Preparation, 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) was synthesized to introduce more aromatic structures into an epoxy resin system. The structure of DGEBF was characterized with Fourier transform infrared and ^{1}H-NMR. 4,4′-Diaminodiphenylmethane (DDM) was used as the curing agent for DGEBF, and differential scanning calorimetry was applied to study the curing kinetics. The glass-transition temperature of the cured DGEBF/DDM, determined by dynamic mechanical analysis, was 260°C, which was about 100°C higher than that of widely used diglycidyl ether of bisphenol A (DGEBA). Thermogravimetric analysis was used to study the thermal degradation behavior of the cured DGEBF/DDM system: its onset degradation temperature was 370°C, and at 700°C, its char yield was about 27%, whereas that of cured DGEBA/DDM was only 14%. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 1476–1481, 2007

Key words: kinetics (polym.); resins; thermal properties

INTRODUCTION

Epoxy resins are widely used in the polymer industry as coatings, structural adhesives, insulating materials, polymer matrices for composite materials, and so on. However, in some cases, the applications of conventional epoxy resins are limited by their heat-resistant and flame-retardant properties.[1,2]

Because of the potential use of epoxy resins, modifications of the molecular backbone and increases in the number of epoxide group functionalities are the methods commonly employed to improve their thermal properties.[3–5] Diglycidyl ether of 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF) as a resin, containing a highly aromatic structure, was first prepared by Korshak et al.[6] They found that the resin, cured with trimellitic anhydride or *m*-phenylenediamine, produced good heat resistance and high thermal stability. The results also showed that polymers with a fluorene or anthrone group between the two phenyl groups had better thermal properties. On the basis of these results, Pearce et al.[7] synthesized epoxy resins from 9,9-bis(4-hydroxyphenyl) fluorene (DGEBF), 3,6-dihydroxyspiro-(fluorene-9,9-xanthane) (DGEFX), 10,10-bis(4-hydroxypheny) anthrone (DGEA), and 9,9,10,10-tetrakis (4-hydroxyphenyl) anthracene (TGETA) to study the relationship between the polymer structures and properties of the cured resins. DGEBF, DGEFX, DGEA, and TGETA, added to a diglycidyl ether of bisphenol A (DGEBA) system, produced increases in the glass-transition temperature (T_g), char yield, and oxygen index with increasing concentrations of these novel epoxy resins. However, the descriptions of the curing kinetics and other fundamental issues about DGEBF epoxy resin and amine systems have not been reported up to now.

To explore the applications of DGEBF, the curing kinetics and thermal properties were examined in detail in this study. DGEBF was synthesized and characterized with Fourier transform infrared (FTIR) spectrometry and NMR. The epoxy resin was cured with diaminodiphenylmethane (DDM). The curing kinetics were studied with differential scanning calorimetry (DSC) and simulated with the method of Kissinger. The thermal degradation behavior was investigated with thermogravimetric analysis (TGA), and the value of the activation energy of degradation (E_d) was determined. Dynamic mechanical analysis

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(DMA) was used to investigate the T_g value of the cured resin.

EXPERIMENTAL

Materials

9,9-Bis(4-hydroxyphenyl) fluorene was obtained from Suqian Ever-Galaxy Pharmacy & Chemical Co. (China). Epichlorohydrin (ECH), tetraethyl ammonium bromide (TEAB), 1,4-dioxane, sodium hydroxide (NaOH), acetone, and ethanol were obtained from Beijing Chemical Co. (China). DDM was received from Shanghai Chemical Co. (China). All chemical agents, which were analytical-reagent-grade, were used without further purification.

Synthesis of DGEBF

The epoxy resin, based on 9,9-bis(4-hydroxyphenyl) fluorene, was synthesized as shown in Scheme 1.[7,8]

9,9-Bis(4-hydroxyphenyl) fluorene (175.21 g), TEAB (21.02 g), ECH (470.25 mL), and 1,4-dioxane (96.71 mL) were added to a three-necked, round-bottom flask equipped with a heating mantle, magnetic stirrer, thermometer, and reflux condenser. The reaction mixture was heated to 65°C, and then 120 mL of 50 wt % aqueous NaOH was dropped gradually over a period of 1 h. After the completion of NaOH addition, the reaction mixture was maintained at 65°C for an additional 2 h, and meanwhile, the excess ECH and solvent were distilled off under reduced pressure. When the reaction was completed, the reaction mixture was filtered to remove the residual sodium chloride, and the organic phase was washed several times with deionized water. After precipitating from cold water and being vacuum-dried, the crude product was purified by recrystallization from a mixture of acetone and absolute ethanol (5 : 1). Then, the white, crystalline powers of DGEBF were obtained, and the synthetic route is shown in Scheme 1.

