

Curing Behavior and Thermal Property of Epoxy Resin with Boron-Containing Phenol-formaldehyde Resin

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ABSTRACT: The curing reaction of bisphenol-A epoxy resin (BPAER) with boron-containing phenol-formaldehyde resin (BPFR) was studied by isothermal and dynamic differential scanning calorimetry (DSC). The kinetic reaction mechanism in the isothermal reaction of BPAER-BPFR was shown to follow autocatalytic kinetics. The activation energy in the dynamic cure reaction was derived. The influence of the composition of BPAER and BPFR on the reaction was evaluated. In addition, the glass transition temperatures (T_g s) were measured for the BPAER-BPFR samples cured partially at isothermal temperatures. With the curing conditions varying, different glass transition behaviors were observed. By monitoring the variation in these T_g s, the curing process and the thermal property of BPAER-BPFR are clearly illustrated. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1054–1061, 2000

Key words: epoxy resin; boron-containing phenol-formaldehyde resin; curing kinetics; glass transition temperature

INTRODUCTION

Epoxy resins are important adhesives and composite matrix materials, and they have been widely used in every aspect of everyday life. In practical application, they can be cured with many kinds of curing agents, such as multiamines and acid anhydrides, and converted into three-dimensional (3-D) networks. However, because of the difference in the structures of these curing agents, the curing behavior, phase behavior, and mechanical and thermal properties of the final products are different. Based on this fact, to gain a desired property of the final network of the epoxy resin, which types of curing agents should be used is the first thing to ascertain.

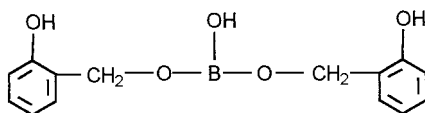
Boron-containing phenol-formaldehyde resin (BPFR) is a modified phenol-formaldehyde resin. It is obtained by introducing boron to the common

phenol-formaldehyde resin, and it can be used to cure the bisphenol-A epoxy resin (BPAER). Recently, several reports have appeared on the synthesis and application of this resin.^{1–3} However, no curing reaction kinetics research reports on it have been seen. To provide a basis for the theory about curing process and properties for the application of BPAER-BPFR, it is necessary to conduct research in the curing kinetics and properties of BPAER-BPFR.

For this article, curing kinetics and properties of BPAER-BPFR were studied. Structure changes of BPAER-BPFR during the curing process were investigated by infrared (IR). The mechanism and kinetics of the curing reaction were studied by isothermal and dynamic differential scanning calorimetry (DSC). The kinetic data were evaluated. Moreover, the glass transition temperatures (T_g s) were measured for the BPAER-BPFR samples cured isothermally at different temperatures for various periods, and by monitoring the difference in these T_g values, the thermal properties and the curing reaction process were identified.

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Scheme 1

EXPERIMENTAL

Materials

BPAER with an epoxide number of 0.44 mol/100 g was purchased from Baoding Fourth Chemical Factory (Hebei Province, China). The BPFR was synthesized according to the literature,³ and its structure is as follows (Scheme 1).

The resin's blends were prepared by solution mixing with three compositions of weight ratio (75 : 25, 65 : 35, 45 : 55) of BPAER : BPFR and then removing the solvent in vacuum at 20°C. The solvent used was acetone (analytical reagent).

IR Measurements

During the isothermal curing, a Hitachi 260-50 IR spectrophotometer was used for the investigation of the structure changes of the BPAER-BPFR. The desired sample was dissolved in acetone and then coated as a thin film on a potassium bromide disk. When the solvent in the film was completely evaporated in vacuum at 20°C for 24 h, the potassium bromide disk was first scanned by the IR instrument. Thereafter, the disk was placed in a heated oven with a fixed temperature of 160°C. During the curing reaction at this temperature, the disk was repeatedly withdrawn at regular time intervals for analysis.

DSC Measurements

Curing studies on the BPAER-BPFR isothermal and dynamic condition were carried out by a Shimadzu DSC-41 differential scanning calorimeter operating in a nitrogen atmosphere. The DSC instrument was calibrated by indium standards, α - Al_2O_3 was used as the reference material.

