# Curing kinetics and properties of epoxy resin–fluorenyl diamine systems

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## ARTICLE INFO

## ABSTRACT

Diglycidyl ether of bisphenol fluorene (DGEBF), 9,9-bis-(4-aminophenyl)-fluorene (BPF) and 9,9-bis-(3-methyl-4-aminophenyl)-fluorene (BMAPF) were synthesized to introduce more aromatic structures into the epoxy systems, and their chemical structures were characterized with FTIR, NMR and MS analyses. The curing kinetics of fluorenyl diamines with different epoxy resins including DGEBF, cyclo-aliphatic epoxy resin (TDE-85) and diglycidyl ether of bisphenol A (DGEBA) was investigated using non-isothermal differential scanning calorimetry (DSC), and determined by Kissinger, Ozawa and Crane methods. The thermal properties of obtained polymers were evaluated with dynamic mechanical thermal analysis (DMTA) and thermogravimetric analysis (TGA). The results show that the values of activation energy ($E_a$) are strongly dependent on the structures of epoxy resin and curing agent. The curing reactivity of epoxy system is restrained by the introduction of rigid fluorene into chain backbone and flexible methyl into side groups. The cured DGEBF/fluorenyl diamine systems exhibit remarkably higher glass transition temperature, better thermal stability and lower moisture absorption compared to those of DGEBA/fluorenyl diamine systems, and display approximate heat resistance and much better moisture resistance relative to those of TDE-85/fluorenyl diamine systems.

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## 1. Introduction

Epoxy resins have gained wide acceptances in advanced composite matrices, surface coating and semiconductor encapsulation applications due to their heat, solvent and chemical resistance, good mechanical and electrical properties and strong adherence to many substrates [1–4]. In high-tech applications, however, epoxy resins with better heat and moisture resistance were required. For this reason, modifications of epoxy resins or curing agents in both backbone and pendant groups have been continuously investigated in order to improve the thermal and physical properties of cured polymers [5–9]. Many studies have been reported for improving the heat resistance of epoxy resins by increasing the crosslink density of cured epoxy resin or introducing bulky structures such as dicyclopentadiene, biphenyl, naphthalene, fluorene, maleimide or silsesquioxane [10–16].

Polymers containing fluorenyl structure in the backbone (so-called 'Cardo-type polymers') have many excellent improved properties, such as good heat resistance, high char yield, high limited oxygen index, good flameproofing, and excellent solubility in common organic solvents. Therefore, the development of these

polymers has attracted extensive research interests during past few years [17–20]. The introduction of fluorene moieties into the crosslink network is expected to greatly improve the thermal stability, mechanical property and moisture resistance of the cured epoxy resins. Lin et al. and Chen et al. reported several epoxy resins bearing fluorene structure and studied the effect of chemical structure on the curing and thermal properties of the cured resins [13,21–25]. The studies showed that fluorene-based epoxy resins exhibited much higher glass transition temperature ($T_g$), char yield and oxygen index compared to bisphenol A epoxy resin when cured with trimethoxyboroxane. Though a number of articles have been devoted to the study of fluorene-based epoxides cured with heteroatom curatives in the past two decades, only few works have so far been published on fluorene-based epoxide/aromatic diamine systems [26]. Fluorenyl diamines have been widely used as the functional monomers to prepare high performance polyimides [27–29] or polyamides [30,31] for the applications of gas separation or proton exchange membranes in direct methanol fuel cells. It is expected that the cured epoxy resin/fluorenyl diamine polymers would exhibit high glass transition temperature and low moisture absorption due to the rigid fluorene moieties [32]. Nevertheless, the curing kinetics and other fundamental issues about epoxy/fluorenyl diamine systems have not been reported up to now.

In this study, DGEBF, BPF and BMAPF were synthesized and characterized with IR, NMR and MS. Curing kinetics of DGEBF/

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fluorenyl diamine was studied with dynamic DSC method and compared with general epoxy/fluorenyl diamine systems, and the thermal properties and moisture resistance of the cured polymers were further investigated with DMTA, TGA, etc.

## 2. Experimental

### 2.1. Materials

9,9-Bis-(4-hydroxyphenyl)-fluorene (BHPF, 99.2%) was synthesized according to literature [33]. Fluorenone (99.5%) was obtained from Harbin Yinhe Chemical Co. (China). Methylsulfonic acid was purchased from Sinopharm Group Chemical Reagent Co., Ltd. (China). Epoxy resins of DGEBA (Epoxy equivalent weight (EEW) of 228 g/mol) and TDE-85 (EEW of 120 g/mol) were obtained from Wuxi Resin Co. (China) and Tianjin Synthetic Materials Research Institute (China), respectively. All solvents and other chemicals were of reagent grade or better and used without further purification. Fig. 1 shows the structural formula of materials used in this research work.