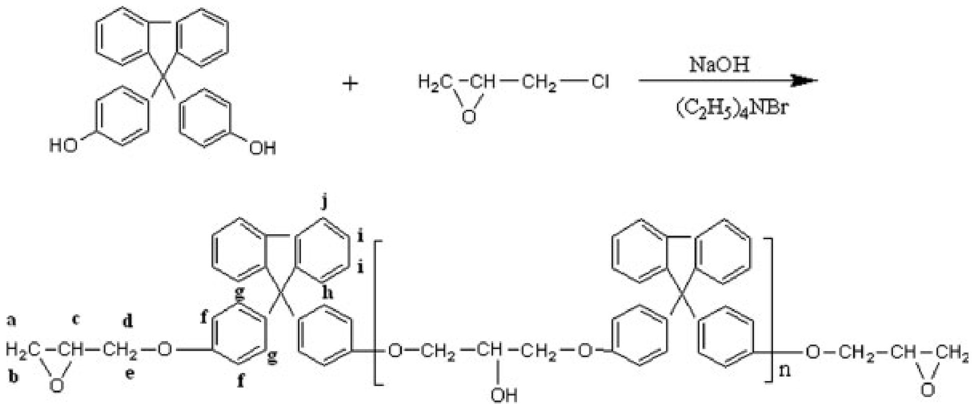
Characterization

^{1}H-NMR characterizations were carried out on a Bruker AM400 instrument operating at 400 MHz. Deuterated chloroform was used as a solvent, and tetramethylsilane was used as an internal standard. FTIR spectra were recorded on a Bruker Equinox 55 spectrometer in the range of 4000–400 cm^{-1}. The resin was ground with potassium bromide, and then the powder of the mixture was pressed into disks for FTIR measurements.

DSC measurements were performed with a Mettler–Toledo 822^e under a constant flow of a nitrogen atmosphere of 20 mL/min. The instrument was calibrated with a high-purity indium standard, and α-Al_2O_3 was used as the reference material. The reactants of DGEBF and DDM were mixed homogeneously in 1 : 1 equivalent ratio. About 5 mg of a sample was weighed into a hermetic aluminum sample pan at 10°C, which was then sealed, and the sample was tested immediately. The dynamic scanning experiments ranged from 25 to 300°C at heating rates of 5, 10, 15, and 25°C/min.

Thermal analyses were performed on a PerkinElmer Pyris 1 thermogravimetric analyzer at heating rates of 10, 20, 30, and 40°C/min in a nitrogen atmosphere from 25 to 750°C. About 5 mg of a sample, which had been cured and ground into a powder, was put into a platinum cell and placed on a detector plate. The char yield at 700°C was defined as the residual weight percentage of the polymer under a nitrogen atmosphere in a TGA measurement.

The dynamic thermal mechanical properties of the cured DGEBF/DDM were characterized with a Rheometric Scientific dynamic mechanical analyzer. The sample (8 mm × 5 mm × 1.5 mm) was loaded in a single-cantilever mode at a heating rate of

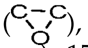


Scheme 1 Syntheses of DGEBF.

5°C/min from the ambient temperature to 300°C at a frequency of 1 Hz.

