Curing Behavior and Thermal Properties of Trifunctional Epoxy Resin Cured by 4,4′-Diaminodiphenylmethane

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ABSTRACT: A novel trifunctional epoxy resin (TMBPBTH-EPOXY) was synthesized in our laboratory, and its curing behavior and performance were studied by curing with 4,4′-diaminodiphenylmethane (DDM) with the mass ratio of 30 : 100 of TMBPBTH-EPOXY and DDM. The mixtures of TMBPBTH-EPOXY/DDM were cured at 100, 140, and 160°C, respectively. The curing state was kept for different time from 1 to 6 h. The transition reaction of epoxide group during curing process was monitored by Fourier transform infrared spectroscopy. It was found that curing reaction was both dependent on the curing temperature and curing time, and the curing temperature has more effect on the curing reaction than the curing time. The curing activation energy was investigated by differential scanning calorimetry to be 55.13 and 55.10 kJ/mol. The glass transition temperature of TMBPBTH-EPOXY/DDM system was 240.2°C. The thermal decomposition temperature at different temperatures and time were studied by thermogravimetric analyzer. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 114: 1976–1983, 2009

Key words: trifunctional epoxy resin; curing behavior; curing activation energy; glass transition temperature; thermal decomposition temperature

INTRODUCTION

Epoxy resins have been known to possess good mechanical properties and excellent adhesive properties, and thus have been widely used in industry, such as adhesive, coating, laminating, electronic encapsulating materials, and composite applications.[1–6] However, the conventional epoxy resins are inefficient to satisfy the required properties in the field of advanced materials, which require high thermal and flame resistance.[7–9] The properties can be improved by the modification of epoxy backbone, i.e., either during synthesis or cure using agents of different structures.

A new generation of multifunctional epoxy resin (with a level of functionality of 3–5) has a great impact on the market because their properties are better than those of conventional (i.e., bifunctional) epoxy resin.[10] At the same cure level, multifunctional resins have better crosslink densities and glass transition temperatures, providing a considerable increase in their thermal, dynamic, mechanical, and adhesive properties in comparison with their bifunctional predecessors.[11,12] Some multifunctional epoxy resins were reported, for example, novolac epoxy resin,[13] cycloalphatic epoxy resin, tetraglycidyl diamine diphenol methane (TGDDM),[14] and so on, and the structures of some typical epoxy resin are showed in Figure 1. The resin used in this work is a new kind of trifunctional resin synthesized in our laboratory,[15] and it is notable for its excellent thermal resistance with 4,4′-diaminodiphenyl sulfone (DDS) or 4,4′-diaminodiphenylmethane (DDM) as hardener.

The properties and performance of epoxy resins are dependent on the type of epoxy resin, the curing agent, and curing conditions.[16] So the aromatic primary amines are known to impart high glass transition temperature (T_g) to cured resins, such as DDS, DDM, and so on.

The aim of this work is to investigate the curing behavior and thermal stability of the novel TMBPBTH-EPOXY cured with 4,4′-diaminodiphenylmethane (DDM) by Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA), and thermogravimetric analysis (TGA). The FTIR was used to monitor the residual epoxide functional groups during the curing process with the curing temperatures changing from 100 to 160°C, and curing time lasting from 1 to 6 h. DSC was used to investigate the curing kinetics of TMBPBTH-EPOXY/DDM system. DMTA and TGA were used to characterize the glass transition temperature and decomposition temperature of cured materials as a function of cure temperature, respectively.

EXPERIMENTAL

Materials

Epichlorohydrin was supplied by Beijing Chemical Plant (Beijing, China). Quaternary ammonium salt
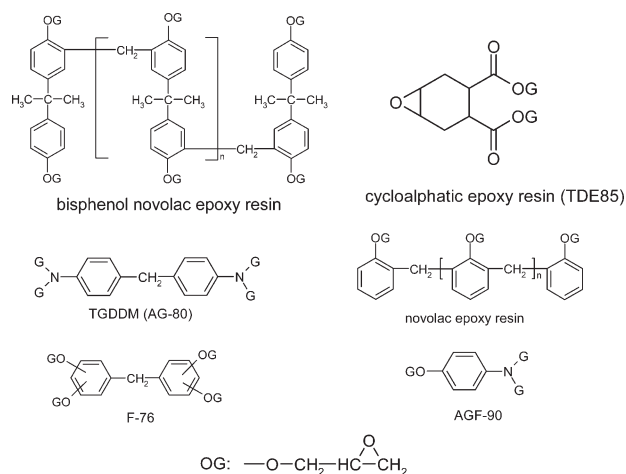

Figure 1 The structures of some typical multifunctional epoxy resins.

was obtained from Tianjin Jinke Fine Chemical Institute (Tianjin, China) used as phase transition catalyst. NaOH was used as analytical reagent supplied by Beijing Chemical Plant. DDM was purchased from Shanghai SSS Reagent and used as curing agent.