About 10 mg of the blend was placed in a sample cell. In the dynamic analysis, the samples were scanned at five heating rates: 2.5, 5, 7.5, 10, 12.5°C \times min⁻¹. Isothermal analysis was performed at temperatures ranging from 190 to 220°C in 10°C increments. Before loading the sample, the furnace was first heated up to a desired fixed temperature and kept for a certain period of time. When the system reached the equi-

librium state, the sample cell was quickly set on the calorimetric detector plate. The reaction was considered complete when the rate curve leveled off to a baseline. The total area under the exotherm curve was used to calculate the heat, ΔH_i , evolved in the isothermal cure at a given temperature. After each isothermal run, the sample was rapidly cooled to 10°C and then reheated at 10°C \times min⁻¹ to determine the residual heat of reaction, ΔH_r . Therefore, the total heat evolved during the curing reaction is $\Delta H_0 = \Delta H_i + \Delta H_r$.

The glass transition temperature (T_g) of the cured sample was measured with DSC. According to the operation procedure mentioned above, a series of samples with the same weight (10 mg) were cured in the DSC-41 at isothermal curing temperatures from 120 to 200°C for various periods, after which, the cured samples were cooled rapidly to at least 50°C below the expected T_g , and then subjected to a dynamic scan at 20°C \times min⁻¹ to determine the T_g . The T_g is taken as the midpoint of the heat capacity change (ΔC_p). In addition, the softening temperature (T_s) of the BPAER was also measured in the DSC-41 at the same heating rate and determined as the T_g .

RESULTS AND DISCUSSION

Structure Changes

IR spectra of BPAER-BPFR detected by IR spectrometer are shown in Figure 1. Features of the spectra are the appearance of the characteristic group absorptions: benzene ring at 1600 cm⁻¹, boron acid ester linkage at 1350 cm⁻¹, phenolic hydroxyl at 1250 cm⁻¹, ether linkage at 1050 cm⁻¹, epoxide group at 910 cm⁻¹. It is observed that the absorption peak of the epoxide group at 910 cm⁻¹ disappears after curing for 60 min. Moreover, the absorption peak of the boron acid ester linkage at 1350 cm⁻¹ gradually decreases with increasing curing time.

Isothermal Curing

The isothermal curing DSC curves of BPAER-BPFR are shown in Figure 2. It is evident that the heat flow rate is greatly affected by the curing temperature [Fig. 2(a)]. If the curing temperature is lower, no apparent exothermic behavior will be observed within the limited sensitivity of the apparatus. If the curing temperature is higher, some exothermic behavior will not be recorded

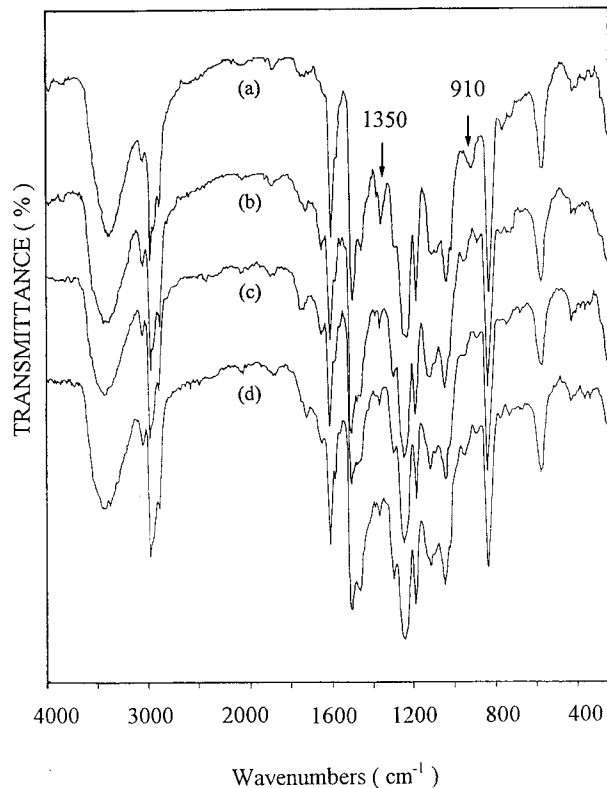


Figure 1 The IR spectra of BPAER-BPFR at: (a) room temperature; and after curing at 160°C for (b) 60 min; (c) 180 min; (d) 240 min.

because of the limited response rate to the rapid reactions. Therefore, the curing temperatures were chosen according to the values of the heat flow rate to gain an apparent exotherm peak. In addition, the heat flow rate is affected by the BPFR content. At a given temperature, with the BPFR content rising, the heat flow rate is increased [Figure 2(b)].