RESULTS AND DISCUSSION

Preparation and characterization of DGEBF

The synthesized DGEBF was characterized with ^{1}H-NMR and FTIR. Figure 1 shows the FTIR spectrum of DGEBF: 728, 742 (*o*-phenylene), 816 (*p*-phenylene), 910 (), 1175 (Ar—H), 1235 (Ar—O—R), 1495 (—Ar—), 1576 and 1598 (phenylene), 2862 and 2908 (methylene), and 2992 and 3030 cm^{-1} (arylene). The ^{1}H-NMR spectrum of DGEBF is shown in Figure 2. According to their chemical shifts, the peaks labeled a–j correspond to the structure shown in Scheme 1. The ^{1}H-NMR spectra and characteristic bands in the IR spectra are in agreement with the results reported in ref. 9, which identified the structure of DGEBF. The resin had a melting point of 147°C, which was measured with DSC. The epoxy value, according to the GB-1677-81 standard method (China), was 0.40–0.41 mol/100 g.

Curing kinetics of the DGEBF/DDM system

Curing is the essential process for the application of epoxy resins. The study of the curing kinetics is very useful in optimizing the curing conditions. The curing kinetics of epoxy resins can be investigated with different techniques, such as FTIR, thermomechanical analysis, and DSC.[10,11] DSC has been used extensively to characterize the curing kinetics of thermoset resins in dynamic or isothermal modes.[12,13] In this study, we used the nonisothermal DSC method to obtain the kinetic parameters.

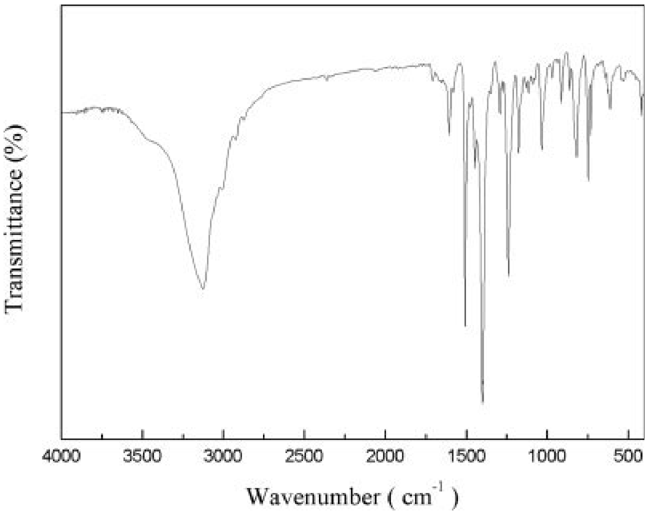


Figure 1 IR spectrum of DGEBF.

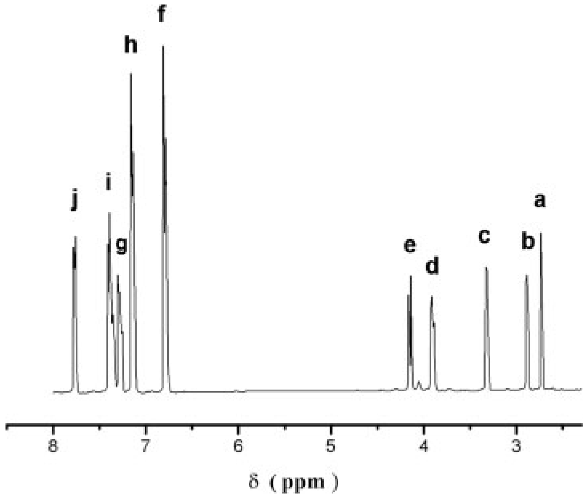


Figure 2 ^{1}H-NMR spectrum of DGEBF.

The curing DSC curves of the DGEBF/DDM system at different heating rates are shown in Figure 3. The exothermic peak temperature (T_p) of the curing curves shifts to a higher temperature with an increasing heating rate (β).

Kissinger's method is based on the fact that T_p varies with β, and it assumes that the maximum reaction rate ($d\alpha/dt$) occurs at peak temperatures.[14] The equation can be expressed as follows:

$$-In\left(\frac{\beta}{T_p^2}\right)=In\left(\frac{E}{R}\right)-In(An)-(n-1)In(1-x)_p+\frac{E}{RT_p} \tag{1}$$

where E is the activation energy; R is the gas constant; and A, n, and x are the pre-exponential factor, the order of the reaction, and the extent of the reaction, respectively. The scatter graph of $\ln(\beta/T_p^2)$ against $1/T_p$ is shown in Figure 4. The calculated value of E was 51.65 kJ/mol, and the linear correlation coefficient was 0.9992.