### 2.2. Synthesis of DGEBF [26]

DGEBF was synthesized from BHPF and epichlorohydrin by the method reported previously (yield 93.6%; melting point 108–114 °C; EEW 248 g/mol). IR (KBr, cm$^{-1}$): 2930 (–CH$_2$O–), 1240, 1028 (C–O–C), 914 (oxirane). $^1$H NMR (400 MHz, CDCl$_3$, ppm): 6.790–7.774 (m, 16H, ArH), 4.144–4.180 (dd, $J = 11.2$ Hz, $J = 3.2$ Hz, CH$_2$ of glycidyl, 2H), 3.887–3.929 (dd, $J = 11.2$ Hz, $J = 5.6$ Hz, CH$_2$ of glycidyl, 2H), 3.309–3.343 (m, CH of epoxy, 2H), 2.878–2.900 (t, $J = 4.4$ Hz, CH$_2$ of epoxy, 2H), 2.733–2.752 (dd, $J = 4.8$ Hz, $J = 2.8$ Hz, CH$_2$ of epoxy, 4H), 1.60 (s, 2H, OH).

### 2.3. Monomer synthesis

#### 2.3.1. Synthesis of BPF [32]

Fluorenone (18.0 g, 0.10 mol), aniline (74.6 g, 0.80 mol) and methylsulfonic acid (4.80 g, 0.050 mol) were added to a 250 mL three-necked, round-bottomed flask equipped with a heating mantle, magnetic stirrer, reflux condenser, thermometer and nitrogen inlet. A stream of nitrogen was introduced and the mixture was heated at 145–150 °C for 10 h with vigorous stirring. The water formed in the condensation reaction was retained in the flask throughout the reaction. The flask was cooled and its contents were poured into 300 mL of ethanol containing 2.0 g of sodium hydroxide. The off-white precipitated product was filtered, washed with ethanol until the effluent was colorless. The product was then dried under vacuum, recrystallized from 1,4-dioxane and dried under vacuum at 100 °C for 24 h. A white powder with a melting point of 237–238 °C was obtained (yield 58.6%; purity (HPLC) 99.4%). IR (KBr, cm$^{-1}$): 3375, 3511 (N–H), 1178 (C–N), 826 (C–H$_{Ar}$). $^1$H NMR (400 MHz, CDCl$_3$, ppm): 6.540–7.771 (m, 16H, ArH), 3.550 (s, 4H, NH$_2$). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 64.16 (quaternary carbon). MS ($m/z$): calcd for C$_{25}$H$_{20}$N$_2$, 348.44; found, 349.5 [M + H]$^+$.

#### 2.3.2. Synthesis of BMAPF

According to the aforementioned method, the off-white powder with a melting point of 230–232 °C was obtained (yield 56.4%; purity (HPLC) 99.4%). IR (KBr, cm$^{-1}$): 3434, 3316 (N–H), 1282 (C–N), 808 (C–H$_{Ar}$). $^1$H NMR (400 MHz, CDCl$_3$, ppm): 6.538–7.770 (m, 16H, ArH), 3.567 (s, 4H, NH$_2$), 2.065 (s, 6H, CH$_3$). $^{13}$C NMR (100 MHz, CDCl$_3$, ppm): 64.23 (quaternary carbon), 17.59 (CH$_3$). MS ($m/z$): calcd for C$_{27}$H$_{24}$N$_2$, 376.19; found, 377.4 [M + H]$^+$.

### 2.4. Resin casting preparation

The epoxy resins were initially heated up to 125–130 °C and degasified for 10–15 min under vacuum. A theoretical mass stoichiometric proportion of curing agent was added to the epoxy resins, and the contents were thoroughly mixed. The treated epoxy resins were then cast into a preheated steel mold (130–135 °C) coated with a mold release agent. Deaeration was carefully conducted again and the resins were cured in sheet molds by heating in an air circulated oven at programmed curing process. The cured resins were allowed to cool down to ambient temperature, and then removed from the oven and cut into a suitable size.
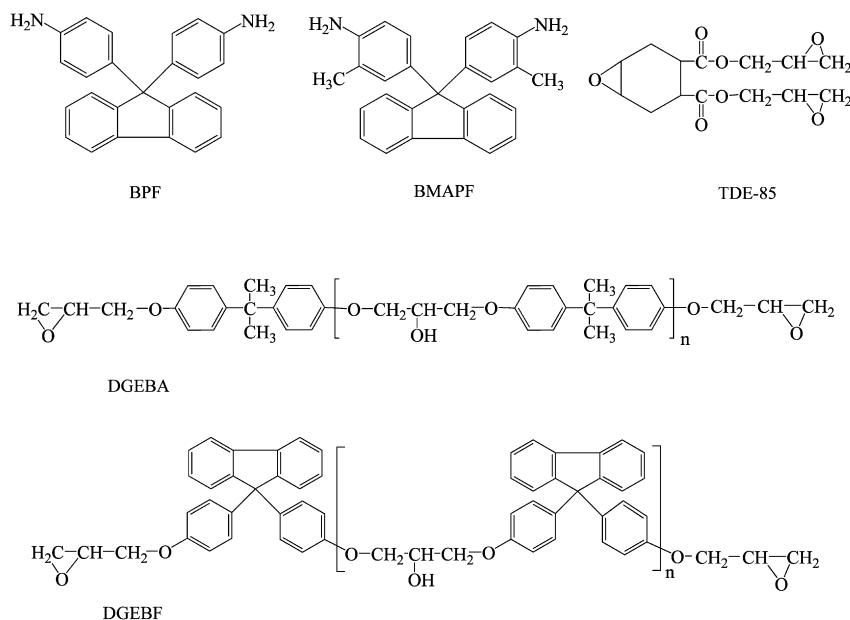