Synthesis of trifunctional epoxy resin

4-(3,3-Dihydro-7-hydroxy-2,4,4-trimethyl-2H-1-benzo-pyran-2-yl)-1,3-benzenediol (TMBPBTH) used in the synthesis of trifunctional epoxy resin was prepared in our laboratory with the reaction of resorcinol and acetone in the presence of hydrochloride,[15] and the reaction mechanism is showed in Scheme 1. Figure 2 shows the spectrum of synthesized TMBPBTH (calcd mass 468) measured by the electron spray impaction mass spectroscopy (ESI-MS). Three strong singles were observed at m/z ($[M+NH_4]^+$) = 486.4, ($[M+Na]^+$) = 491.4, and ($[M+K]^+$) = 507.4, respectively, indicating the formation of TMBPBTH-EP-

OXY. The calculated yield of the TMBPBTH reached 99.2% based on the amount of acetone, and its purity was up to 94.35% analyzed by HPLC as showed in Figure 3.

TMBPBTH-EPOXY was synthesized by the reaction of THBPBTH and epichlorohydrin through well-known two-step process with quaternary ammonium salt as catalyst. The epoxide equivalent weight (EEW) of TMBPBTH-EPOXY was 161–164 analyzed by hydrocholoride–acetone method. Accordingly, based on the determined EEW value, TMBPBTH-EPOXY was mixed with DDM at the weight ratio of 100 : 30.

Analysis and measurement

HPLC measurements

An American Waters 600E liquid chromatograph equipped with an inert C18 analytical column was used to determine the purity of synthesized multiphenol. Methanol/water (w/w 60/40) or acetonitrile/water was used as the mobile phase at a constant flow rate of 1.0 mL/min and 10 μL sample. The 220 nm wavenumber of ultra violet detector was selected.

ESI/MS measurements

An American Waters ceuattro premier XE MS ESI-MS was used to determine the ionized molecular weight of TMBPBTH-EPOXY with acetonitrile/water (w/w, 60/40) as mobile phase. The operating conditions for ESI in electrospray ionization mode were as follows: spray voltage, 4500 V; capillary temperature, 350°C; sheath gas (N_2), 80 PSI; auxiliary gas (N_2), 40 mL/min. ESI on the ion trap mass spectrometer were as follows: spray voltage, 5.5–6.6 kV; capillary temperature, 250°C; capillary voltage, 8 V; tube lens
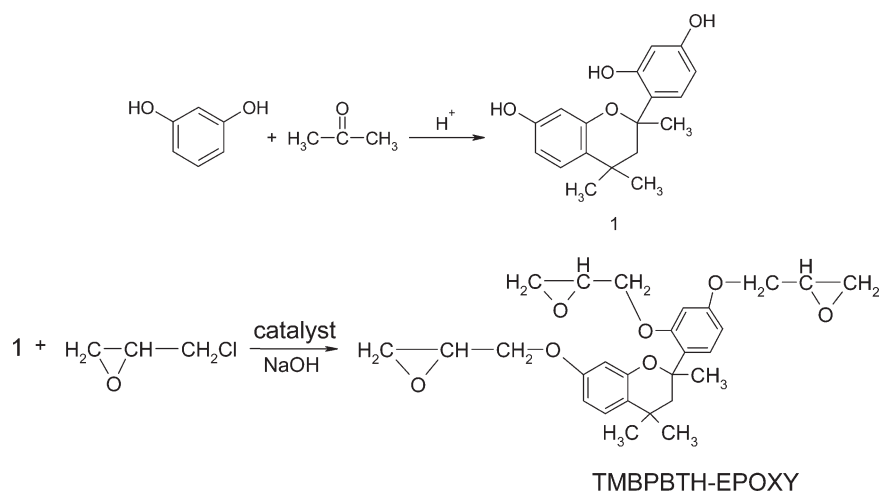
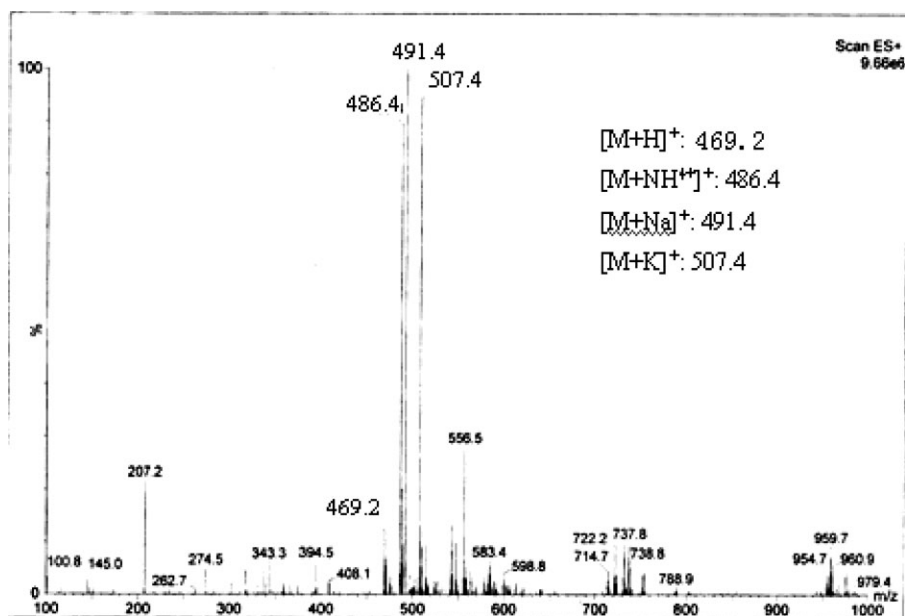**Scheme 1** Reaction mechanism of TMBPBTH and TMBPBTH-EPOXY.

