

Crystal Structure, Curing Kinetics, and Thermal Properties of Bisphenol Fluorene Epoxy Resin

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ABSTRACT: Diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF) monomer was successfully synthesized and characterized in detail. The crystal structure of DGEBF was measured by single-crystal X-ray diffraction analysis. Curing kinetics of DGEBF with 4,4-diaminodiphenyl sulfone (DDS), thermal properties, and decomposition kinetics were investigated using nonisothermal differential scanning calorimetry (DSC) according to Kissinger, Ozawa and Crane methods. The glass transition temperature (T_g), thermal properties of cured polymer were estimated by DSC,

dynamic mechanical analysis, and thermogravimetric analyses. Epoxy value of DGEBF monomer up to theoretical value leads to higher crosslink density of cured polymers. The cured DGEBF/DDS system exhibited obvious higher T_g and better thermal stability compared to those of DGEBF/diamine systems reported previously. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 827–833, 2010

Key words: crystals; curing kinetics; thermal properties; decomposition kinetics; resins

INTRODUCTION

Epoxy resins are widely applied in polymer industry fields as coatings, structural adhesives, insulating materials, polymer matrixes for composite materials, and so on. However, the widespread use of epoxy resins is limited in many high-performance applications because of their thermal properties.^{1–4} Modifications of the molecular backbone and increases in the number of epoxide group functionalities are the common methods used to improve their thermal properties.^{5–8}

The compound that contains fluorene ring usually has excellent heat resistance, high refractive index, high transparency, and low linear expansion coefficient. Therefore, with the addition of fluorene group to the backbone of polymers, the improved polymers are considered worthy of further study in terms of their properties.^{9–12} The introduction of fluorene group into epoxy resins has been reported and studied during past few years.^{13–17} Korshak et al. and Chen et al. synthesized diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF) and studied the effect of chemical structure on the curing and thermal properties of the cured resins.^{13,14} They found that polymers with a fluorene between the two phenyl groups show a better thermal property. Recently, Dai et al. and Liu et al. reported the curing

kinetics of several different epoxy/fluorenyl diamine systems and some fundamental issues about DGEBF epoxy resin.^{15–17} Their studies showed that epoxy/fluorenyl diamine systems exhibited higher thermal properties and lower reactivity compared to diglycidyl ether of bisphenol A (DGEBA). Nevertheless, the epoxy value of synthesized epoxy resin achieved theoretical value has not been reported, and there has been no description on precise crystal structure of epoxy resin monomer with no molecular weight distribution. What's more, curing kinetics of DGEBF/DDS system has not been reported up to now.

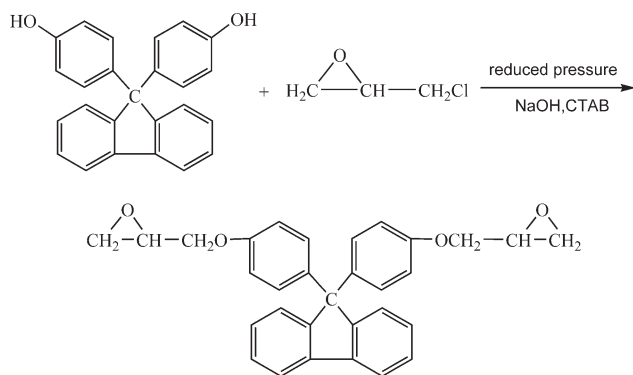
In our work, DGEBF with crystal structure was synthesized and characterized by IR, NMR, X-ray, and DSC. Crystal structure of DGEBF monomer was analyzed by single-crystal X-ray. Thermal properties of cured DGEBF/DDS system was measured by dynamic mechanical analyzer (DMA) and thermogravimetric analyses (TGA). The curing kinetics of DGEBF/DDS system was studied with dynamic DSC method and compared with normal DGEBF reported previously.

