Curing Kinetics, Thermal Property, and Stability of Tetrabromo-bisphenol-A Epoxy Resin with 4,4′-Diaminodiphenyl Ether

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ABSTRACT: The curing reaction of tetrabromo-bisphenol-A epoxy resin (TBBPAER) with 4,4′-diaminodiphenyl ether (DDE) was studied by isothermal differential scanning calorimetry (DSC) in the temperature range of 110–140°C. The results show that the isothermal cure reaction of TBBPAER–DDE in the kinetic control stage is autocatalytic in nature and does not follow simple nth-order kinetics. The autocatalytic behavior was well described by the Kamal equation. Kinetic parameters, including 2 rate constants, k_1 and k_2, and 2 reaction orders, m and n, were derived. The activation energies for these rate constants were 83.32 and 37.07 kJ/mol, respectively. The sum of the reaction orders is around 3. The glass transition temperatures (T_gs) were measured for the TBBPAER–DDE samples cured partially in isothermal temperature. With the degree of cure varies, different glass transition behaviors were observed. By monitoring the variation in these T_gs, it is illustrated that the network of the system is formed via different stages according to the sequence reactions of primary and second amines with epoxides. It is due to the presence of the 4 bromine atoms in the structure of TBBPAER that this curing process can be clearly observed in DSC curves. The thermal stability of this system studied by differential thermal analysis–thermogravimetric analysis illustrates that the TBBPAER–DDE material can automatically debrominate and takes the effect of flame retarding when the temperature reaches 238.5°C. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 70: 1991–2000, 1998

Key words: tetrabromo-bisphenol-A epoxy resins; curing kinetics; aromatic amine; glass transition temperature; thermal stability; differential scanning calorimetry

INTRODUCTION

It is well known that epoxy resins are important adhesives and composite matrix materials. An accurate description of the curing kinetics and the properties of these materials is the most important aspect of the practical model and fundamental theory. The mechanism and kinetics of the curing reaction about different epoxy resins have been studied by many researchers. In the modeling of industrial processing, the curing kinetics, curing rate at various temperatures, and reaction activation energy are usually required. These kinetic data in dynamic and isothermal conditions provide us the knowledge of the mechanism of curing reactions. Moreover, the glass transition temperatures of these materials can be used to illustrate the thermal property and the curing reaction process. The thermal stability of these thermosetting polymers can guide us to properly select the practical model condition. And all these parameters and properties can be determined by different methods.

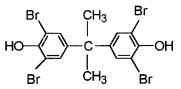Tetrabromo-bisphenol-A epoxy resin (TBB-PAER) is a novel epoxy resin with the flame-

retarding function,[1] and it has been gained use in the electronic industries. But the studies on the fundamental theory about TBBPAER application have been lacking until now. In order to provide a basis for the theory about curing process and properties for the application of TBBPAER, it is necessary to conduct the research in the curing kinetics and properties of TBBPAER–aromatic amines.

In this article, curing kinetics and properties of TBBPAER with 4,4′-diaminodiphenyl ether (DDE) was studied. Structure changes of TBBPAER–DDE during curing process were investigated by infrared (IR) analysis. The mechanism and kinetics of these curing reactions were studied by isothermal differential scanning calorimetry (DSC). The kinetic data were evaluated. Moreover, the glass transition temperatures (T_gs) were measured for the TBBPAER–DDE samples cured isothermally at different temperatures for various periods and by monitoring the difference in these T_g values, the thermal property and the curing reaction process was illustrated. In addition, the thermal stability of the material was also investigated by differential thermal analysis–thermogravimetric analysis (DTA–TGA).

EXPERIMENTAL

Materials

Tetrabromo-bisphenol-A (TBBPA), having the following form

was purified by recrystallized in toluene, and its mp is 180°C. TBBPAER was synthesized according to Rainer et al.,[2] and its molecular structure has the following approximate form:

where, $n = 0$–1. The equivalent epoxy molecular weight of TBBPAER is 500 g/eq (that is, 0.20 mol/100 g), which was determined by the hydrochloric acid–acetone method. Curing agent, DDE, is analytical reagent, with an equivalent amine hydrogen molecular weight of 50 g/eq. The TBB-PAER–DDE samples were prepared with a stoichiometric ratio of one epoxy group with one amine hydrogen, and they were mixed uniformly. Trichloromethane and acetone (analytical reagent) were used as solvent.