Figure 2 ESI/MS spectrum of TMBPBTH-EPOXY.

offset, 30 V; sheath gas (N_2), 70 PSI; auxiliary gas (N_2), 3 mL/min.

FTIR measurements

A Nicolet Nexus 670 spectrometer was used to monitor the variation of epoxide functional groups of TMBPBTH-EPOXY/DDM system as the function of curing temperature and curing time during the curing process. The sample was made into powder and mixed with potassium bromide, and then it was made as a thin film at room temperature and the resolution was 4 cm^{-1}. The potassium bromide was used as the background.

DSC measurements

A Perkin-Elmer Pyrisl differential scanning calorimeter was used to investigate the curing behavior of TMBPBTH-EPOXY/DDM in nitrogen atmosphere. TMBPBTH-EPOXY/DDM mixtures (about 4.0 mg each) were subjected to DSC scans at heating rates of 5, 10, 15, 20 K/min, respectively.

DMTA measurements

An American Rheometric Scientific DMTA V DMTA was used to determine the T_g of cured TMBPBTH-EPOXY sample. The bending method was used with a frequency of 1 Hz and a strain level of 0.04% in
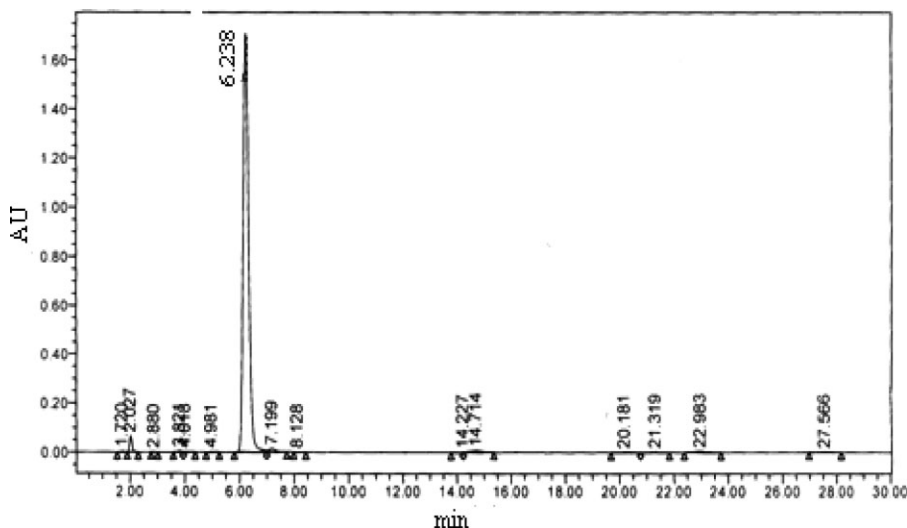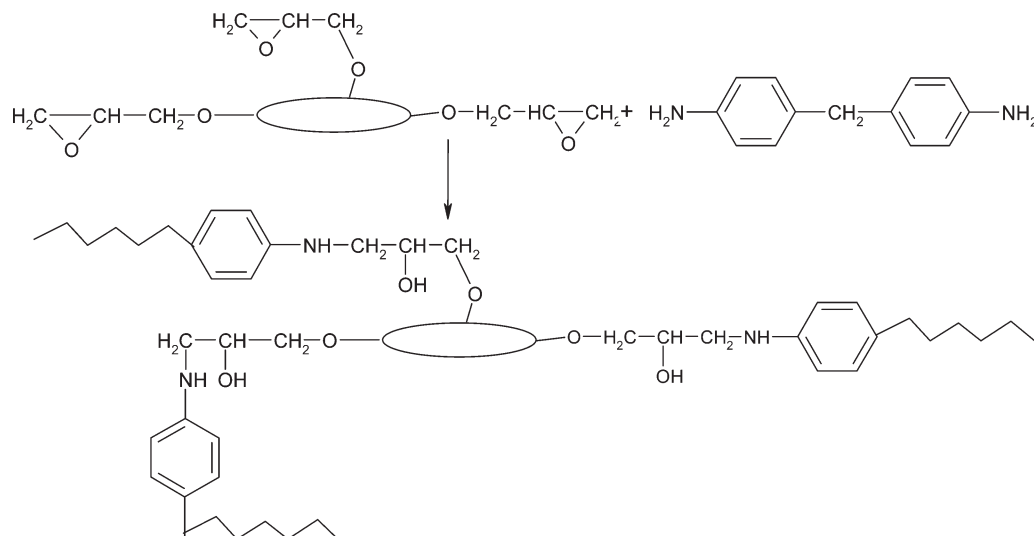

Figure 3 HPLC spectrum of TMBPBTH.

Scheme 2 The curing reaction mechanism of TMBPBTH-EPOXY with DDM.

the temperature range from 20 to 350°C. The heating rate was 5 K/min. The testing was performed by using rectangular bars of approximate $50 \times 8 \times 2$ cm³. The exact dimensions of each specimen were measured before the scanning.

TGA measurements