**Fig. 1.** Molecular structures of 9,9-bis(3-methyl-4-aminophenyl)-fluorene (BMAPF), 9,9-bis(4-aminophenyl)-fluorene (BPF), 4,5-epoxyhexyl-1,2-dimethyl acid diglycidyl ester (TDE-85), diglycidyl ether of bisphenol A (DGEBA) and digylcidyl ether of 9,9-bis(4-hydroxylphenyl)-fluorene (DGEBF).

## 2.5. Characterization

FTIR spectra were recorded on a Nicole Avatar 370 FTIR spectrometer in the range of 4000–500 cm$^{-1}$. $^1$H NMR and $^{13}$C NMR characterizations were performed on a Bruker AVANCE-400 NMR spectrometer using chloroform-$d$ (CDCl$_3$) as the solvent and tetramethylsilane (TMS) as internal standard. HPLC data were collected from an Agilent 1100 HPLC system with a mobile phase of methanol–acetonitrile–water system (73:7:20, v/v/v). Mass spectrographic analyses were obtained on an Agilent 1100SL mass spectrometer. DSC measurements were evaluated on a NETZSCH 204F1 differential scanning calorimeter (DSC) ranged from 25 to 300 °C at heating rates of 5, 10, 15, and 20 °C/min under nitrogen atmosphere at a constant flow of 20 mL/min. The reactants of epoxy resin and curing agent were mixed homogeneously in 1:1 molar equivalent ratio. About 10 mg of sample was weighed into a hermetic aluminum sample pan at 25 °C, which was then sealed, and the sample was tested immediately. Thermogravimetric analyses (TGA) were performed on a TA Q5000 thermogravimetric analyzer at a heating rate of 10 °C/min from 50 to 700 °C under nitrogen atmosphere at a flow rate of 50 mL/min. The dynamic mechanical thermal properties of the epoxy thermosets were measured with a TA Q800 dynamic mechanical analyzer. The rectangular samples (20 × 5 × 2 mm) were loaded in single cantilever mode at a temperature ramp of 3 °C/min from 50 to 300 °C at a frequency of 1 Hz under air atmosphere. Moisture absorption was determined as follows: the rectangular samples (20 × 5 × 2 mm) were dried under vacuum at 100 °C for 12 h, cooled to room temperature, weighed and placed in 100 °C water for a period of time and reweighed. The moisture absorption was calculated as percent weight gain: moisture absorption% = $(W/W_o - 1) \times 100\%$, where $W$ is the weight of the sample after dipping in 100 °C water for a period of time, $W_o$ is the initial weight of the sample after placing in vacuum oven for 12 h.

## 3. Results and discussion

### 3.1. Curing kinetics of epoxy resin–fluorenyl diamine systems

For theoretical and practical purposes, DGEBA, TDE-85 and DGEBF were employed to discuss the thermal curing behaviors of epoxy/fluorenyl diamine systems at heating rates of 5, 10, 15 and 20 °C/min by DSC technique (Fig. 2). To evaluate the kinetic parameters of epoxy/fluorenyl diamine systems, many methods have been used to investigate the kinetics of the curing reaction of epoxy resins [34,35]. Kissinger and Ozawa methods [36,37] were applied to calculate activation energy ($E$) and frequency factor ($A$) because they were both simple ways to deal with the dynamic curing process of epoxy/amine system. The kinetic parameters obtained from Kissinger and Ozawa methods are without the need of any assumption about conversion-dependent equation. Kissinger's equation can be expressed as follows

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

where $A$, $R$ are Arrenihus constant and ideal gas constant, respectively. Therefore, $E_k$ could be obtained from the slope of $\ln(\beta/T_p^2)$ vs. $1/T_p$ plot (Fig. 3). Ozawa's equation gives

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

where $E_o$ could be obtained from the slope of $\ln(\beta)$ vs. $1/T_p$ plot (Fig. 4). According to Kissinger's method, $A$ can be calculated with the following equation.

$$A = \frac{\beta E_a \exp[E_a/RT_p]}{RT_p} \tag{3}$$

Furthermore, the curing reaction order ($n$) could be obtained when Crane method [38] as depicted in Eq. (4) is applied.

$$\frac{d(\ln \beta)}{d(1/T_p)} = -\left[\frac{E_{a,k}}{nR} + 2T_p\right] \tag{4}$$

where $E_{a,k}$ is activity energy calculated by Kissinger method, and $n$ could be derived from the slope of $\ln(\beta)$ vs. $1/T_p$ plot when $E_{a,k}/nR$ is much higher than $2T_p$.