IR Measurements

During the isothermal curing, a Hitachi 260-50 IR spectrophotometer was used for the investigation of the structure changes of the TBBPAER–DDE. The desired sample was dissolved in trichloromethane, then coated it into a thin film on a potassium bromide plate. When the solvent in the film was completely evaporated in vacuum, the potassium bromide plate was first scanned by the IR instrument. Thereafter, the plate was placed in a heated oven with a fixed temperature of 90°C. During the curing reaction at this temperature, the plate was repeatedly withdrawn at a regular time interval for analysis.

DSC Measurements

Curing studies on the TBBPAER–DDE isothermal condition was carried out by a Shimadzu DSC-41 differential scanning calorimeter operating in a nitrogen atmosphere. The DSC instrument was calibrated by the indium standards. α-AL_2O_3 was used as the reference material.

About 10 mg of this mixture was placed in a sealed aluminum sample cell. Isothermal analysis was performed at temperature ranging from 110 to 140°C in 5°C increments. Prior to 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 equilibrium state, the sample 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/min to 260°C in order 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), as a function of the degree of cure and curing temperature, was measured with DSC. According to the operation procedure mentioned above, a series of samples with the same weight (10 mg) were cured

in DSC-41 at isothermal curing temperatures from 120 to 180°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/min 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 TBBPAER was also measured in DSC-41 at the same heating rate and determined as the T_g.

DTA–TGA Measurements

Simultaneous differential thermal analysis–thermogravimetric analysis (DTA–TGA) of the cured sample was determined in a static air atmosphere by using a Shimadzu DTC-40 analyzer. About 10 mg of the sample, which had been completely cured, was put in a platinum cell and placed on the detector plate, then the furnace was heated at 2°C/min.

RESULTS AND DISCUSSION

Structure Changes
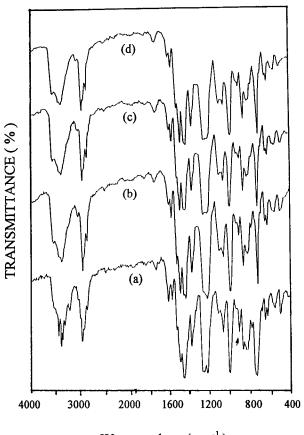
The IR spectrum of TBBPAER–DDE detected by an IR spectrometer are shown in Figure 1. The most significant feature is the appearance of the epoxide group absorption (marked by an arrow). It is observed that the absorption peak of the epoxide group at 910 cm^{-1} gradually decreases with the time increasing. After the curing time increases to 135 min, the absorption becomes a tiny peak. In addition, the IR absorption in carbonyl region is almost no change.

Kinetic Models

During the curing reaction of the thermosetting resins, the heat evolution recorded by DSC is proportional to the extent of consumption of the epoxide group in the epoxy resin or the reactive group in the curing agent;[3,4] namely, the heat is proportional to the extent of the reaction.[5] According to this assumption, curing kinetics was studied, and the kinetics data were determined.[6,7]

On modeling the kinetics, the expression for the reaction rate as a function of the temperature is

$$\frac{d\alpha}{dt} = \mathrm{k}(T)f(\alpha) \qquad (1)$$

Figure 1 The IR spectrum of TBBPAER–DDE at (a) room temperature and after curing at 90°C for (b) 60, (c) 90, and (d) 135 min.

where α is the extent of the reaction, k(T) is the rate constant at temperature T, and $f(\alpha)$ is the function of α, which represents the reaction mechanism.
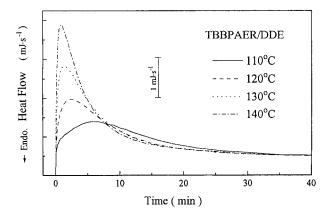
The rate constant k(T) generally takes the Arrhenius equation form, as follows:

$$\mathrm{k}(T) = A \, \exp(-\frac{E}{RT}) \qquad (2)$$

where all parameters have usual Arrhenius significance, and T is the absolute temperature.

The nth-order and autocatalytic are the 2 general categories that can describe most thermoset curing mechanism.[8] The nth-order and autocatalytic kinetics can be expressed as follows. Nth-order kinetics:

$$\frac{d\alpha}{dt} = \mathrm{k}(T)(1 - \alpha)^n \qquad (3)$$

Figure 2 Isothermal DSC curves for the curing of TBBPAER–DDE at different temperatures.