The reaction heat obtained by the DSC curves varies for different BPFR contents. At a given temperature, as the BPFR concentration is increased, the heat values are found to decrease and show a maximum at the 75 : 25 ratio. In theory, the heat evolution recorded by DSC is assumed to be proportional to the extent of consumption of the reactive groups in BPAER-BPFR. According to this assumption, the extent of reaction and the reaction rate at anytime during an experiment can be described by

$$\alpha = \frac{\Delta H_t}{\Delta H_0} \quad (1)$$

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_0} \times \frac{dH}{dt} \quad (2)$$

where ΔH_t is the partial heat of reaction at time t , ΔH_0 is the total heat of reaction, and dH/dt is the flow rate of heat.

According to the above two equations, the α and $d\alpha/dt$ were calculated by integrating the DSC curves, and the plots of $d\alpha/dt$ versus α at different temperatures or different compositions are shown in Figure 3. It is seen that the reaction rate is affected by three factors: isothermal curing temperature; conversion; and composition ratio. As expected, at a given temperature and composition, the reaction rate is observed to increase with conversion initially and pass through a maximum, and then gradually slow down, finally tending to zero at a certain degree of conversion. In addition, at a given temperature and conversion, the higher the BPFR content in the composition, the higher the reaction rate [Fig. 3(b)]. Moreover, at a given composition and conversion, the reaction rate increases with increasing temperature [Fig. 3(a)].

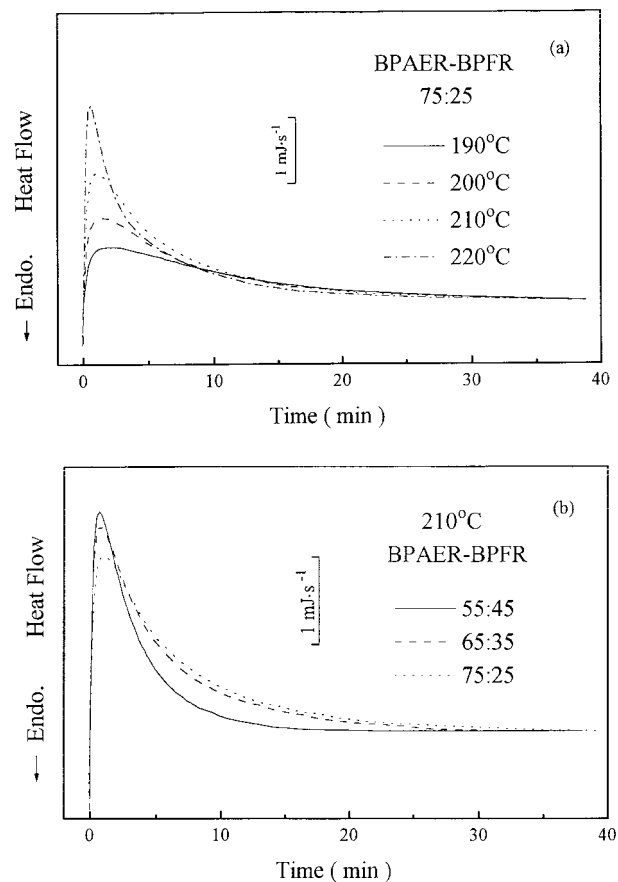


Figure 2 Isothermal DSC curves of BPAER-BPFR for curing of (a) the same composition at different temperatures, (b) different compositions at 210°C.