A German TG209C TGA produced by NetZSCH Company was used to determine the thermal decomposition temperatures of cured materials in dynamic nitrogen atmosphere at heating rate of 20 K/min. The onsets are at about 5% weight loss, and the test specification is from room temperature to 600°C.

RESULTS AND DISCUSSION

FTIR study of curing reaction

The epoxide functional group is the characteristic group in the epoxy resin, and epoxide rings will open under the attack of amine molecule during the curing reaction of epoxy resins by amine curing agent, which will decrease the content of epoxide groups drastically. The curing mechanism of TMBPBTH-EPOXY and DDM is showed in Scheme 2. Thus, FTIR is an effective method to investigate the curing behavior of epoxy resin by determining the change of functional groups before and after curing reactions of epoxy resin. In our experiments, cured compound was powdered and mixed with potassium bromide. Then, FTIR measurement was carried out to investigate the residual epoxide groups after curing reaction under different curing conditions by using KBr film at room temperature with a

resolution of 4 cm⁻¹. The experimental results are showed in Figure 5 and Table I.

Figure 4 presents the FTIR spectra of the TMBPBTH-EPOXY/DDM system during the curing reaction. The assignments of the absorption features are as follows: about 1613, 1581, 1517, and 1502 cm⁻¹ to phenyl group, 1255 cm⁻¹ to the aromatic ether φ—O—C, 1112 and 1031 cm⁻¹ to the deformation of the aromatic CH, 910 cm⁻¹ to epoxide group, 835 cm⁻¹ to the out-of-plane deformation of the aromatic CH.