Autocatalytic kinetics (Kamal equation[9]):

$$\frac{d\alpha}{dt} = (k_1 + k_2\alpha^m)(1 - \alpha)^n \qquad (4)$$

where α is the fraction of epoxide reacted at time t, and m and n are the reaction orders, k_1 and k_2, are reaction rate constants with 2 different activation energies and preexponential factors. The 2 models are classified by different characters. Systems obeying nth-order kinetics will obviously have the maximum reaction rate at $t = 0$, while systems obeying autocatalytic kinetics will attain a maximum value at some intermediate conversion ($\alpha = 0.3 \sim 0.4$).

If the total heat of reaction for completing cure is ΔH_0, then the extent of reaction and the reaction rate at any time during an experiment can be described by

$$\alpha = \frac{\Delta H_t}{\Delta H_0} \qquad (5)$$

$$\frac{d\alpha}{dt} = \frac{1}{\Delta H_0} \times \frac{dH}{dt} \qquad (6)$$

where ΔH_t is the partial heat of reaction at time t, ΔH_0 is the total heat of reaction, and $\frac{dH}{dt}$ is the flow rate of heat.

Parameters Determination

The isothermal curves of TBBPAER–DDE are shown in Figure 2. The heat evolution of the curing reaction of TBBPAER–DDE was recorded as a function of reaction time, and the average value of the total heat of TBBPAER–DDE developed during the isothermal DSC tests was 98.79 J/g^{-1}.

Figure 3 shows the plots of the curing reaction rate $d\alpha/dt$ versus conversion α at different temperatures. It is seen that the reaction rate is affected by the iso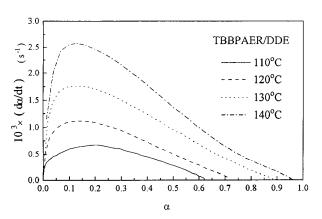thermal curing temperature and the conversion. At a given temperature, the reaction rate is observed to increase with conversion initially and pass through a maximum, and then gradually slow down, finally tending to zero at certain degree of conversion. Additionally, at a given conversion, a higher isothermal curing temperature gains a higher reaction rate. Moreover, the higher the isothermal temperature, the higher the final degree of conversion.

Of course, it would be also observed that the final degree of conversion at 140°C is quite high; consequently, it may be confirmed that the system is close to complete cure. However, it should be noticed that a relative scale of degree of cure has been used in the calculation of α and $d\alpha/dt$. Defined in equations (5) and (6), the α and $d\alpha/dt$ are from the heat of reaction values measured by DSC. But the total reaction heat does not mean that the crosslinking reaction is complete; this is only part heat, which can be detected by DSC. In fact, it is not possible to obtain the whole reaction heat, which is generated by consuming all the reactive functions, for the sensitivity of the apparatus is limited and little change in heat cannot be detected, especially in high conversion.[10,11] When the curing reaction proceeds very slowly, no further sign of reaction can be seen in the traces of DSC. Nevertheless, little heat may be still evolving. Therefore, it may be possible that the data of α and $d\alpha/dt$ calculated from equations (5)

Figure 3 The plots of the curing reaction rate $d\alpha/dt$ versus conversion α at different temperatures.

Table I   Values of *m* and *n* Estimated at Different Temperatures

Temperature (°C)	m	n
110	0.65	2.14
115	0.54	2.92
120	0.5	2.75
125	0.48	2.97
130	0.43	2.51
135	0.40	2.35
140	0.51	2.49

and (6) are some higher than the real values. Additionally, when the curing temperature is set above 140°C, the value of the total reaction heat measured by DSC tends to decrease since part of the heat is lost during the stabilization time of the DSC. So it is difficult to establish the curing kinetics at high temperature, and the ultimate isothermal curing temperature in the study was not over 140°C.

Based on the above experimental phenomenon and not considering individual reactions in the curing process, the phenomenological approach is used to identify a kinetic model to describe the kinetic reaction. As already stated, 2 different models have been used in the literature for the expression of kinetic reaction. Therefore, in order to deduce the kinetics model, a common simple approach is used. First, the experimental phenomenon is compared with the features of the 2 models, and then an appropriate kinetics model is chosen to test the experimental data, and the parameters of the model are determined. At last, by comparing the model results with the experimental data, the applicability of the model is illustrated.