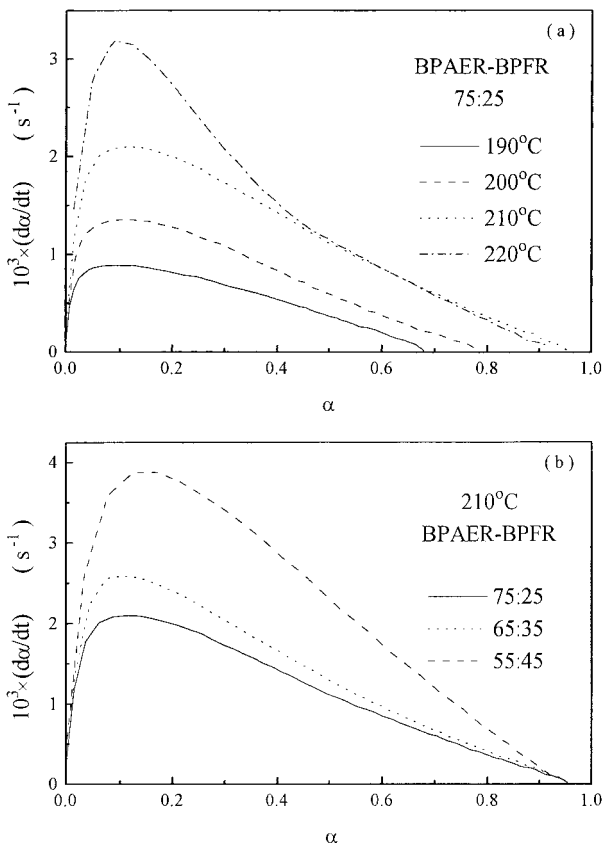


Figure 3 The plots of reaction rate $d\alpha/dt$ versus conversion α for curing of (a) the same composition at different temperatures, (b) different compositions at 210°C.

To model the curing kinetics, the following two equations are used to describe the reaction rate and the reaction rate constant.

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (4)$$

where α is the extent of the reaction, $k(T)$ is the rate constant at temperature T , $f(\alpha)$ is the function of α that represents the reaction mechanism, other parameters have the usual Arrhenius significance, and T is the absolute temperature.

As reported in the literature,⁴ n th-order and autocatalytic kinetics are the two reaction mechanisms to describe the curing reaction. They can be expressed as follows.

n th-order kinetics:

$$\frac{d\alpha}{dt} = k(T)(1 - \alpha)^n \quad (5)$$

autocatalytic kinetics⁵

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

where α is the fraction of epoxide reacted at time t , m and n are the reaction orders, k_1 and k_2 , are reaction rate constants with two different activation energies and preexponential factors.

According to Eqs. (5) and (6), systems obeying n th-order kinetics will obviously have the maximum reaction rate at $t = 0$; whereas, systems obeying autocatalytic kinetics will attain a maximum value at some intermediate conversion ($\alpha = 0.3 \sim 0.4$). Based on the characters of the two reaction mechanisms, and in view of the above experimental phenomena, in which the reaction rate of the BPAER-BPFR system reaches a maximum at $\alpha = 0.1 \sim 0.2$ [Fig. 3(a, b)], the isothermal curing kinetic reaction of BPAER-BPFR can be deduced to follow autocatalytic kinetics.

Dynamic Curing

The dynamic DSC curing curves of BPAER-BPFR at the heating rate of $5^\circ\text{C} \times \text{min}^{-1}$ are shown in Figure 4. It can be seen that there is an endotherm peak before the beginning of the curing process. This is attributed to a dehydrating reaction process between hydroxymethyls in the

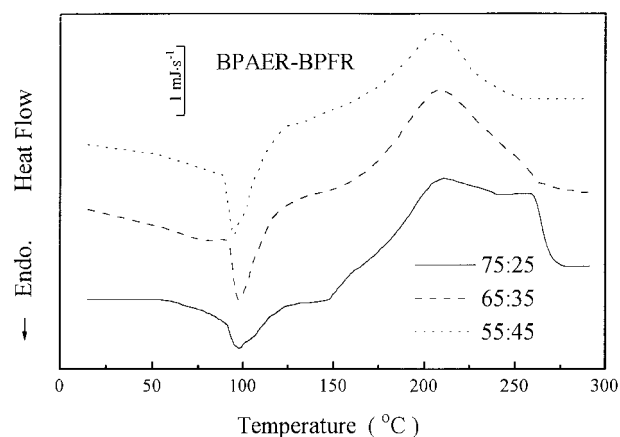


Figure 4 Dynamic DSC traces of the BPAER-BPFR with different compositions at the heating rate of $5^\circ\text{C} \times \text{min}^{-1}$.