EXPERIMENTAL

Materials

9,9-Bis(4-hydroxyphenyl) fluorene was obtained from Suqian ever-galaxy pharma & chem. Co. (China). 3-Chloro-1,2-epoxypropane (ECH) was purchased from SINOPEC Baling Petrochemical Branch. 4,4-Diaminodiphenyl sulfone (DDS), hexadecyl trimethyl ammonium bromide (CTAB), acetone, chloroform,

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Scheme 1 Syntheses of DGEBF.

and 1,4-dioxane were all obtained from Sinopharm Chemical Reagent Co. All chemical agents were of analytical-reagent grade and used without further purification.

Synthesis of DGEBF

Synthesis of DGEBF had been reported previously,^{13–15} we improved the method and got DGEBF monomer with high epoxy value.

9,9-Bis(4-hydroxyphenyl) fluorene (20.0 g, 0.057 mol), ECH (70.0 mL, 0.900 mol), CTAB (0.5 g, 0.001 mol), and 1,4-dioxane (11 mL) were added to a three necked flask. The mixtures were heated to 65°C slowly and stirred for 0.5 h with magnetic stirrer. Then, 13 mL of 50 wt % hot aqueous NaOH was added drop by drop over a period of 1 h under reduced pressure atmosphere. After the completion of aqueous NaOH addition, the reaction was maintained at 60°C for an additional 2 h under reduced pressure. Then, the obtained viscous solution was poured into deionized water, washed several times till the pH of organic phase was 7. The organic phase was readded to three necked flask and heated. After the excess ECH and solvent were distilled off under reduced pressure, we got crude powder DGEBF precipitated from deionized water. After being vacuum-dried, the crude product was purified by recrystallization from a mixture of acetone and absolute ethanol (5 : 1). Then, colorless crystalline powers of DGEBF were obtained. We got single-crystal DGEBF by single-crystal cultivation in mixture solvent of acetone and chloroform (1 : 1) at room temperature. The synthetic route is shown in Scheme 1.

Curing procedure

The epoxy resin was heated to be melting under vacuum, then a equivalent ratio of curing agent DDS was added to the DGEBF and thoroughly mixed. After that, the mixtures were cured at its optimal

curing condition decided by dynamic DSC analyses: the curing and postcuring temperature were 180°C and 240°C with curing time were 4 h and 3 h, respectively. The cured resins were allowed to cool down to room temperature, and then cut into suitable sizes for DSC measurement.

Characterization

FTIR spectra were recorded on a WQF-410 FTIR spectrometer in the range of 4000–400 cm^{-1} . NMR spectra were carried out on a INOVA-400M (Varian) instrument ($^1\text{H-NMR}$, 400 MHz) using chloroform-d (CDCl_3) as the solvent, Chemical shifts of 1H (δ ppm) were calibrated using tetramethylsilane as internal standard (δ 0.0). Single-crystal X-ray diffraction analysis was performed in Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences using a SMART-APEX instrument. TG-DSC analysis was performed on a NETZSCH STA 449C equipment. Dynamic curing kinetics of DGEBF/DDS system was measured ranged from 25 to 300°C under nitrogen atmosphere at heating rates of 5, 10, 15, and 20°C/min, respectively. The dynamic thermal mechanical properties of the cured DGEBF/DDS were characterized by a Rheometric Scientific DMA. The sample size was 50 mm \times 6 mm \times 2 mm. The analyses were done in a single-cantilever mode at a frequency of 1 Hz. The samples were heated from 50°C to 350°C at a heating rate of 5°C/min.

RESULTS AND DISCUSSION

IR, $^1\text{H-NMR}$, DSC characterization

IR (KBr, cm^{-1}): 914 (oxirane), 1242, 1034 (C–O–C), 1448 (Ar), 1506, 1606 (phenylene), 2873, 2922 (methylene), 3001, 3057(arylene). $^1\text{H-NMR}$ (400 MHz, CDCl_3 , ppm): 6.750–7.754 (m, 16H, ArH), 4.118–4.146 (dd, 2H, CH_2 of glycidyl), 3.885–3.927 (m, 2H, CH_2 of glycidyl), 3.287–3.325 (m, 2H, CH of epoxy), 2.862–2.884 (t, 2H, CH_2 of epoxy), 2.704–2.723 (m, 2H, CH_2 of epoxy).