Correspondingly, the characters of the curing reaction was first examined in the study. Figure 3 shows that the reaction rate of the system reaches a maximum at time $t > 0$, and the maximum rate is observed at the conversion of $\alpha = 0.1-0.2$, which is characteristic of a autocatalytic reaction, so the autocatalytic kinetics model is appropriate to describe the isothermal curing behavior of the system. In this article, equation (4) was employed to test the experimental data.

According to the literature,[12,13] to compute the four parameters, k_1, k_2, m, and n, in equation (4) from experimental data, the nonlinear regression technique was used. The values of m and n obtained for each curing temperature are shown in

Table I. The overall reaction order $m + n$, is around 3, with the average value $m = 0.49$ and $n = 2.55$, respectively. Rate constants k_1 and k_2 are shown as an Arrhenius plot in Figure 4, which yield the values of 83.32 and 37.07 kJ/mol for the associated activation energies.

In an ideal condition, a successful model should describe well the experimental data throughout the whole range of cure. But in this work, it is should be indicated that the effect of the diffusion and the etherification reaction was not taken into account in the kinetic model. In order to demonstrate the curing behavior described by the Kamal equation, it is necessary to compare the model prediction results with the experimental data. Figure 5 shows that the model curves of $d\alpha/dt$ versus α at different temperatures fit the experimental data quite well in the early stage of the curing reaction. However, deviations are observed in the later stage, which is attributed to the effect of diffusion.

According to this idea and in view of the relationship between $d\alpha/dt$ and α, as many other epoxy resins curing reactions reported, kinetic control stage and diffusion control stage are the 2 stages in the curing process of TBBPAER–DDE system. In the early stage, the curing reaction is controlled by chemical kinetics and the reaction rate increases with rising time. The kinetic behavior described by the kinetics model coincides with the experimental data. Whereas in the later stage, the chemical kinetics cannot be satisfactorily represent the experimental data, and the system becomes controlled mainly by diffusion. Correspondingly, the reaction rate decreases gradually with rising time, and the experimental data
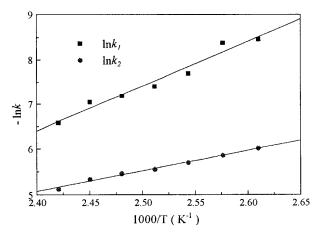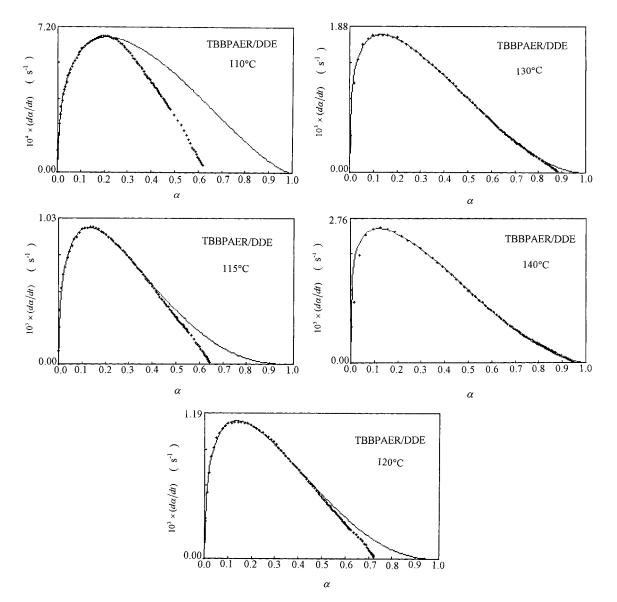