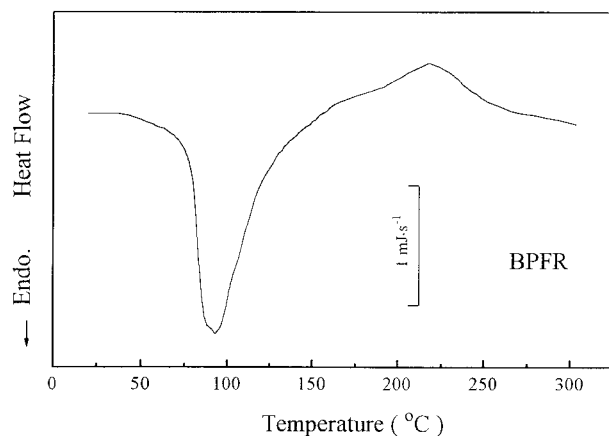


Figure 5 DSC traces of the BPFER at the heating rate of $5^{\circ}\text{C} \times \text{min}^{-1}$.

BPFER molecules (Fig. 5). The weight loss during this process is found to be proportional to the BPFER concentration. In addition, there is a slight difference in the shapes of the exothermic peaks for different compositions. This is caused by the influence of the BPFER content on the curing reaction rate. With a higher BPFER content, the epoxide groups in the BPAER–BPFER are easier to react. For 75 : 25, following the main exotherm peak, there is a shoulder, after which the rate drastically decreases and at last stabilizes at a certain value. This is because the BPFER content in the composition is too low, and not all the epoxide groups can be reacted in the rapid curing reaction process. For the 65 : 35 and 55 : 45, the peak shapes are similar. Furthermore, with the content of BPFER rising, the curing reaction covers a narrower temperature range.

In addition, the peak temperature (T_m) is observed to decrease with the increasing BPFER concentration. The T_m indicates the temperature for the maximum rate of the curing reaction. All the T_m s of the DSC curves under different heating

rates are listed in Table I. Based on the fact that the exotherm peak temperatures varies with the heating rates, curing activation energies E and frequency factor A were determined by the Kissinger equation⁶:

$$\ln\left(\frac{\beta}{T_m^2}\right) = \ln\left(\frac{AR}{E}\right) - \frac{E}{RT_m} \quad (7)$$

where β is the linear heating rate and the other parameters have the same significance as described earlier. Kissinger's technique assumes that the maximum reaction rate occurs at peak temperatures, where $(d^2\alpha/dt^2) = 0$, therefore, by plotting $\ln(\beta/T_m^2)$ versus $1/T_m$, E and $\ln A$ were obtained from the slope and intercept of the line. The results are listed in Table I. From the results, it can be seen that the reaction activation energy decreases with the BPFER content increasing. This indicates that the reaction rate is enhanced with BPFER content rising, and the reaction is catalyzed by hydrogen in the B—OH of BPFER.

Thermal Property and the Curing Reaction Process

The properties of the final curing product were reported to be affected by its molecular structure, which, in turn, reflects the properties of the product. The glass transition temperature (T_g) is one of the most important parameters, determining its physical state and influencing other properties. Generally, the T_g of a crosslinked system is related to the conversion of reactioning groups^{7,8}; whereas, the degree of conversion depends upon such curing conditions as temperature, time, and curing agent content. Therefore, with these curing conditions varying, the T_g of the system will vary. By monitoring the difference in T_g s of the partially cured sample, the thermal properties of the material will be indicated, and the curing process will be better understood.