The structural changes can be identified from Figure 4. After curing at 100°C for 1 h, the relative absorption intensity of epoxide group still remained obviously. And, even if the curing time was increased up to 6 h, the absorption peak at 910 cm⁻¹ hardly decreased [see Fig. 4(a,b)]. When the curing temperature was up to 140°C, the absorption intensity at 910 cm⁻¹ weakened when compared with that cured at 100°C, and 6 h curing time had a little influence on the opening reaction of epoxide ring when compared with 1 h curing [see Fig. 4(c,d)]. Furthermore, when the curing temperature rose to 160°C, the absorption intensity of residual epoxide groups at 910 cm⁻¹ was not clear, especially for the curing time of 6 h [see Fig. 4(e,f)]. The FTIR analysis

TABLE I
The Epoxide Groups Index of TMBPBTH-EPOXY/DDM System

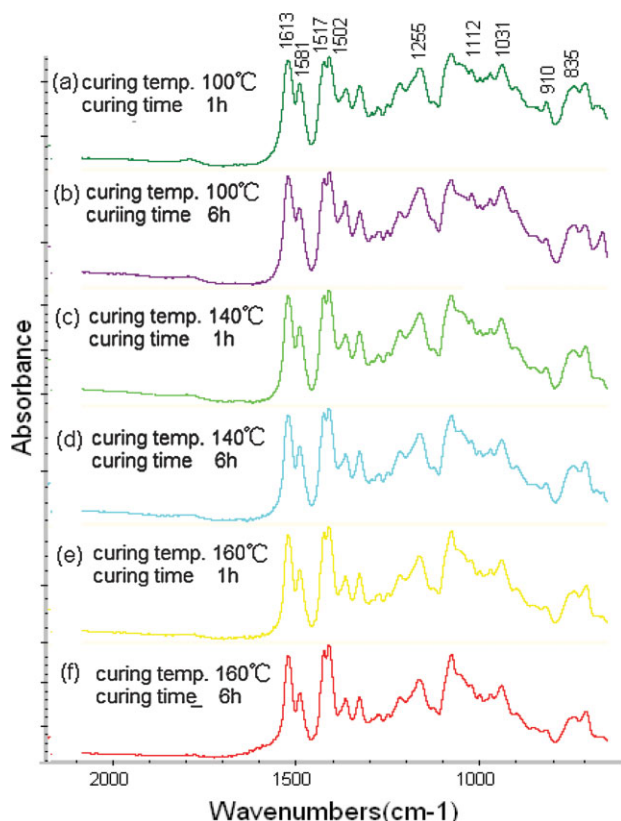| Time (h)	T (°C)		
	100	140	160
1	0.0551 ± 0.0004	0.0401 ± 0.0005	0.0242 ± 0.0005
6	0.0427 ± 0.0007	0.0323 ± 0.0006	0.0179 ± 0.0006

Figure 4 FTIR spectra of the TMBPBTH-EPOXY/DDM system cured at different temperatures. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

results elucidated that curing temperature impacted on the curing reaction more obvious than curing time. To show the changes of residual epoxide group with the curing temperature and curing time, the epoxide group index was calculated by using the absorption intensity of phenyl groups as internal standard and by the following equation:

$$\text{Epoxide group index} = \frac{\text{epoxide group's peak area}}{\text{phenyl group's peak area}}$$
$$= \frac{A_{926-889}}{A_{1670-1548}}$$

The calculated results are showed in Table I.

Curing kinetics

The curing reaction kinetic parameters can be evaluated with a multiple-heating-rate method by determining the exothermic peak temperatures at several heating rates. In practice, two convenient multiple-heating-rate methods are generally used. One is the maximum reaction rate method proposed by Kissinger,[17] which is based on the fact that the exother-

mic peak temperature (T_p) varied with the heating rates. The other is the isoconversion method proposed by Flynn, Wall, and Ozawa,[18,19] which is based on the fact that isoconversion can be reached at different temperatures with various heating rates.

Kissinger's approach assumed that the maximum reaction rate occurred at peak temperatures, where d^2/dt^2 can be expressed as

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) - \frac{E_a}{RT_P} \tag{1}$$

where, β is the linear heating rate (K/min), T_p is he peak temperature (K), A is the pre-exponential factor, E_a is the activation energy, and R is the universal gas constant [$R = 8.314$ kJ/(mol K)]. Therefore, a plot of $\ln(\beta/T_p^2)$ versus $1/T_p$ gives the values of E_a and A.

Flynn-Wall-Ozawa method assumes that the degree of conversation at peak temperatures for different heating rates is constant. It can be expressed as follows:

$$\ln\beta = -\frac{E_a}{ART_p} + C \tag{2}$$

where C is a constant, T_p is the isoconversion temperature, and other parameters are the same as described earlier. By plotting $\log°C$ versus $1/T_p$, the activation energy can be obtained from the slope.