Figure 4   Arrhenius plots of rate constants k_1 and k_2 for different temperatures.
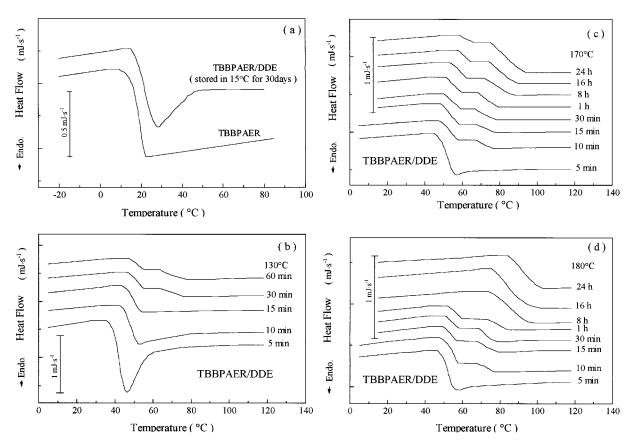
Figure 5   Comparison of experimental data (x symbols) with the kinetic model results (dots) for TBBPAER–DDE at different temperatures.

no longer fit the kinetic model. So the kinetic model does not provide a good description for the slowly reaction stage.

As a result of comparison, the influences of diffusion on the curing reaction are apparently observed in the low curing temperatures (for example, curing at 110°C; Fig. 5). With an increase in the curing temperature, the effect of the diffusion tends to decrease and becomes indistinct at 140°C. This may be associated with the T_g of the fully cured material. If the curing temperature is in the vicinity of the glass transition region (that is, 84–103.4°C, obtained by a second DSC scan after cured at 180°C for 24 h; Fig. 6) of the highly

cured material, the free volume is reduced, and the segmental mobility within the polymer decreases, thus reducing the rate of diffusion of molecular to reactive sites, which, in turn, reduces the reaction rate.[10,14] So it is evidently observed that the reaction rate is seriously affected by the diffusion when curing at 110°C. On the other hand, as the curing temperature increases, the thermal energy provides sufficient molecular mobility to recommence the curing process,[15] causing an increase in the reaction rate (for example, curing at 115°C; Fig. 5). If the curing temperature is above the T_g of the fully cured material, the effect of the diffusion on the reaction

Figure 6 DSC traces (a), (b), (c), and (d) of the TBBPAER and the TBBPAER–DDE cured isothermally at different temperatures for various periods.

reduces.[10] Therefore, the higher the curing temperature over the T_g, the higher the degree of cure at the onset of diffusion control (Fig. 5). As a result, at a high temperature (for example, 140°C), the final degree of cure appears to be quite high.

Thermal Property and the Curing Reaction Process

It is generally accepted that the thermal property of the polymer material is affected by its T_g, and there is a one-to-one relationship between the T_g and the degree of cure. Therefore, by monitoring the difference in T_gs of the partially cured samples, the thermal property of the material will be indicated, and the formation process of the network will be deduced.

Based on the above viewpoint, the T_g values were measured for the TBBPAER–DDE samples cured isothermally at different temperatures for various periods. The T_s of the TBBPAER was also determined, and the transition process is similar as a glass transition in the DSC curve. As a re-

sult, some DSC curves measured in the second scan are shown in Figure 6, and all the T_g values obtained from DSC measurements are summarized in Tables II and III. Figure 7 shows how to determine the glass transition temperature (T_g) and the heat capacity (ΔC_p) change.

As shown in Figure 6 and Tables II and III, different glass transition behaviors occurred for the samples with different degrees of cure. When the degree of cure is lower, the sample exhibits a single glass transition process, which is above the T_s (16°C) of TBBPAER. When the degree of cure reaches a higher value, the sample exhibits the following 2 glass transition processes: T_{g1} is observed at above 48°C, and T_{g2} is located in above 68°C. Normally, at a given temperature, with the time increasing, the sample gives the 2 higher T_g values; and within a given time, with the isothermal curing temperature rising, the sample also gives the 2 higher T_g values. However, after the degree of cure surpasses a specific value, the first glass transition disappears, and only does the

Table II T_g **Values (°C) of the Samples Cured Isothermally at Different Temperatures for Various Periods within 60 Min**