The value of E was introduced into Crane's equation:[15]

$$\frac{d(In\beta)}{d(1/T_p)}\approx-\frac{E}{nR} \tag{2}$$

The scatter plot of ln(β) and $1/T_p$ is also shown in Figure 4. Therefore, n obtained from the slope was 0.87, and the linear correlation coefficient was 0.9994.

According to Kissinger's method, A, which can be calculated with the following equation, was 3.259×10:^{5}

$$A\approx\frac{\beta E\exp E/RT_p}{RT_p^2} \tag{3}$$

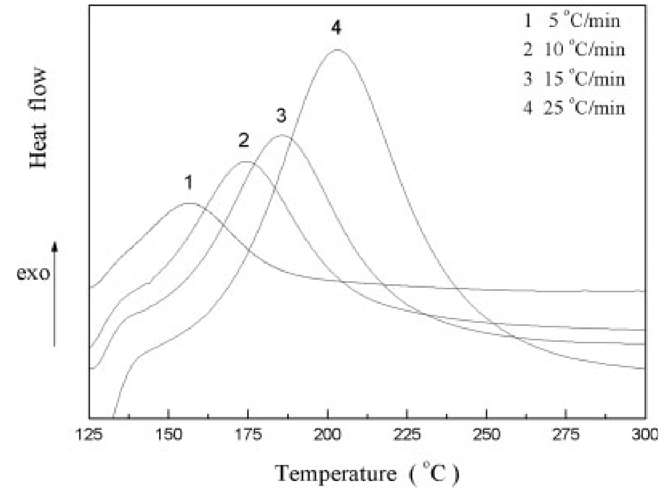


Figure 3 Dynamic curing curves of the DGEBF/DDM system at different heating rates.

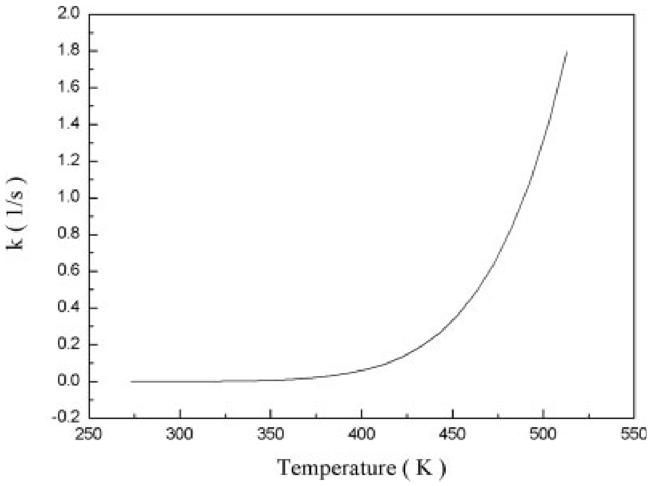


Figure 5 Curing reaction rate constant (k) values at different temperatures.

The values of E and A, determined from the curing kinetic data, were used to calculate the reaction rate constant (k) from an Arrhenius equation:

$$k = A\exp(-E/RT) \tag{4}$$

The k values at different temperature are shown in Figure 5. The value of k was dependent on the temperature and increased with an increasing curing temperature.

The starting temperature of the exothermic reaction corresponded to the crosslink temperature. T_p was relative to the curing temperature. The postcuring temperature was associated with the terminal temperature of the exothermic reaction. Then, β was extrapolated to zero so that we could approximately determine the curing temperature. Therefore, the crosslinking temperature, the curing temperature, and the postcuring temperature were 125, 155, and 185°C, respectively, as shown in Figure 6.