The melting point (T_m) of DGEBF was 155.1°C measured by DSC, which is higher than that of Dai and Liu's value (147 and 108–114°C),^{15,16} as melting point increase along with increasing of the degree of crystallization.¹⁸ The epoxy value (determined by acetone-hydrochloride method according to GB-1677-1981) also increase from 0.40 (Dai and Liu's value)^{15,16} to 0.43 mol/100 g. Figure 1 shows DSC thermograms for uncured DGEBF.

Crystal structure

The ORTEP diagrams of DGEBF are shown in Figure 2. The overall structure of molecule can be described as a

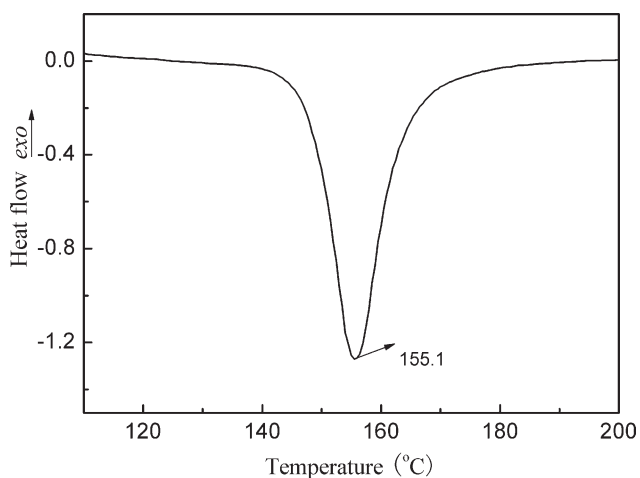


Figure 1 DSC thermograms for uncured DGEBF at 10°C/min heating rate under nitrogen atmosphere.

bat with fluorene group formed the “bat body” and “bat wings” made of two side chains consisted of two benzene rings, two propylene oxide groups, which is much more clearly in crystal cell shown in Figure 3. The two side chains connected to the center atom (C1) are not symmetrical as they twisted and the C14–C1–C2–C7 torsion angle is 115.7° compared to –120.6° for C23–C1–C2–C7. The bond length of C1–C2 (1.531 Å) is slightly shorter than C1–C13 (1.535 Å) due to twist of two benzene rings of fluorene group. There atoms of the fluorene group are not on a perfect plane, so as atoms of the two benzene rings (C2–C3–C4–C5 torsion angle is 0.5°, C8–C9–C10–C11 torsion angle is 0.1°). The angle between two side chains is 111.5°; the distance between C1 and two benzene rings of side chains are 1.543 Å (C1–C14) and 1.538 Å (C1–C23), all longer than C1–C2, C1–C13. The two benzene rings of side chains are not on a plane, bond lengths and angles of the two epoxy groups are different nevertheless both of two epoxy groups all curl inwards.

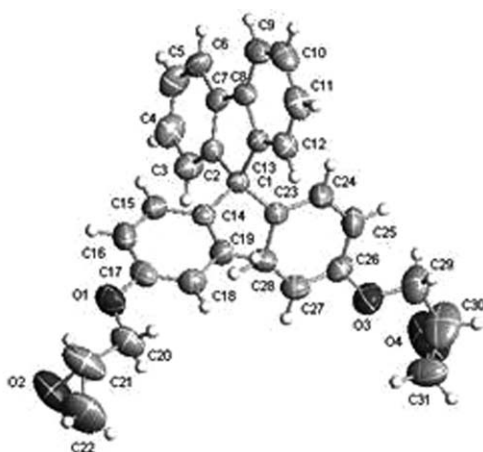


Figure 2 An ORTEP view showing 50% probability ellipsoids of DGEBF.