In Figure 5, the heat flow is plotted as a function of the temperature for four different heating rates. It is seen that the exothermic reaction proceed in a wide temperature range, and the maximum rate temperatures of the curing reaction increased with increasing heating rate. The values of activation energy E_a and A of TMBPBTH-EPOXY/DDM systems can be calculated from the slopes of the linear lines in Figure 6,
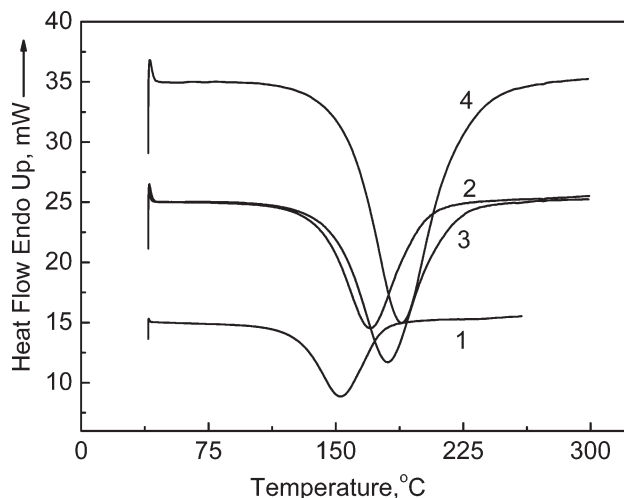

Figure 5 DSC curves of TMBPBTH-EPOXY/DDM. Heating rate: 1, 5K min^{-1}; 2, 10K min^{-1}; 3, 15K min^{-1}; 4, 20K min^{-1}.
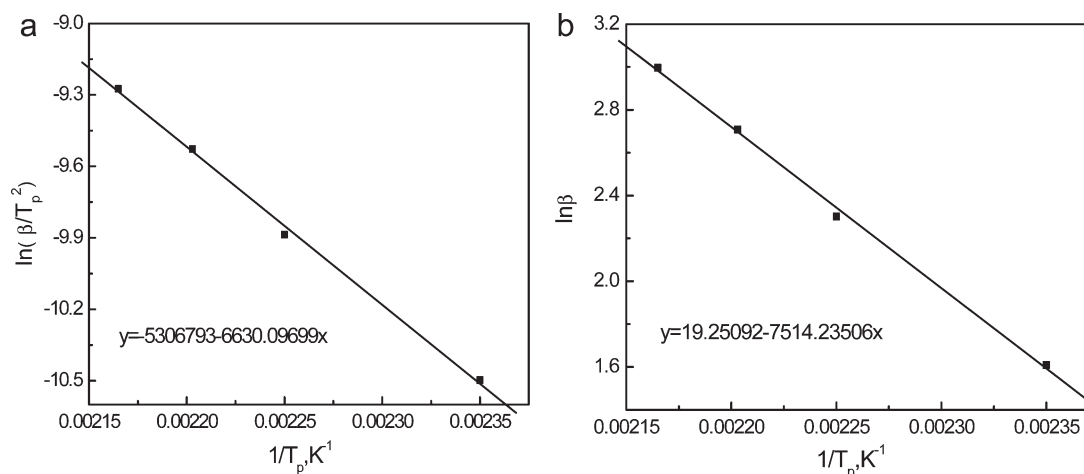
Figure 6 Kinetics analysis of TMBPBTH-EPOXY/DDM curing system. TMBPBTH-EPOXY/DDM: a: $\ln(\beta/T_p^2)$ $-1/T_p$; b: $\ln \beta - 1/T_p$.

and all the exothermic peak temperatures (T_p) of the DSC curves at different heating rates are listed in Table II, and the curing kinetic parameters determined by the Kissinger and Flynn-Wall-Ozawa methods are also summarized in Table II.

According to eq. (1), it was calculated that E_a of TMBPBTH-EPOXY/DDM curing system is 55.13 kJ/mol, and A is 0.882. According to eq. (2), it was calculated that E_a of TMBPBTH-EPOXY/DDM curing system is 55.10 kJ/mol.

Because of thermal hysteresis, curing temperatures were different because of different heating rates. However, materials are often cured at constant temperature or stepped of heating state because at that time the heating rate is 0 K/min. Therefore, the method of extrapolation of T-β is used to get the isothermal curing temperature of curing system, and then the best curing process is determined. The data is showed in Table III, and Figure 7 shows T-β analysis, whereas, T_i, T_p, and T_o means onset temperature, peak temperature, and end temperature, respectively.