According to the literature,⁹ it is necessary to measure the T_g values for the BPAER–BPFER

Table I T_m Values ($^{\circ}\text{C}$) and the Kinetic Parameters of Dynamic Curing of BPAER–BPFER

Composition	Heating Rate ($^{\circ}\text{C} \times \text{min}^{-1}$)					E ($\text{kJ} \times \text{mol}^{-1}$)	$A \times 10^7$ (s^{-1})
	2.5	5	7.5	10	12.5		
55 : 45	195.0	206.3	212.6	218.8	223.1	102.9	4.4
65 : 35	199.2	211.0	218.8	223.0	227.2	104.6	5.1
75 : 25	199.9	211.8	218.1	223.7	225.8	110.9	2.6

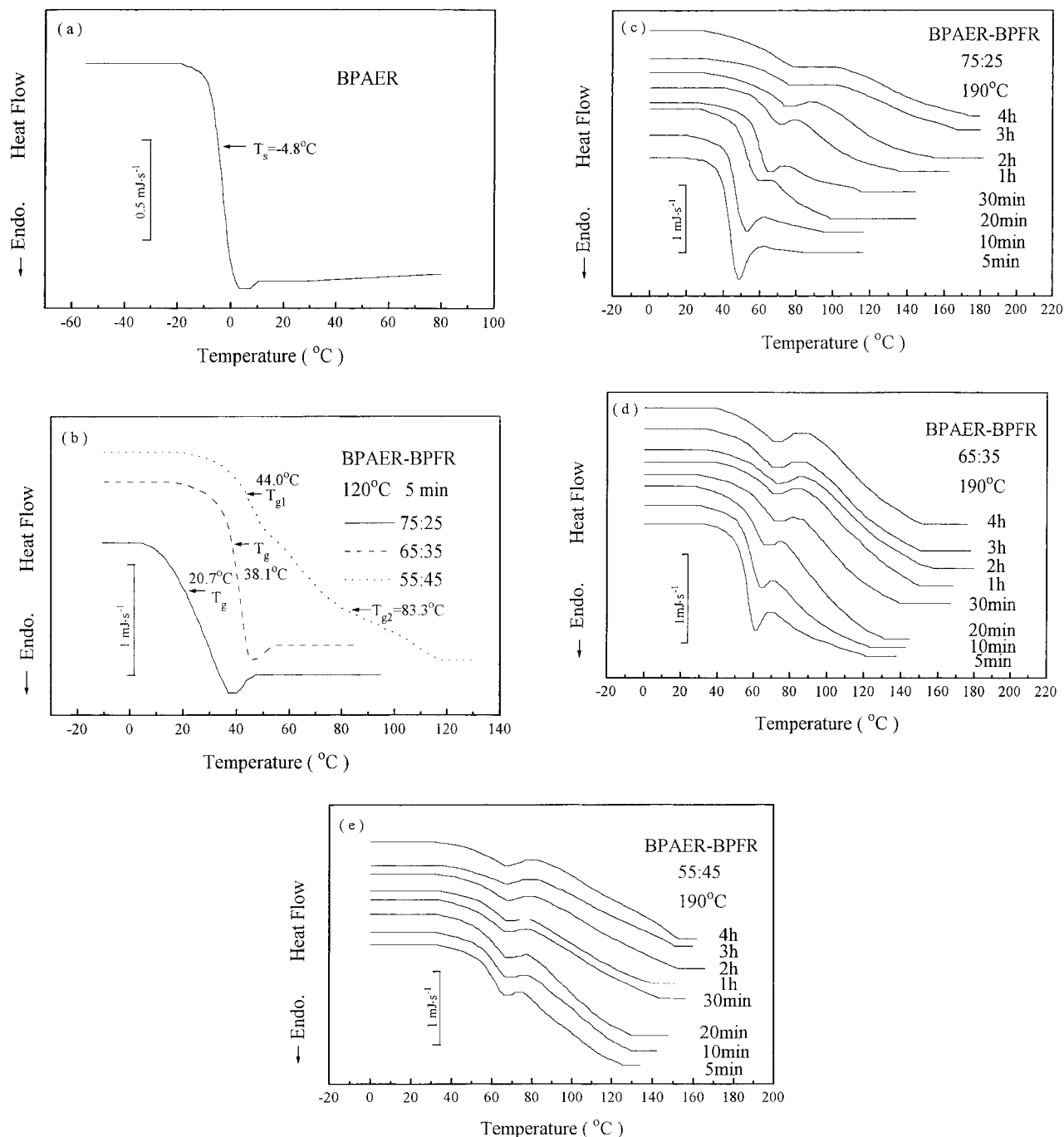


Figure 6 DSC traces of (a) the BPAER, (b, c, d, e) the BPAER-BPFR cured isothermally at different temperatures for various periods.

samples partially cured. In this study, a series of DSC experiments were conducted to determine the T_g s of samples cured isothermally at different temperatures for various periods. Meanwhile, the T_s of the BPAER was also determined. Some DSC curves are shown in Figure 6, and all the T_g , ΔC_p values obtained from DSC measurements are summarized in Tables II, III, IV, respectively.