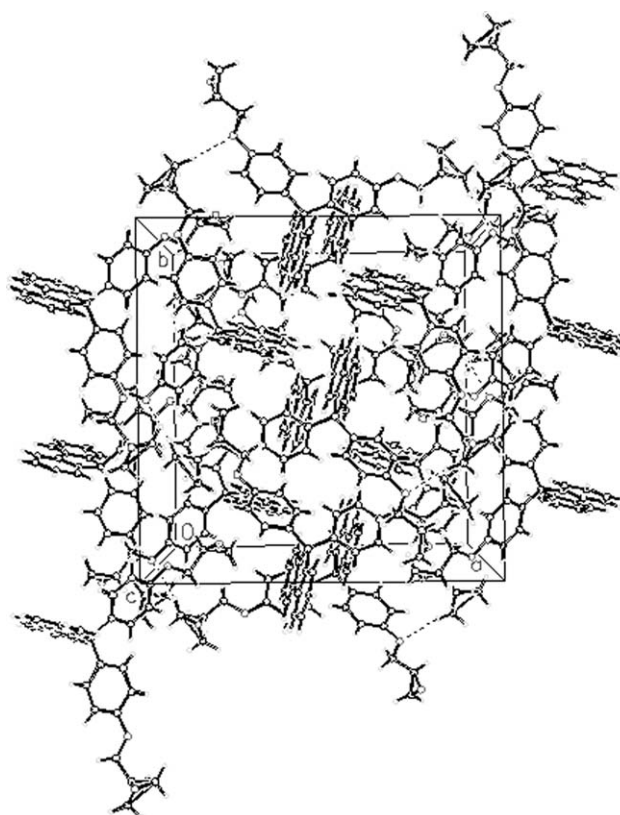


Figure 3 An ORTEP view showing 50% probability ellipsoids of crystal cell of DGEBF.

As well as van der Waals forces, the crystal packing of DGEBF appears to be controlled by several different intermolecular interactions. The most clear-cut is an C–H...O hydrogen bond (indicated by a dashed line in Fig. 3) that links oxygen atom of side chain with hydrogen atom of epoxy group in adjacent molecule. These weak intermolecular interactions which help to establish the crystal packing lead to the twist of two side chains and the distortion of the fluorene group.

The crystallographic data, selected bond lengths, and angles for DGEBF are presented in Tables I and II.

Curing kinetics of the DGEBF/DDS system

DSC has been extensively used for investigating the curing reaction of thermoset polymers. Kinetics can be characterized with DSC by measuring heat generated during the curing reaction as a function of temperature and time. In our work, we used nonisothermal DSC method to study curing kinetics. Kissinger and Ozawa methods^{19,20} were applied to calculate activation energy (E) and frequency factor (A); the order of reaction (n) and the reaction rate constant (k) were obtained from Crane and Arrhenius equation.²¹ Figure 4 shows the DSC curves of DGEBF/DDS at different heat rates.

TABLE I
Crystallographic Data for DGEBF

Formula	C ₃₁ H ₂₆ O ₄
<i>M_r</i>	462.52
Crystal system	Tetragonal
Space group	<i>I4(1)/a</i>
<i>T</i> (K)	293 (2)
<i>a</i> (Å)	17.7223 (10)
<i>b</i> (Å)	17.7223 (10)
<i>c</i> (Å)	30.723 (2)
α (deg)	90°
β (deg)	90°
γ (deg)	90°
<i>Z</i>	16
volume (Å ³)	9649.4 (11)
<i>D_{calc}</i> (g cm ⁻³)	1.273
μ (mm ⁻¹)	0.08
2θ scan range (deg)	4.6–40.4°
range <i>h</i>	–20 to 22
range <i>k</i>	–20 to 22
range <i>l</i>	–38 to 38
reflections measured/ unique	28371/5255
goodness-of-fit on <i>F</i> ²	1.021
<i>R1</i> , <i>wR2</i> [<i>I</i> > 2σ(<i>I</i>)]	0.064, 0.1782

Wavelength: Mo/ *K*α, 0.71073 Å; Refinement method: Full-matrix least-squares on *F*²; $w = 1/[\sigma^2(F_o^2) + (0.102P)^2]$, where $P = (F_o^2 + 2F_c^2)/3$; CCDC register number: CCDC 741,837.