Time (min)	5	10	15	30	60
$T_{g1/120°C}$	40.2	46.6	50.2	50.3	49.7
$T_{g2/120°C}$	—	—	—	—	68.7
$T_{g1/130°C}$	40.8	47.2	48.8	50.7	51.7
$T_{g2/130°C}$	—	—	—	69.4	70.6
$T_{g1/140°C}$	44.2	48	48.2	50.0	51.0
$T_{g2/140°C}$	—	—	68.2	72.8	74.0
$T_{g1/150°C}$	46.5	49.1	50.2	52.0	51.7
$T_{g2/150°C}$	—	—	68.0	71.8	73.0
$T_{g1/160°C}$	50.7	50.4	55.7	54.1	53.0
$T_{g2/160°C}$	—	—	74.5	73.0	72.9
$T_{g1/170°C}$	50.6	52.6	53.4	54.7	55.5
$T_{g2/170°C}$	—	72.1	73.1	72.6	74.2
$T_{g1/180°C}$	51.7	54.5	55.2	53.2	55.7
$T_{g2/180°C}$	—	72.6	73.3	74.3	77.8

second one exist. Subsequently, the value of T_{g2} is observed to continue to increase with the rise in curing time. Moreover, accompanying the variation in T_gs, ΔC_p is continuously changing. These experimental results reflect the variation in the reaction during the network formation process.

In theory, the difference in T_gs of the partially cured samples is essentially the reflection of the different structures, and ΔC_p reflects the changes in the entropy of the system. Therefore, by monitoring the difference in T_gs and tracing the variation of the ΔC_p associated with the transition, the curing reaction process will be better understanding.

In general, the epoxide groups can react with primary and secondary amines, and it is recognized that the addition occurs mainly in 2 stages in the reaction between epoxides and amines.[10,14,16] Based on this assumption and taking into account both of the difference in T_gs and the variation in ΔC_p of the partially cured samples, the following
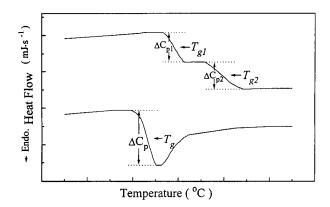
Table III T_g **Values (°C) of the Samples Cured Isothermally at 170 and 180°C for Various Periods from 8 to 24 h**

Time (h)	8	16	24
$T_{g1/170°C}$	57.8	60.6	62.6
$T_{g2/170°C}$	77.3	81.3	84.7
$T_{g1/180°C}$	—	—	—
$T_{g2/180°C}$	86.4	88.2	93.9

curing reaction process for TBBPAER–DDE system is proposed.

At the beginning of the curing reaction process, only primary amines are contained in the system, so primary amines in DDE first react with epoxide groups in TBBPAER, and small linear moleculars are formed. This process is characterized by a gradual increase in molecular weight. At this stage, the degree of cure is low, and the sample gives 1 significant glass transition process in the DSC curve (Fig. 6). The extent of the ΔC_p in the transition process shows that the movable chain segment is long, and there is more free volume for them to move. So in this stage, only the primary amines are in reaction, and the secondary amines do not get the chance. Certainly, this transition behavior is the reflection of the movement of the linear molecular chain in the system. With the molecular weight increases, T_g increases while ΔC_p decreases; this is ascribed to the decreasing configurational entropy.[17] Since only linear molecular chains exist in this stage, there are many chances for the moleculars to collide, and this results in a high reaction rate.

With the reaction of primary amines proceeding, some secondary amines gradually gain the chance to react with epoxide groups. As a result, crosslinking has occurred, and the weight-average molecular weight increases. Meanwhile, besides the first glass transition process, the sample gives another glass transition process in the DSC curve (Fig. 6), suggesting that different structures exist in the system. Naturally, the second transition behavior is the reflection of the movement of the crosslinked molecular chain segment, whereas the first one is still the result of the movement of the linear chain segment. With the increase of the crosslink points, the linear chain
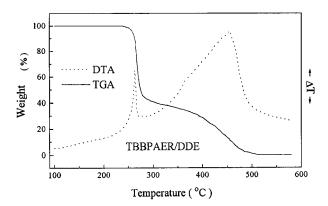

Figure 7 Determination of the glass transition temperature (T_g) and heat capacity (ΔC_p).

segment within the system tends to reduce relatively, and its mobility is restricted by the crosslinked chain. Consequently, both T_{g1} and T_{g2} are enhanced, and ΔC_{p2} gradually increases, while ΔC_{p1} continues to decrease. In addition, viewing the movement of all the chains in the system, the mobility of the chain is decreased, and the chances for the moleculars to collide with each other is reduced. Therefore, the reaction rate decreases.