To ensure the better properties of the resins, we investigated the influence of the curing and postcuring times at 155 and 185°C, as shown in Figure 7. DSC measurements were used to evaluate the T_g values at different curing times. T_g was used directly as a parameter to evaluate the degree of cure, and it reflected the movement of the molecular chain in the system. At the beginning of curing reaction, the process was a gradual increase in the molecular weight. The crosslinking density further increased with the reaction time rising, so the T_g value became higher. However, it decreased a little when the curing time was prolonged because the extra curing time led to pyrolysis or cracking in the molecular chain. Therefore, it was better to control the curing time within 4 h. Then, we raised the temperature to 185°C for

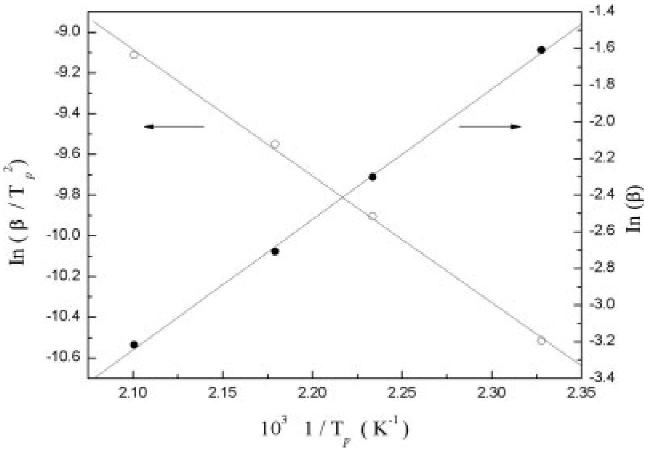


Figure 4 Curing kinetic analysis and calculation of the curing activation energy of DGEBF/DDM.

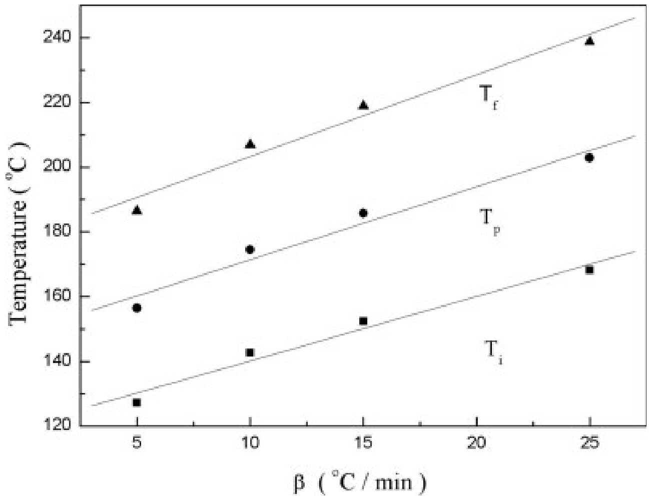


Figure 6 Temperatures of crosslinking, curing, and postcuring for DGEBF/DDM.

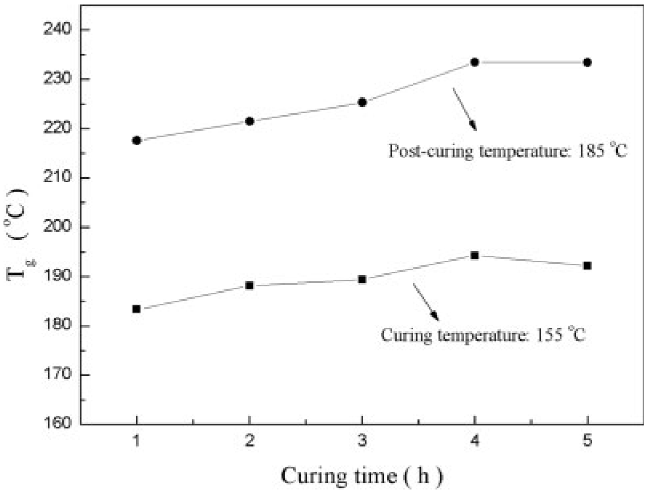


Figure 7 T_g values of the epoxy resin at different curing and postcuring times.

the postcuring so that the system could be cured completely, and the same trend was observed. Therefore, the curing condition was 155°C for 4 h and 185°C for 4 h.

Thermal properties and degradation kinetics

The thermal degradation kinetics of the cured DGEBF/DDM were also studied with a dynamic method.[16,17] Figure 8 shows the thermogravimetry (TG) curves at four different heating rates. The TG curves shifted to higher initial degradation temperatures with increasing heating rates, and the thermal degradation was controlled by a single E_d value.