Kissinger's method is based on the fact that the exothermic peak temperature T_p varies with the heating rates and the maximum reaction rate ($d\alpha/dt$)

TABLE II
Selected Bond Lengths (Å) and Angles (deg) for DGEBF

Bond lengths	
C1–C2	1.531 (3)
C1–C13	1.535 (3)
C1–C14	1.543 (3)
C1–C23	1.538 (3)
C7–C8	1.463 (4)
C21–C22	1.380 (6)
C30–C31	1.330 (9)
O2–C21	1.356 (5)
O4–C30	1.375 (6)
Bond angles	
C2–C1–C13	100.8 (2)
C23–C1–C14	111.5 (2)
C7–C2–C1	110.7 (2)
C8–C13–C1	110.7 (2)
C2–C1–C23	107.4 (2)
C13–C1–C14	108.43 (19)
C21–O2–C22	58.6 (3)
C30–O4–C31	57.4 (5)
Torsion angles	
C14–C1–C2–C7	115.7 (2)
C23–C1–C2–C7	–120.6 (2)
C1–C2–C7–C8	–1.2 (3)
C2–C3–C4–C5	0.5 (5)
C8–C9–C10–C11	–0.1 (4)
C17–C18–C19–C14	–0.4 (4)
C26–C27–C28–C23	–0.5 (4)

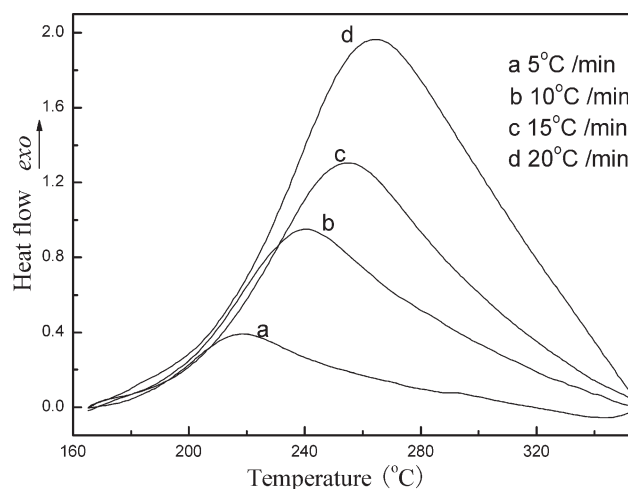


Figure 4 Dynamic DSC thermograms for DGEBF/DDS system under nitrogen atmosphere at different heating rates.

occurs at the peak temperatures.¹⁹ The equation can be expressed as follows

$$E_k = -R \frac{d[\ln(\beta/T_p^2)]}{d(1/T_p)} \quad (1)$$

where E_k , R , β are the activation energy, the gas constant and the heating rate, respectively. So the E_k values of curing can be obtained from the plot of $\ln(\beta/T_p^2)$ vs. $1/T_p$ (Fig. 5). The calculated value of E_k was 55.28 kJ/mol, linear correlation coefficient was 0.9989.

For Ozawa's method, it is on the assumption that the degree of conversion at peak temperatures for different heating rates is constant,²⁰ Ozawa's equation is shown in eq. (2).

$$E_o = -\frac{R}{1.052} \frac{d \ln \beta}{d(1/T_p)} \quad (2)$$

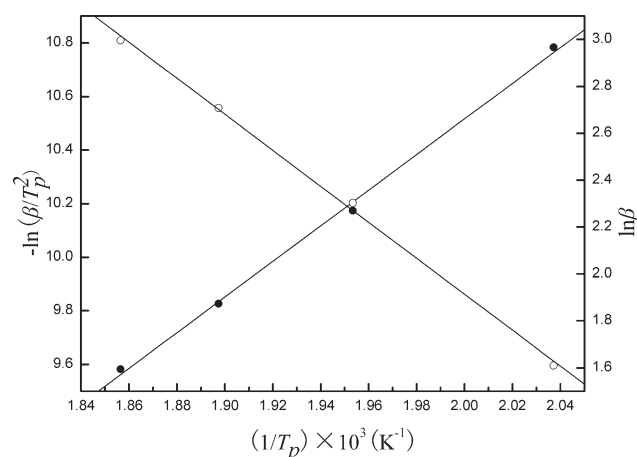


Figure 5 Plot for determination of the E by Kissinger method and Ozawa method.