As shown in Figure 6 and Tables II, III, different glass transition behaviors occur to the samples with different degrees of cure, and the glass transition temperatures are affected by the investigated factors, including temperature, time, and agent content. When cured at low temperature and for a short period of time [e.g., 120°C, 5 min; Fig. 6(b)], 75 : 25, 65 : 35 samples exhibit a single

Table II T_g Values (°C) of the Samples Cured Isothermally at Different Temperatures for Various Periods

Time (min)		5	10	20	30	60	120	180	240
75 : 25	$T_{g1/190^\circ\text{C}}$	39.9	40.3	51.7	56.4	58.8	62.0	65.1	66.1
	$T_{g2/190^\circ\text{C}}$	70.2	79.0	82.7	95.9	108.2	120.1	134.4	139.0
	$T_{g1/200^\circ\text{C}}$	41.1	49.4	56.0	58.0	62.1	63.6	65.7	66.4
	$T_{g2/200^\circ\text{C}}$	84.0	85.6	92.3	102.4	118.5	137.1	140.1	141.3
65 : 35	$T_{g1/190^\circ\text{C}}$	52.3	53.9	55.3	58.5	58.5	59.6	56.9	59.0
	$T_{g2/190^\circ\text{C}}$	96.3	97.5	108.1	112.8	118.4	122.6	119.0	120.8
	$T_{g1/200^\circ\text{C}}$	52.2	57.0	58.2	57.7	59.1	58.4	58.0	57.2
	$T_{g2/200^\circ\text{C}}$	94.9	106.5	110.1	114.7	127.7	121.6	132.4	122.2
55 : 45	$T_{g1/190^\circ\text{C}}$	54.4	54.3	53.5	55.4	53.6	53.2	53.4	54.1
	$T_{g2/190^\circ\text{C}}$	101.0	103.7	106.1	110.8	109.8	117.2	111.6	118.3
	$T_{g1/200^\circ\text{C}}$	52.4	53.0	52.8	53.2	54.4	52.0	53.0	53.6
	$T_{g2/200^\circ\text{C}}$	89.3	105.9	112.5	117.4	120.8	117.6	116.9	118.0

glass transition process; whereas, the 55 : 45 ratio of BPAER : BPFR shows two processes that are not apparently separated in the DSC curve. With the curing temperature and time rising, the two glass transition processes obviously can be separated in the related DSC curves, and the two T_g s are gradually enhanced [Fig. 6(c, d, e)].

Based on the above experimental phenomena and taking into account the characters of the reactive groups in the molecules of BPAER and BPFR, the following curing process is proposed.

At the beginning of the curing reaction process, the hydroxymethyl in the BPFR first reacts with the epoxide group in BPAER, which results in the crosslinking between the molecules of BPFR and BPAER and decreases the mobility of the molecular chains. As a result, the sample gives one significant glass transition process in the DSC curve [Fig. 6(b)], and the T_g is higher than T_s [-4.8°C , Fig. 6(a)] of the BPAER.

With the curing reaction proceeding, the crosslinking density is increased, which reduces the chance of collision between the molecules of BPFR and BPAER. For this reason, the self-

crosslinking reaction is more likely to occur between the molecules of BPFR (Fig. 5), which results in crosslinking and further decreases the mobility of the molecular chains in the system. Therefore, in addition to the first glass transition process, the other one can be seen in the DSC curves [Fig. 6(c, d, e)].

With the reaction temperature and time rising, the crosslinking density further increases, and both T_{g1} and T_{g2} are enhanced [Tables II, III, Fig. 6(c, d, e)]. Correspondingly, the chance for unreacted molecules to collide with each other is seriously reduced. Finally, the curing process cannot proceed further, and the network is completely formed.

According to the above reaction process, it is confirmed that different structures exist in the final network of the BPAER–BPFR. The two T_g s are a reflection of the network structure.