With the reaction time rising, the crosslinking density further increases, and the unreacted epoxide groups in the linear chain segment get a chance to react with secondary amines. Subsequently, only the second glass transition process can be seen in the DSC curve (Fig. 6), indicating that the linear segment may be absent within the system and that the structure is almost a network. So only T_{g2} is the T_g of the network. Consequently, with a rise in the curing time, the T_g of the network is enhanced with a decrease in the distance between crosslink points. Correspondingly, there is some variation in ΔC_p. Finally, the increasing crosslinking density makes the intramolecular reaction not to proceed any longer. At this time, the sample has been highly cured.

As a matter of fact, it is attributed to the presence of the 4 bromine atoms in the structure of TBBPAER that the 2 glass transition processes can be clearly observed during the second DSC scans for the partially cured TBBPAER–DDE samples. First, in the presence of the 4 bromine atomes in the system, the 2 structures, linear and crosslink chain segments, may exhibit significant difference in the thermal property. As a reflection, 2 ΔC_ps are distinctly showed in the DSC curves during the second scans for the samples with some intermediate degree of cure, and 1 ΔC_p can be observed for the samples with a lower or higher degree of cure, respectively. Second, the 4 bromine atoms occupied a larger space in the structure of TBBPAER, and this enhances the steric hindrance in the attack from the amines to epoxied groups, especially for the secondary. Therefore, the reaction in the later stage proceeds slowly. As a result, the difference in the onset of the sequence reactions of the primary and secondary amines are obviously monitored in the series second DSC scans for the partially cured TBBPAER–DDE samples.

According to the above reaction process, it is clearly affirmed that the previous kinetics analysis only involves the quick reaction stage and does not cover the entire reaction process. So the ki-

Figure 8 DTA–TGA curves for the cured TBBPAER–DDE at the heating rate of 2°C/min.

netic experimental results, which are obtained with the ΔH measurement method by DSC, can only indicate a basic trend for the variation in $d\alpha/dt$ versus α and cannot represent the actual reaction behavior. Different with the ΔH parameter, T_g can be measured more accurately and displays significant changes over the entire range of conversion from the unreacted state up to high conversion.[10]

Thermal Stability

The DTA–TGA thermograms of the cured TBBPAER–DDE are shown in Figure 8. It can be seen that thermal degradation of the cured TBBPAER–DDE occurs in 2 stages. In the first stage, the DTA curve shows a narrow exothermic peak in the 238.5–270°C range. Correspondingly, the TGA curve shows a rapid weight loss process in this region. It corresponds to the process of the debromination, and the weight loss, nearly 58.50%, is as the same as the bromine content in the material. It is attributed to the exothermic change in the bromine radical coupled reaction that the exothermic peak appears in the DTA curve during the process of the debromination. This indicates that the material can automatically debrominate and takes the effect of flame retarding when the temperature reaches 238.5°C.

After undergoing the debromination process, the reaction enters the second reaction stage. In this stage, the DTA curve shows a broad exothermic peak in the 290–520°C range. Correspondingly, the TGA curve shows a slow weight loss process, it represents the oxidation of the residue after the debromination. The weight loss in this step is nearly 41.50%, and this illustrates that all

the residue are oxidated when the temperature reaches 520°C.

CONCLUSIONS

1. The curing kinetic behavior of the TBB-PAER–DDE, studied using the isothermal DSC, shows that the curing reaction in the kinetic control stage follows autocatalytic kinetics and the Kamal equation, which includes 2 reaction orders, m and n, and 2 rate constants, k_1 and k_2, was well described the cure kinetics; whereas in the diffusion control stage, the model results do not fit the experimental data.

2. T_gs were studied for the TBBPAER–DDE samples cured partially; and by monitoring the difference in these T_gs, the curing reaction process and the thermal property of the TBBPAER–DDE are illustrated. The results show that the network is formated via different stages according to the sequence reactions of primary and second amines with epoxide groups. Namely, primary amines first react with epoxide groups in the initial stage, and then secondary amines gradually get the chance to react with epoxides with the reaction proceeding. Subsequently, linear chains disappear gradually, and the network is formed. Finally, secondary amines continue the reaction until stopped. It is due to the presence of the 4 bromine atoms in the structure of TBBPAER that this curing processes can be clearly observed in DSC curves.

3. The thermal stability of the material studied by DTA–TGA illustrates that the TBBPAER–DDE material can automatically debrominate and takes the effect of flame retarding when the temperature reaches 238.5°C.

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