Therefore, the E_o value of curing can be obtained by plotting $\ln \beta$ vs. $1/T_p$ (Fig. 5). Value of E_o calculated by Ozawa's method was 60.67 kJ/mol, the linear correlation coefficient was 0.9992.

Take value of activity energy E_k calculated by Kissinger's method into Crane's equation:²¹

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\frac{E}{nR} + 2T_p \quad (3)$$

where $\frac{E_k}{nR}$ is much higher than $2T_p$, the order of reaction n can be determined from plotting $\ln \beta$ vs. $1/T_p$ (Fig. 5). Therefore, n obtained from the plotting was 0.87.

According to Kissinger's method, A can be calculated by the eq. (4). The value was 1.07×10^5 .

$$A = \frac{\beta E_a \exp[E_a/RT_p]}{RT_p^2} \quad (4)$$

The E value calculated by Ozawa's method is slightly higher than that of Kissinger's method. The value of E_k is lower than that of DGEBA/DDS system (62–69 kJ/mol),²² implying that DGEBF exhibits higher curing reactivity toward DDS than DGEBA. Nevertheless, the E_k values of DGEBF/amines system are all higher than that of DGEBA/amines system reported in previously papers.^{16,17} Therefore, we cannot simply conclude that the steric hindrance of DGEBF decrease the curing reactivity compared to DGEBA. However, the E value is higher than that of DGEBF/DDM system (about 51.6 kJ/mol)¹⁵ which means higher curing temperature required. Lower curing energy of DGEBF/DDS than DGEBA/DDS system may attribute to the singleness of epoxy resin with no molecular weight distribution, and further investigation should be carried out to complete the curing kinetic model.

Thermal properties and decomposition kinetics of cured epoxy resins

Thermal stability was evaluated by TGA under nitrogen atmosphere. The TG and DTG thermograms of cured DGEBF at different heating rates are shown in Figure 6.

The degradation temperature at 5% weight loss ($T_{5\%}$), temperature corresponding to 10% weight loss ($T_{10\%}$) were 369°C and 379°C, both of which taken as indexes of resin thermal stability. The char yield of (Y_c) the cured resin at 820°C was 20%. All the values are according to DSC heating rate at 10°C/min. The temperature at $T_{5\%}$, $T_{10\%}$ are about 30–50°C higher than DGEBF/fluorenyl diamine systems, even Y_c at 820°C is 2% higher than Y_c at 700°C of DGEBF/fluorenyl diamine systems.¹⁶