When the T-β analysis in Figure 7 are extrapolated until β equals to 0, T_i, T_p, and T_o of isothermal curing would be gained. T_i, T_p, and T_o of TMBPBTH-EP-OXY/DDM system is 44.9, 143.4, and 168.6°C, respectively. The curing system was heated from 44.9 to 143.4°C gradually, and then cured at 143.4°C for isothermal curing; at last, it was heated to 168.6°C and remained for a certain time. The best

curing process was determined, and the results is showed in Table IV.

Glass transition temperature of epoxy resin network

T_g of an epoxy resin network is the reflection of the structure for different epoxy resins when the curing reaction is complete.

DMTA is used to determine the dynamic mechanical property of materials in a certain temperature range. It can determine continuously in wide temperature or frequency range and get the relationship of rigidity and damping with temperature, frequency, or time in a short time. At the aspect of determining material's glass transition and secondary transition, it has better sensitivity than DTA and DSC. Here, TMBPBTH-EPOXY/DDM curing system was studied by DMTA at fixed frequency.

Figure 8 shows the DMTA spectra of TMBPBTH-EPOXY/DDM. The T_g of TMBPBTH-EPOXY/DDM curing system is about 240.2°C.

Thermal decomposition temperature of TMBPBTH-EPOXY/DDM system

The thermal decomposition temperatures of cured compounds are different depending on the curing conditions of different curing temperature and time. TGA was used to determine the thermal decomposition temperatures of TMBPBTH-EPOXY/DDM

TABLE II
Kinetics Data of TMBPBTH-EPOXY/DDM

β (K/min)	5	10	15	20
T_p(K)	425.779	443.459	453.832	461.879
$1/T_p$ ($\times 10^{-3}$ K)	2.349	2.255	2.203	2.165
$\ln \beta$	1.609	2.303	2.708	2.996
$\ln(\beta/T_p^2)$	-10.498	-9.887	-9.527	-9.275

TABLE III
DSC Data of TMBPBTH-EPOXY/DDM Curing System

β (K/min)	5	10	15	20
T_i (K)	327.734	347.988	365.223	367.424
T_p (K)	425.779	443.459	453.832	461.879
T_o (K)	463.954	504.941	528.411	549.314

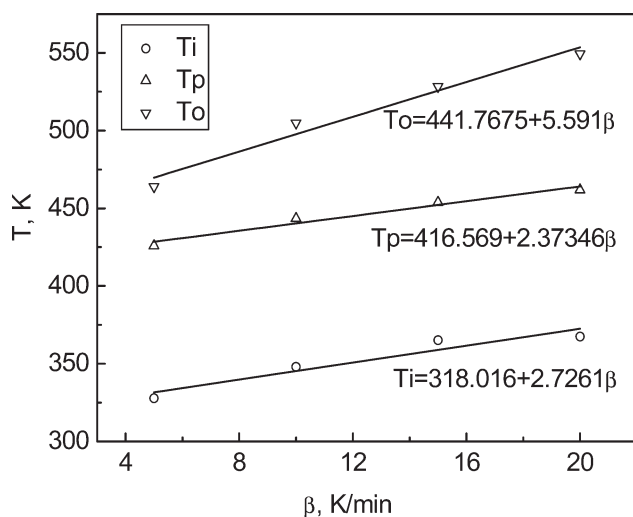**Figure 7** T-β analysis of TMBPBTH-EPOXY/DDM curing system.

curing system at curing temperatures of 100, 140 and 160°C for curing time of 1, 2, 4, and 6 h, respectively. The testing temperature range for the determination is from room temperature to 600°C, and the heating rate is 20 K/min. The measurement results of the sample cured at 100°C are plotted in Figure 9, and all results of the samples with T_o, T_i, and T_e data are listed in Table V, whereas, T_o, T_i, and T_e are onset temperature, middle temperature, and offset temperature of thermal decomposition, respectively.

It indicates that thermal decomposition temperature increased slightly with the increasing of curing time from 1 to 6 h at the same curing temperature of 100°C. This change was attributed to the increase of density of crosslinking caused by curing for longer time, which in turn results in well crosslinking network. Moreover, it can be seen from the experimental data in Table V that the decomposition temperature increased gradually with increasing time even at later curing stage, which elucidated that the curing time influenced the curing reaction largely at relatively lower curing temperature.

