent activation energies for curing reactions are similar, regardless of the reaction extents, with E_a of 47.29 kJ·mol^{-1}. Combining with the FTIR analysis [7] of the system, we can see that the condensation reaction between primary amine and epoxide is dominant at low reaction extent, and that between hydroxyl and epoxide is the main reaction at high extent in the temperature range of 140–180°C, with the apparent activation energies of the two condensation reactions being quite similar, which is in agreement with the previous reference [10].

For the curing reaction of epoxy resin, presuming $f(\alpha)=(1-\alpha)^n$, then,

$$d\alpha\ /\ (1-\alpha)^n = k\mathrm{d}t \tag{5}$$

for $n=0$, $n=1$, $n\leq2$, integration leads to:

$$\alpha - \alpha_o = K(t - t_o)$$

$$-\ln(1-\alpha) = k(t - t_o) + \text{constant}$$

$$1/(1-\alpha)^{n-1} = (n-1)k(t-t_o) + \text{constant}$$

where t_o is the reference time.

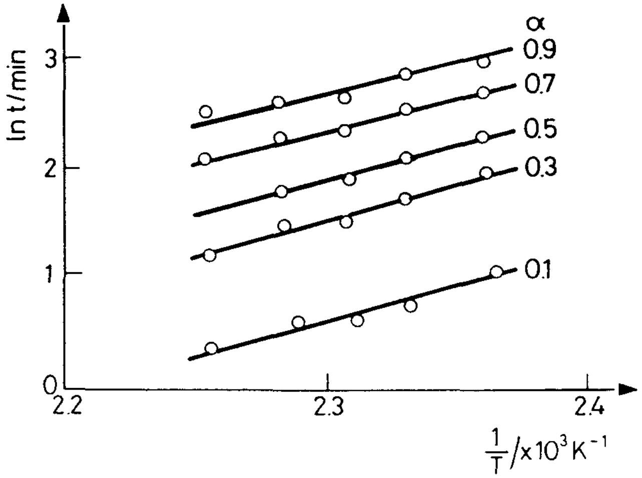


Fig. 4 Plots of ln$t$ *vs.* $1/T$ of isothermal curing curves with different reaction extent for sample No. 5

However, as reported in many references, due to the existence of tertiary amine or hydroxyl which has catalytic effect on the curing reaction of epoxy resin, it is more suitable to describe by using the kinetic equation [11, 12] of the autocatalyzed curing reaction, that is,

$$\mathrm{d}\alpha/\mathrm{d}t = (k_1 + k_2\alpha^m)(1-\alpha^n) \tag{6}$$

where k_1 and k_2 are rate constant, m and n are constants, $m+n$ is the overall order of the reaction; k_1 and k_2 can be obtained through experiment.

dα/dt is plotted against α for isothermal curing curve of the studied system at temperatures 150, 160 and 170°C, and dα/dt *vs.* α in the form of Eq. (6) for $m=1$, $n=1$ and $m=1$, $n=2$ (plots are omitted). Comparing these curves, it shows that the experimental curve at 170°C agrees relatively with the calculated curve from Eq. (6) for $m=1$, $n=1$, and the experimental curve at 150 or 160°C lies between the two calculated curves. The curing reaction kinetics of Ag-80/*SED* is rather complicated, because of the occurrence of many reactions simultaneously. It is very difficult to model only after an n order or an $m+n$ order kinetic formula within the experimental temperature range.

Conclusions

In the non-isothermal DSC of the novel Ag-80/*SED* system: The low temperature exothermic peak corresponds mainly to the condensation reactions between the primary amine and epoxide and between hydroxyl and epoxide, while the high temperature one to that between secondary amine and epoxide.

Using Kissinger method to calculate the kinetic parameters further indicates that different equivalent ratios of amine-epoxide give rise to different curing mechanisms.

Applying the Arrhenius method to carry out the kinetic analysis shows that apparent activation energies of reactions between the primary amine and epoxide and between hydroxyl and epoxide are very close to each other.

Isothermal curing reaction, which includes many reactions, is rather complicated and cannot be modelled after an n order or an $m+n$ order kinetic equation.

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Zusammenfassung — Mittels nichtisothermer und isothermer DSC wurde der Mechanismus und die Kinetik der Härtungsreaktion von tetrafunktionellem Epoxyharz (Ag-80)/neuartigem Diaminhärtungs(SED)System untersucht. Verschiedene entsprechende Verhältnisse von Amin und Epoxid verursachen verschiedene Härtungsmechanismen. Die wichtigste Kondensationsreaktion kann der Reaktion zwischen primärem Amin und Epoxid und der Reaktion zwischen Hydroxyl und Epoxid zugeschrieben werden, wenn die Temperatur unter 200°C liegt, oberhalb von 200°C hingegen der Reaktion zwischen sekundärem Amin und Epoxid. Die entsprechenden scheinbaren Aktivierungsenergien betragen 58.3 kJ/mol und 99.3 kJ/mol. Die scheinbare Aktivierungsenergie der Kondensationsreaktionen zwischen Amin und Epoxid und zwischen Hydroxyl und Epoxid sind fast gleich, nämlich 47.3 kJ/mol.