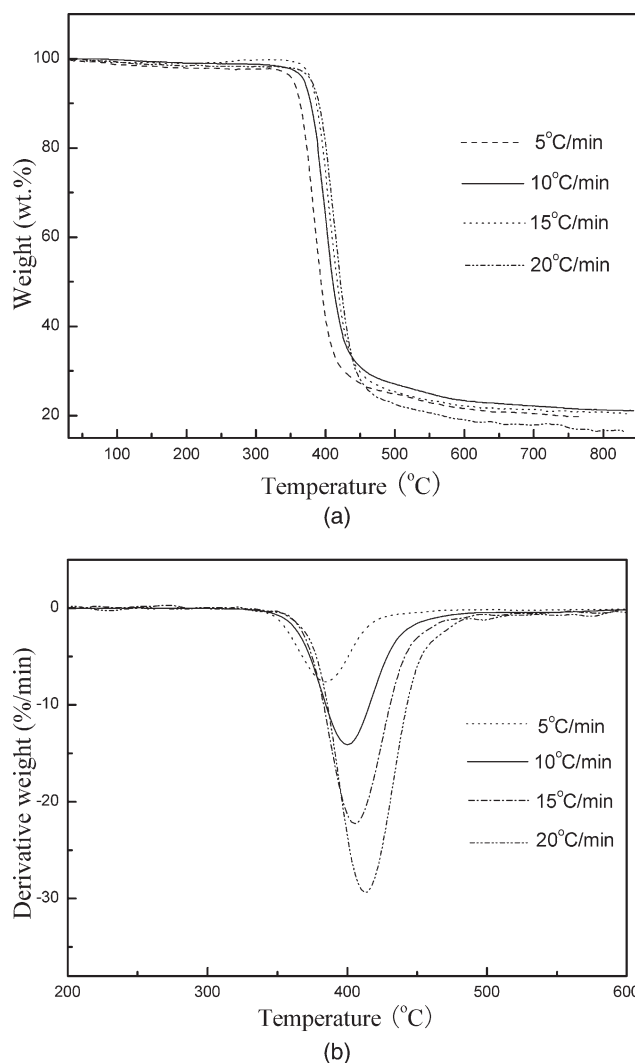


Figure 6 TG and DTG thermograms for cured DGEBF under nitrogen atmosphere.

There are several dynamic methods and an isothermal method for calculating kinetic parameters which depend on both the experimental conditions and the mathematical treatment of the data. We applied Kissinger and Ozawa's methods to evaluate the activation energies of the decomposition, E_d .^{19,20}

Kissinger's method only needs to know the temperature value at which the rate of weight loss conversion is at maximum without any assumptions about the reaction mechanism. E_d is obtained from the maximum reaction rate where $d(d\alpha/dt)/dt$ is zero under a constant heating rate condition, α is the conversion of thermal decomposition. Kissinger's equation can be expressed as follows

$$\frac{d[\ln(\beta/T_m^2)]}{d(1/T_m)} = -\frac{E_d}{R} \quad (5)$$

where T_m is the temperature at which the maximum degradation rate is exhibited. Thus, E_d can be

obtained from plots of $\ln(\beta/T_m^2)$ versus $1/T_m$. The average value was 171 kJ/mol.

For Ozawa's method, the values of E_d according to the nonisothermal kinetic theory can be written as follows:

$$\ln \beta = -1.105 \frac{E_d}{RT} + \ln \left[\frac{0.0048AE}{f(\alpha)} \right] \quad (6)$$

here $f(\alpha)$ is the differential expression of a kinetic model function, α is the conversion of thermal decomposition, A and R are pre-exponential factor and ideal gas constant.^{20,23} Value of E_d is determined from plotting $\ln \beta$ vs. $1/T$ (Fig. 7). The average E_d was 165 kJ/mol.

E_d obtained by Kissinger's method is slightly higher than that by Ozawa's method. Epoxy value up to theoretical value (0.43) ensures high crosslink density of cured resin; furthermore, high rigid aromatic ring content of both epoxy resin and curing agent have steric hindrance to molecular motion. Therefore, cured DGEGBF/DDS system has high degradation temperature. High char yield corresponds to molecular internal aromatization and cyclization of fluorene ring as molecular internal interaction is critical in chain breaking reaction at the later stage of decomposition.¹⁷

Dynamic mechanical properties

The dynamic-mechanical spectra in terms of storage modulus (E'), loss modulus (E''), and loss factor ($\tan \delta$) at 1 Hz for cured DGEGBF/DDS system were reported in Figure 8. The relaxation taking places at high temperature corresponds to the glass transition temperature (T_g) in the $\tan \delta$ plot. In this region, the storage modulus exhibits a sharp drop and then