As shown in Fig. 2, the exothermic peak temperatures ($T_p$s) of the curing curves shifted to higher temperature with increasing heating rate ($\beta$). The DSC exothermic peaks of fluorenyl diamine/epoxy systems are very similar to those of other common aromatic diamine/epoxy systems such as diaminodiphenyl sulfone (DDS)/DGEBA or diaminodiphenyl methane (DDM)/DGEBA and these epoxy/fluorenyl diamine systems might be directly used in practical applications. The peak temperatures of cure exotherms obtained from the dynamic DSC scans at multiple heating rates are summarized in Table 1. On the basis of the experimental results from the dynamic DSC study, $E$, $A$ and $n$ of the epoxy/fluorenyl diamine systems were obtained using Eqs. (1)–(4), which are summarized in Table 2.

There are a few differences in $T_p$ and $E_a$ values among DGEBA/fluorenyl diamine, DGEBF/fluorenyl diamine and TDE-85/fluorenyl diamine systems, implying that these three epoxides have different reactivities. DGEBF shows lower reactivity towards fluorenyl diamines than DGEBA. This result may be attributed to the steric hindrance based on the fluorene structure in DGEBF, which may reduce the molecular mobility and depress the reactivity of reactive site. TDE-85 shows relatively higher $E_a$ than that of DGEBF, whereas $T_p$ of TDE-85 is lower, and this result might be induced by the cooperation effect of the steric hindrance of rigid cycloaliphatic group and the reactivity differences among the three epoxy groups of TDE-85. The $T_p$ and $E_a$ of BMAPF/epoxy systems are both higher than those of BPF/epoxy systems, and this result means that BMAPF exhibits lower curing reactivity compared to BPF. The decreased reactivity of amino group towards oxirane group for BMAPF might result from the further steric hindrance due to the methyl in side groups and its poor solubility in epoxy resins. This deduction is supported by the fact that a small endothermal peak exists near the melting point of BMAPF (about 230 °C in Fig. 2(d)–(f) at the heating rate of 5 °C/min), which infers that BMAPF could not dissolve well in aforedescribed epoxy reins.

The values of $E_k$ and $E_o$ are 53.04–73.99 and 57.14–77.45 kJ mol$^{-1}$, respectively. Taking fluorenyl diamine/DGEBA as an example, the value of $E_k$ is lower than that of DDS/DGEBA system (around 62–69 kJ mol$^{-1}$) [39]. It may be concluded that the fluorenyl diamines, in spite of their larger size, display higher reactivity than DDS. Nevertheless, the $E_k$ value of DGEBF/BPF system is higher than that of DGEBF/DDM system (around 51 kJ mol$^{-1}$) [26]. It implies that BPF might have lower reactivity towards epoxy groups due to the steric hindrance of fluorene moieties, and it is possible to be used in tailoring the processing factors in the manufacturing process of microelectronic encapsulation, heat-resistant adhesives and high performance composite matrices. Moreover, the cure reaction may proceed complicatedly because the reaction orders for the epoxy/fluorenyl diamine systems were all less than 1. Thus, further investigation should be carried out to characterize the curing kinetic model in later communications.