Accordingly, thermal decomposition temperatures of samples cured at 140°C are higher than cured at 100°C, which meant that curing temperature of 140°C is more helpful for complete curing reaction and cured compounds had much higher crosslinking density. Moreover, it can be seen from the experi-

TABLE IV
Curing Processes of TMBPBTH-EPOXY/DDM
Curing System

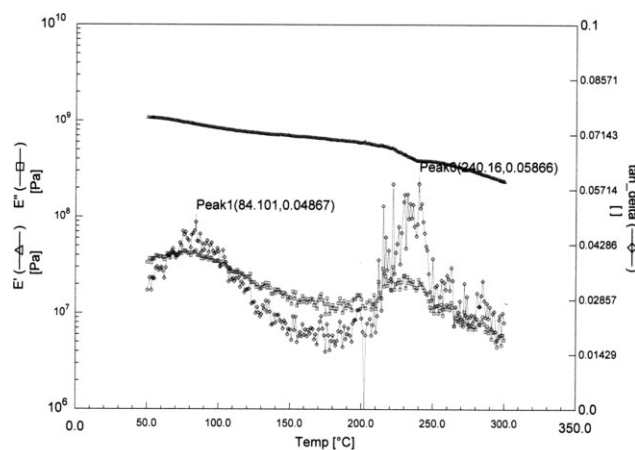| Curing system	Curing process (°C/h)
TF-EPOXY/DDM	140/2 + 170/4

Figure 8 DMTA curve of TMBPBTH-EPOXY/DDM curing system.

mental data in Table V that the decomposition temperature increased slowly with increasing time at later curing stage, which elucidated that the curing time influenced the curing reaction nonobviously at relatively higher curing temperature.

Finally, the curing temperature was raised to 160°C and the thermal decomposition temperature supposed to be higher than that cured at 140°C. However, the fact was just reverse, and the thermal decomposition temperatures of samples cured at 160°C are lower than cured at 140°C and declined slightly with the increasing curing time. This change can be explained to excess crosslinking of epoxy resin and hardener or overcured which gave inner stress and then deficiency appeared. These deficiencies made the thermal decomposition temperature to decline. With the increase of curing time, the
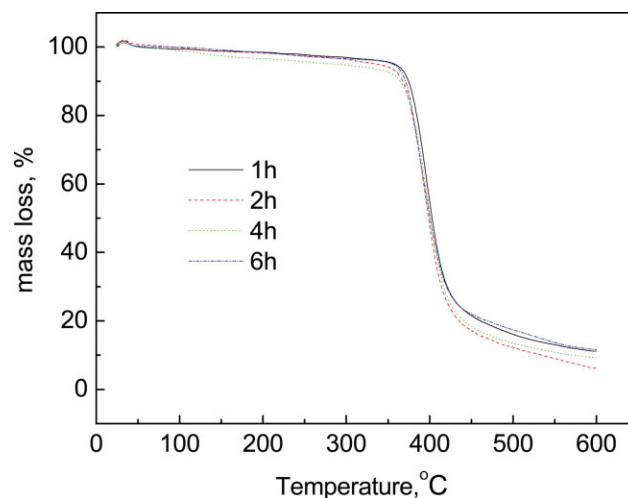

Figure 9 TGA curves of TMBPBTH-EPOXY/DDM curing system at 100°C with 20°C/min heating rate. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE V
Thermal Decomposition Temperatures of
TMBPBTH-EPOXY/DDM

Curing temperature (°C)	Curing time (h)	T_o (°C)	T_i (°C)	T_e (°C)
100	1	370.2	395.2	420.3
	2	370.0	395.1	420.1
	4	371.1	396.9	422.7
	6	373.5	398.0	422.4
140	1	378.7	398.9	419.1
	2	381.2	400.7	420.2
	4	380.1	400.2	420.4
	6	380.8	400.9	420.9
160	1	376.4	398.5	420.7
	2	375.8	398.9	420.0
	4	374.5	398.1	421.6
	6	370.6	394.7	418.8

deficiencies became more serious and decomposition temperature decreased gradually.

CONCLUSIONS

FTIR studies indicated that the state-of-cure of TMBPBTH-EPOXY/DDM curing system was mainly dependent on the curing temperature and it is increased with increasing temperature; however, it changed a little with increasing curing time at the same curing temperature. DSC studies showed that the curing activation energies of TMBPBTH-EPOXY/DDM systems are 55.13 and 55.10 kJ/mol. The DMTA studies elucidated that the glass transition temperature (T_g) of TMBPBTH-EPOXY/DDM was as higher as 240.2°C. TGA studies showed that the thermal decomposition temperature increased with the increasing curing temperature and time, but it is declined at 160°C because of overcuring.

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