According to the nonisothermal kinetic theory, the thermal degradation of a resin can be expressed by the following function:

$$\frac{d\alpha}{dT} = \frac{A}{\beta}\exp\left(\frac{-E_d}{RT}\right)f(\alpha) \qquad (5)$$

where $f(\alpha)$ is the differential expression of a kinetic model function, α is the conversion of thermal degradation, and T is the temperature.

E_d of the system was obtained with Ozawa's method,[18,19] which was deduced from eq. (5). The Ozawa equation can be written at a fixed conversion as follows:

$$\ln\beta = \ln\left[\frac{0.0048AE}{f(\alpha)}\right] - 1.10516\frac{E_d}{RT} \qquad (6)$$

Plots of ln β versus $1/T$ at several degradation conversions are shown in Figure 9. The E_d values for this system under different conversions were calculated, and the average value at $\alpha = 0.1$–0.4 was 175.90 kJ/mol. We also calculated E_d of the DGEBA/DDM system with the same method; the average value of E_d was 149.58 kJ/mol.

The TGA curves showed that the onset degradation temperature of the cured DGEBF/DDM system was about 370°C, and the char yield of the cured resin at 700°C was about 27%. Char formation is one of the important factors related to the flammability of materials. A linear relationship between the oxygen index and the char residue upon pyrolysis for halogen-free polymers has been proposed.[20] Increased char formation limits the production of combustible gases, decreases the exothermicity of the pyrolysis reaction, and decreases the thermal conductivity of the surfaces of the burning materials. Consequently, higher char yields are related to lower flammability for epoxy resins. Compared with that of cured DGEBF/DDM, the char yield of cured

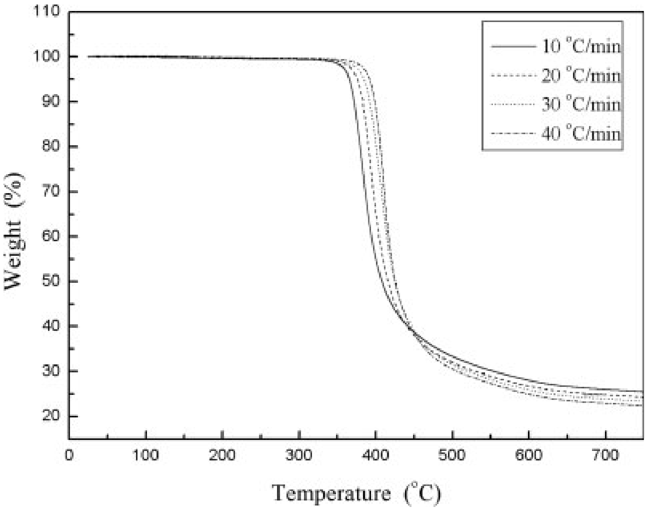


Figure 8 TG curves of the cured DGEBF/DDM system at four different heating rates.

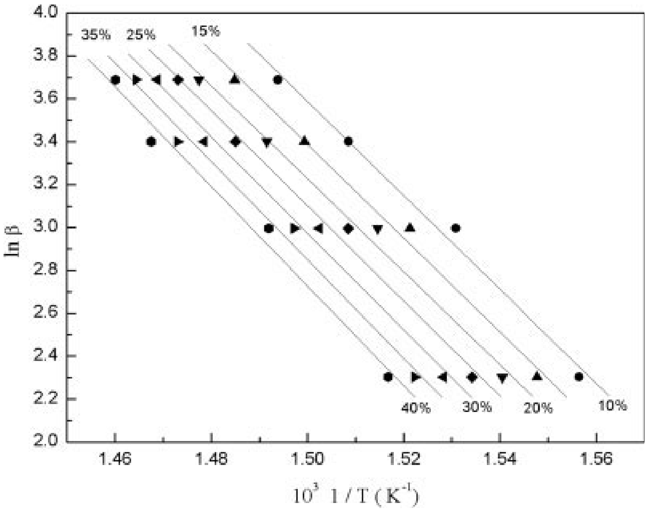


Figure 9 Plots of ln β versus $1/T$ for cured DGEBF/DDM at several fixed degradation conversions.