### 3.2. Dynamic mechanical thermal analyses

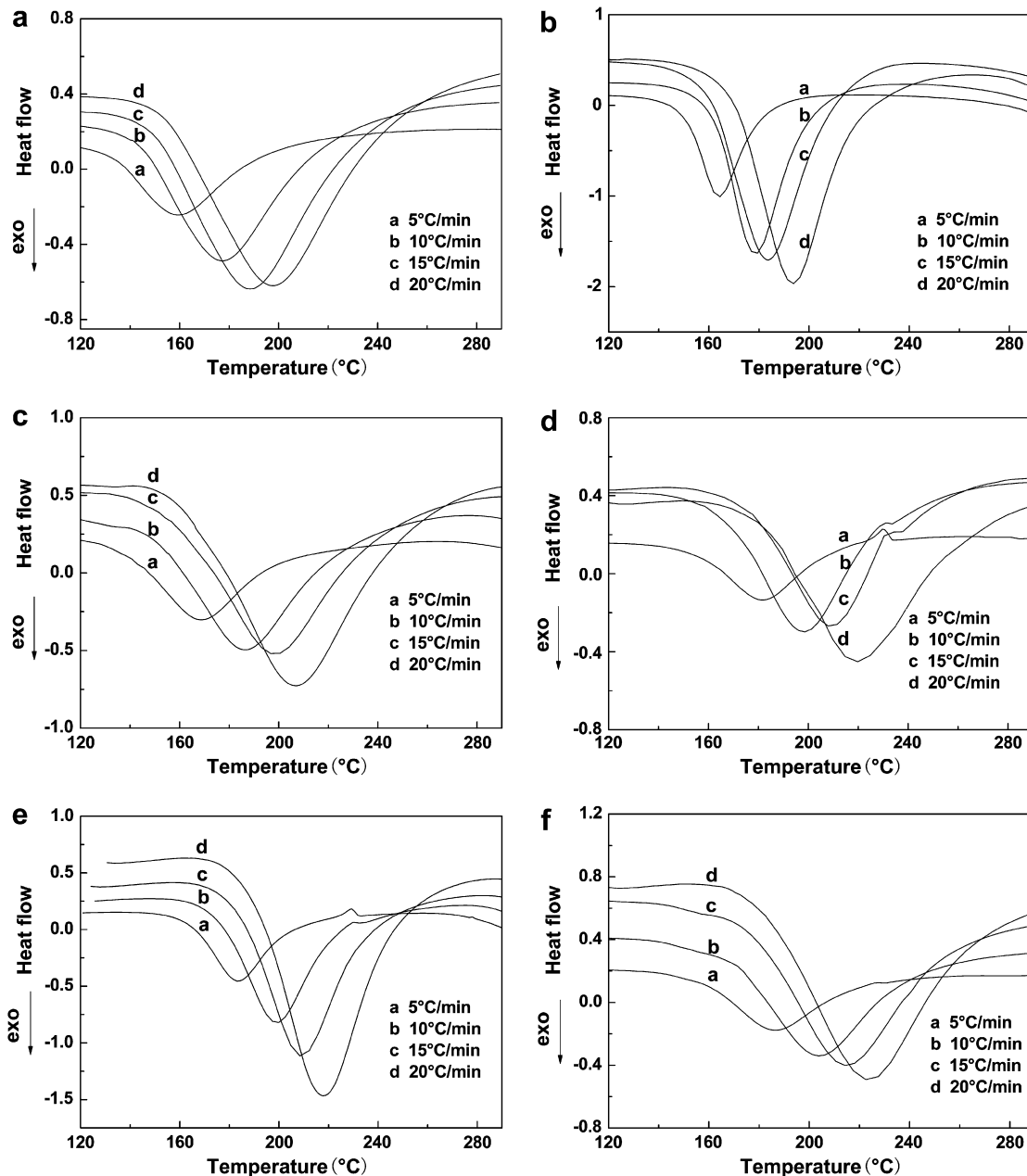Dynamic mechanical measurements were carried out to analyze the dynamic elastic modulus ($E$) and the occurrence of

**Fig. 2.** Dynamic DSC thermograms for the epoxy/fluorenyl diamine systems at heating rates of 5, 10, 15 and 20 °C/min under nitrogen atmosphere. (a) DGEBA/BPF; (b) TDE-85/BPF; (c) DGEBF/BPF; (d) DGEBA/BMAPF; (e) TDE-85/BMAPF; (f) DGEBF/BMAPF.

glass transition of different cured epoxy systems. Temperature dependence curves of $E$ and tan $\delta$ of different cured polymers are shown in Fig. 5(a) and (b), respectively. The value of $E$ of DGEBF/BPF is higher than that of DGEBA/BPF and TDE-85/BPF both in the glassy and rubbery regions characterized by the temperature corresponding to the maximum peak of tan $\delta$, which was taken as the glass transition temperature ($T_g$) (Fig. 5(b)). $T_g$ is affected both by the backbone rigidity of the epoxy monomer and by crosslink density. The glass transition temperature of the cured polymers can be elevated drastically by introducing some rigid groups into the backbone of epoxy monomer or by increasing crosslink density of cured polymer [40]. DGEBF 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 [31]. Therefore, the stiff, bulky

cardo moiety must arise from the higher rigidity of fluorene skeleton in the chain backbone, which would restrain the internal rotations and thermal motion of polymer segments. As a result, the $T_g$ for cured DGEBF/BPF is about 50 °C higher than that of DGEBA/BPF. TDE-85, the trifunctional epoxy resin containing two aliphatic epoxide rings and a cycloaliphatic epoxide ring, has much higher epoxy value and longer alkyl chain than DGEBF, which results in a higher crosslinking density of cured epoxide. Thus, the $T_g$s of TDE-85/fluorenyl diamine systems are slightly lower than those of DGEBF/fluorenyl diamine systems. It is deduced that $T_g$ is dominated by crosslink density rather than the content of phenyl group for the TDE-85/diamine systems.