Of course, it should be noted that the influence of the composition of BPAER and BPFR on the reaction can also be seen from the T_g variation. As shown in Figure 6(c, d, e) and Tables II, III, at a given temperature and time, with the composi-

Table III T_g Values (°C) of the Samples Cured Isothermally at Different Temperatures for 5 min

Temperature (°C)		120	160	170	180
55 : 45	T_{g1}	44.0	52.5	51.7	48.7
	T_{g2}	83.3	89.3	90.3	91.7
65 : 35	T_{g1}	38.1	45.9	47.3	45.5
	T_{g2}	—	71.3	72.3	72.6
75 : 25	T_{g1}	20.7	34.9	38.8	37.4
	T_{g2}	—	—	58.8	63.2

Table IV ΔC_p Values ($\text{J} \times \text{g}^{-1} \times \text{K}^{-1}$) of the Samples Cured Isothermally at Different Temperatures for Various Periods

Time (min)		5	10	20	30	60	120	180	240
75 : 25	$\Delta C_{P1/190^\circ\text{C}}$	0.287	0.267	0.185	0.218	0.170	0.158	0.126	0.106
	$\Delta C_{P2/190^\circ\text{C}}$	0.012	0.035	0.120	0.092	0.166	0.172	0.146	0.154
	$\Delta C_{P1/200^\circ\text{C}}$	0.274	0.269	0.206	0.125	0.103	0.112	0.102	0.085
65 : 35	$\Delta C_{P2/200^\circ\text{C}}$	0.022	0.055	0.069	0.165	0.193	0.185	0.188	0.192
	$\Delta C_{P1/190^\circ\text{C}}$	0.198	0.176	0.163	0.088	0.075	0.063	0.086	0.058
	$\Delta C_{P2/190^\circ\text{C}}$	0.103	0.150	0.174	0.206	0.193	0.197	0.185	0.192
	$\Delta C_{P1/200^\circ\text{C}}$	0.198	0.131	0.124	0.110	0.112	0.147	0.132	0.141
55 : 45	$\Delta C_{P2/200^\circ\text{C}}$	0.112	0.178	0.211	0.213	0.219	0.229	0.235	0.229
	$\Delta C_{P1/190^\circ\text{C}}$	0.113	0.104	0.098	0.093	0.105	0.105	0.069	0.075
	$\Delta C_{P2/190^\circ\text{C}}$	0.188	0.196	0.188	0.207	0.208	0.227	0.209	0.201
	$\Delta C_{P1/200^\circ\text{C}}$	0.145	0.122	0.080	0.105	0.087	0.090	0.106	0.103
	$\Delta C_{P2/200^\circ\text{C}}$	0.152	0.239	0.237	0.228	0.237	0.259	0.256	0.247

tion varying, the difference in the T_g s for different systems can be seen. With the BPFR content increasing, both T_{g1} and T_{g2} decrease for the samples with higher conversion. In addition, the results in Figure 6(b) show that the curing reaction proceeds much more rapidly in the system with more BPFR.

In addition, the following phenomena should be noted from Table IV: with the degree of cure increasing, ΔC_{p1} generally decreases, and ΔC_{p2} increases; however, the total heat capacity change ($\Delta C_p = C_{p1} + \Delta C_{p2}$) of the sample accompanying the glass transition process is almost a constant. It is shown that the entropy of the system is almost constant during the reaction.

CONCLUSIONS

1. The curing kinetic behavior of the BPAER-BPFR, studied using the isothermal DSC, shows that the curing reaction follows autocatalytic kinetics. Dynamic DSC shows that there is a dehydrating endotherm peak before the beginning of curing process. In isothermal and dynamic DSC curing processes, the reaction rate is enhanced with BPFR content rising.
2. The curing reaction process and the thermal properties of the BPAER-BPFR are

illustrated by monitoring the difference in T_g s of the partially cured samples. The results show that the network is formed via different stages according to the sequence reactions of different reaction groups. With the BPFR content increasing, both T_{g1} and T_{g2} decrease for the samples with higher conversion. The total heat capacity change ($\Delta C_p = C_{p1} + \Delta C_{p2}$) of the sample accompanying the glass transition process is almost constant.

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