DGEBA/DDM was 14%. The increase in the char yield from DGEBA to DGEBF corresponded to the aromatization and cyclization of these resins. Therefore, the higher char residue and higher E_d value implied that the flame retardancy of the epoxy resin were elevated by the introduction of a fluorene structure into the backbone of the resin.

DMA

More detailed information was obtained from the measurements of the dynamic mechanical behavior of the cured epoxy resin as a function of temperature. The modulus and tan δ curves of the DGEBF/DDM and DGEBA/DDM systems are shown in Figure 10.

The T_g values of these systems were determined from the peak temperature of the tan δ curve. The results indicated that the resin had a high T_g at about 260°C; it was about 100°C higher than that of the cured DGEBA/DDM system. The increase in T_g from DGEBA to DGEBF appeared to correspond to an increase in the chain stiffness, which was due to the rigid structure of fluorene and the low degree of free conformational rotation. It also illustrated that DGEBF had better thermal stability. Therefore, the T_g value of the cured resin could rise remarkably with the introduction of the fluorene group into the molecular backbone.

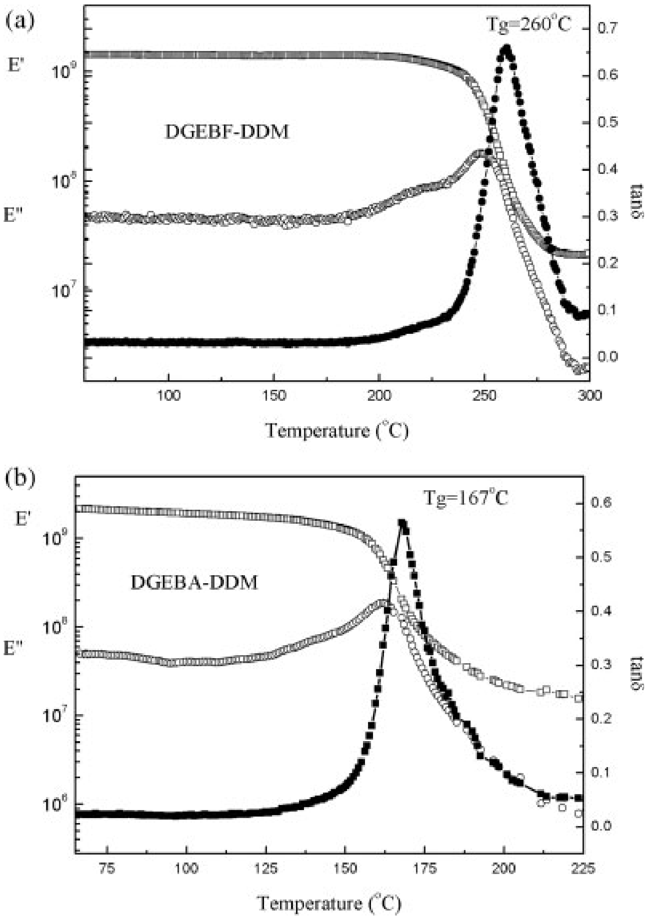


Figure 10 DMA curves of cured (a) DGEBF/DDM and (b) DGEBA/DDM systems at a heating rate of 5°C/min (E' is the storage modulus, and E'' is the loss modulus).

CONCLUSIONS

Diglycidyl ether of 9,9-bis (4-hydroxyphenyl) fluorene was synthesized and characterized in detail. The nonisothermal curing processes of DGEBF and DDM were studied with DSC. E and n were 51.65 kJ/mol and 0.87, respectively. The optimal curing condition was 155°C for 4 h and 185°C for 4 h. TGA curves showed that the cured resin had one-stage degradation, and the average value of E_d of cured DGEBF/DDM at α = 0.1–0.4 was 175.90 kJ/mol on the basis of the Ozawa equation. The T_g value of cured DGEBF/DDM was 260°C, and the char yield was about 27% at 700°C in nitrogen; these values were much higher than those of DGEBA/DDM. The results demonstrated that the DGEBF/DDM system exhibited higher thermal performance and better flame retardancy. Therefore, the introduction of a fluorene structure into an epoxy skeleton is an effective way of increasing the thermal stability and T_g of resins.

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