By comparing the results of DGEBA and TDE-85 cured with BMAPF, it can be clearly seen that DGEBA/BMAPF has higher $E$ values than that of TDE-85/BMAPF in glassy region, whereas, at temperatures above $T_g$, the situation reverses. Higher retention of $E$
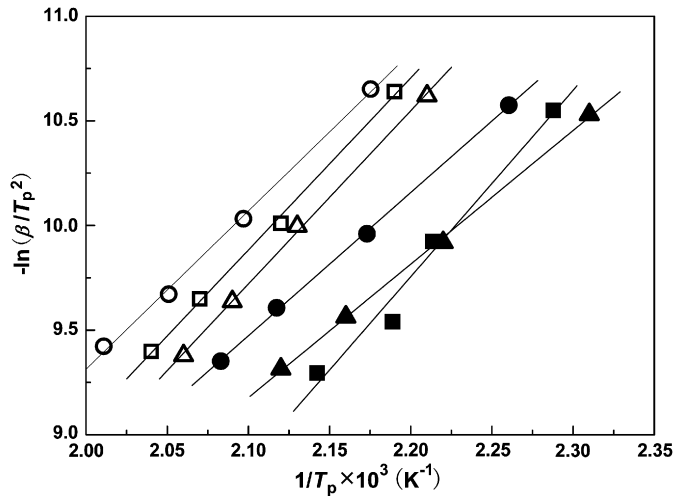
**Fig. 3.** Plot for determination of the $E$ and the $A$ by Kissinger method in different curing reactions: ● DGEBF/BPF; ■ TDE-85/BPF; ▲ DGEBA/BPF; ○ DGEBF/BMAPF; □ TDE-85/BMAPF; △ DGEBA/BMAPF.
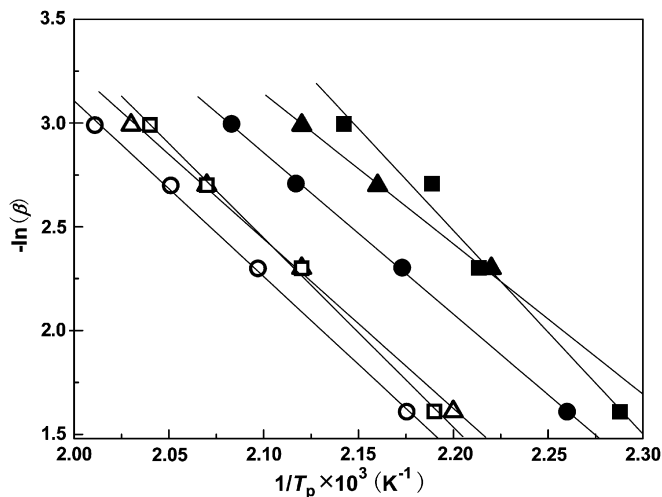


**Fig. 4.** Plot for determination of the $E$ and the $A$ by Ozawa method in different curing reactions: ● DGEBF/BPF; ■ TDE-85/BPF; ▲ DGEBA/BPF; ○ DGEBF/BMAPF; □ TDE-85/BMAPF; △ DGEBA/BMAPF.

for TDE-85/BMAPF at elevated temperature might be attributed to the higher crosslink density of TDE-85/BMAPF compared with DGEBA/BMAPF. The cured TDE-85/BMAPF displays higher $T_g$ (196.8 °C) than that of DGEBA/BMAPF (164.5 °C). This tendency is also reasonably in agreement with the different rigidity between the chains of DGEBA and TDE-85. For DGEBA/BMAPF and TDE-85/BMAPF, the $E$ and $T_g$ of cured polymer decreased strikingly compared with those of the same epoxy/BPF system. One

**Table 1**
Peak temperature ($T_p$, °C) of cure exotherms for the epoxy/fluorenyl diamine systems at different DSC heating rates ($\beta$)

| Samples | $\beta$ (°C/min) | | | |
|---|---|---|---|---|
| | 5 | 10 | 15 | 20 |
| DGEBA/BPF | 159.6 | 177.5 | 188.8 | 197.8 |
| TDE-85/BPF | 163.9 | 178.6 | 183.7 | 193.6 |
| DGEBF/BPF | 169.2 | 187.0 | 199.1 | 206.9 |
| DGEBA/BMAPF | 181.5 | 198.5 | 209.1 | 219.9 |
| TDE-85/BMAPF | 183.6 | 199.0 | 209.2 | 218.0 |
| DGEBF/BMAPF | 186.5 | 203.7 | 214.4 | 224.1 |