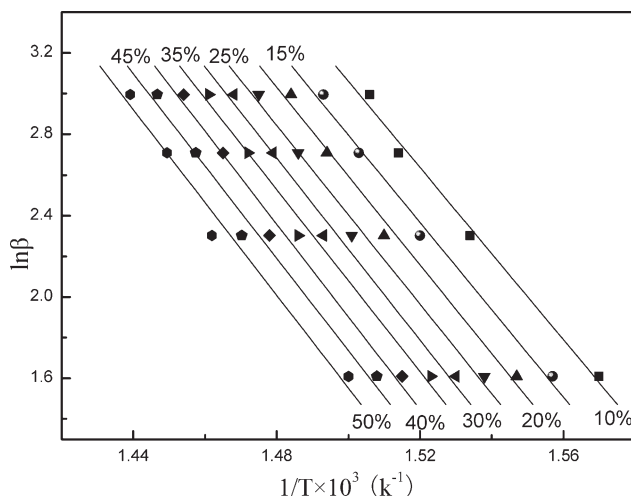


Figure 7 Plots of $\ln \beta$ versus $1/T$ for cured DGEGBF/DDS at several fixed degradation conversions.

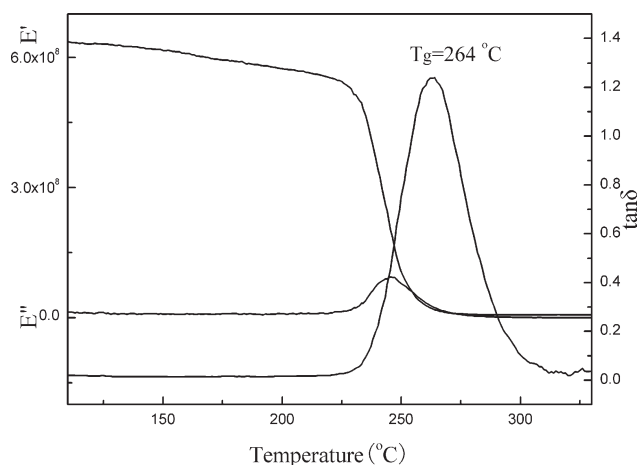


Figure 8 DMA curves of cured DGEGBF/DDS and systems at a heating rate of $5^\circ\text{C}/\text{min}$ (E' is the storage modulus and E'' is the loss modulus).

approaches a constant value (rubbery plateau). The E' plot also shows that E' is not constant at $T < T_g$ but slightly decreases with temperature. The E'' value is almost constant in E'' plot before and after the glass transition.

The glass transition temperature (T_g) is an important physical characteristic of plastics. The T_g value of cured DGEGBF/DDS system was determined from the peak temperature of the $\tan \delta$ plot. The value of T_g for cured DGEGBF/DDS was 264°C , about 30°C higher than DGEGBF/fluorenyl diamine systems.¹⁶

The glass transition temperature is affected by both the backbone rigidity of the epoxy monomer and crosslink density. DGEGBF has a structure in which a bulky fluorene unit protrudes vertically from the polymer main chain. This chemical structure of four phenyl rings connected to a quaternary carbon leads to severe rotational hindrance of the phenyl groups.²⁴ Epoxy value of DGEGBF up to theoretical value means much more epoxy groups, which leads to higher crosslink density of cured polymers. Consequently, the T_g value is enhanced accounted to the stiffness of molecular chain, low degree of free conformational rotation, and high crosslink density.

CONCLUSIONS

High purity diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene was successfully synthesized and characterized. The nonisothermal curing processes of DGEGBF/DDS and decomposition kinetics were studied with DSC by Kissinger, Ozawa and Crane methods. Glass transition temperature, degradation temperature, and char yield were all higher than those of papers reported previously. Epoxy value of DGEGBF monomer up to theoretical value leads to higher crosslink density of cured polymers. Crystal DGEGBF monomer almost without impurities can cut

down chlorine content, which is of vital importance to electronic packaging materials. The results demonstrated that high crosslink density and rigid aromatic ring content enhanced the thermal stability of cured epoxy resin. The correlation between crystallinity of epoxy monomer and thermodynamic performances of cured polymers is underway.

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