**Table 2**
Curing kinetic parameters for the epoxy/fluorenyl diamine systems derived from the multi-temperature scan method

| Samples | Kissinger method | | | Ozawa method | |
|---|---|---|---|---|---|
| | $E_k$ (kJ mol$^{-1}$) | $A$ (s$^{-1}$) | $n$ | $E_o$ (kJ mol$^{-1}$) | $A$ (s$^{-1}$) |
| DGEBA/BPF | 53.04 | $4.394 \times 10^5$ | 0.882 | 57.14 | $1.404 \times 10^6$ |
| TDE-85/BPF | 68.29 | $1.287 \times 10^7$ | 0.902 | 71.98 | $3.453 \times 10^7$ |
| DGEBF/BPF | 56.87 | $9.113 \times 10^5$ | 0.881 | 61.33 | $3.130 \times 10^6$ |
| DGEBA/BMAPF | 60.33 | $1.532 \times 10^6$ | 0.890 | 64.45 | $4.649 \times 10^6$ |
| TDE-85/BMAPF | 73.99 | $1.645 \times 10^8$ | 0.908 | 77.45 | $4.328 \times 10^8$ |
| DGEBF/BMAPF | 62.80 | $2.478 \times 10^6$ | 0.893 | 66.87 | $7.322 \times 10^6$ |

possibility for this result might be assigned to the flexible methyl in side groups, which would increase the chance of thermal movement for the pendent segment in glassy state [41]. Another possible explanation could be the poor solubility of BMAPF in epoxy resins, which might induce a non-uniform curing degree in the epoxy thermosets and finally lead a reduced mechanical and thermal performance of the cured samples. Nevertheless, DGEBF/BMAPF has minor deterioration in both $E$ and $T_g$ relative to DGEBF/BPF. This result could be induced by abundant rigid fluorene skeleton in the molecular chain of DGEBF.

### 3.3. Thermogravimetric analyses

Thermal stability was evaluated by thermogravimetric analyses (TGA) under nitrogen atmosphere. The results are shown in Fig. 6.
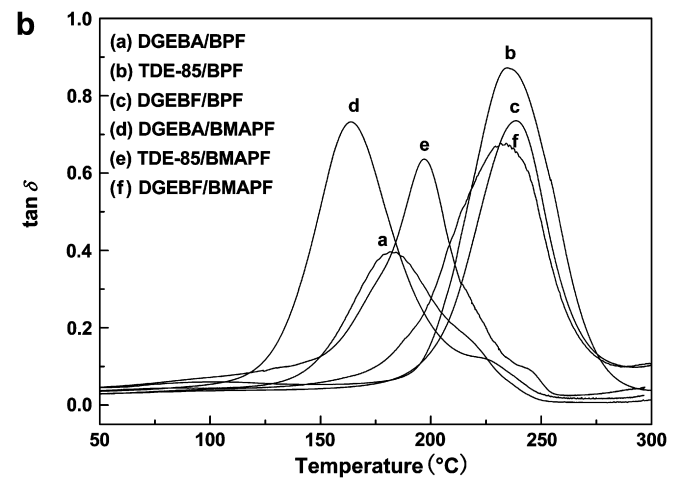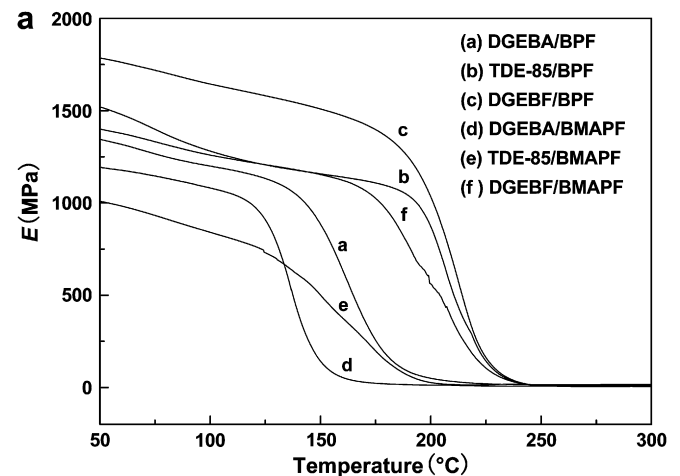




**Fig. 5.** Temperature dependencies of storage modulus ($E$) and tan $\delta$ for the cured DGEBA/BPF, TDE-85/BPF, DGEBF/BPF, DGEBA/BMAPF, TDE-85/BMAPF and DGEBF/BMAPF.
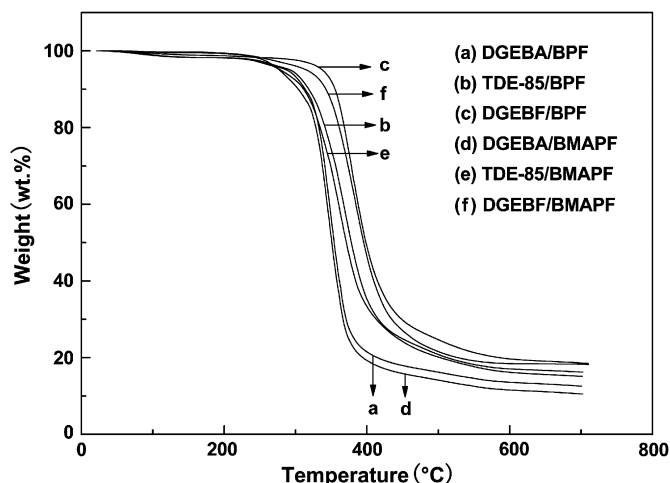
**Fig. 6.** TGA thermograms of the cured epoxy/fluorenyl diamine systems in nitrogen atmosphere.

(a) DGEBA/BPF
(b) TDE-85/BPF
(c) DGEBF/BPF
(d) DGEBA/BMAPF
(e) TDE-85/BMAPF
(f) DGEBF/BMAPF

Thermal property parameters of different epoxy thermosets are given in Table 3.

The temperature corresponding to 5% weight loss ($T_{5\%}$) was taken as an index of thermal stability. $T_{5\%}$ and $Y_c$ values of the DGEBF/BPF polymer are much higher than those of DGEBA/BPF. This result indicates that the introduction of fluorene skeleton into epoxy monomers improved the inherent thermal stability of the thermosets dramatically. Nevertheless, the cured TDE-85 exhibits much lower degradation temperature but slightly lower char yield compared to those of the cured DGEBF. The relatively high char yield of TDE-85 polymers could be due to the higher crosslink density of the curing system. This may suggest that the condensed aromatic rings and higher crosslink density facilitate the formation of char. The $T_{5\%}$ and $Y_c$ of the epoxy/BMAPF polymers are both lower than those of the epoxy/BPF polymers. Since the thermal motion of network in glassy state is believed to include the vibration of side group and the motion of crosslink segment, the flexible methyl in side group may favor these motions and decrease the dimensional stability of the cured polymers at elevated temperature.

## 3.4. Moisture absorption

In the practical application, absorbed moisture was found to plasticize the epoxy resin, resulting in a decrease of the $T_g$ and in turn affecting mechanical properties [42,43]. The moisture absorption measurement results are given in Table 4.

The moisture resistance of all cured DGEBF/fluorenyl diamine polymers (water uptake of DGEBF/BPF and DGEBF/BMAPF, 1.90, 1.40%, respectively, 72 h) is better than those of cured DGEBA/fluorenyl diamine (2.06, 2.01%, 72 h), TDE-85/fluorenyl diamine (7.12,

**Table 3**
Thermal stability parameters for the cured polymers

| Samples | $T_g$ (°C) | $T_{d,5\%}$ (°C) | $T_{d,10\%}$ (°C) | $Y_c$ (%, 700 °C) |
|---|---|---|---|---|
| DGEBA/BPF[a] | 183.0 | 287.8 | 313.4 | 12.55 |
| DGEBF/BPF | 238.5 | 337.8 | 355.6 | 18.60 |
| TDE-85/BPF | 234.6 | 292.8 | 318.5 | 16.22 |
| DGEBA/BMAPF[b] | 164.5 | 277.5 | 303.8 | 10.52 |
| DGEBF/BMAPF | 233.0 | 315.4 | 342.4 | 18.26 |
| TDE-85/BMAPF | 196.8 | 280.0 | 311.4 | 15.13 |

$T_{d,5\%}$: temperature of 5% weight loss. $T_{d,10\%}$: temperature of 10% weight loss. $Y_c$: char yield under nitrogen atmosphere.
[a] The curing process of epoxy/BPF: 150 °C/1 h + 180 °C/3 h + 200 °C/1 h.
[b] The curing process of epoxy/BMAPF: 150 °C/1 h + 180 °C/3 h + 200 °C/2 h.

**Table 4**
Moisture absorption of the cured polymers

| Samples | Water uptake (%) | | | | |
|---|---|---|---|---|---|
| | 12 h | 24 h | 36 h | 48 h | 72 h |
| DGEBA/BPF | 1.44 | 1.70 | 1.79 | 1.95 | 2.06 |
| DGEBF/BPF | 1.60 | 1.74 | 1.84 | 1.88 | 1.90 |
| TDE-85/BPF | 2.93 | 4.18 | 5.10 | 6.10 | 7.12 |
| DGEBA/BMAPF | 1.39 | 1.59 | 1.69 | 1.86 | 2.01 |
| DGEBF/BMAPF | 1.10 | 1.24 | 1.20 | 1.34 | 1.40 |
| TDE-85/BMAPF | 2.74 | 4.02 | 4.92 | 5.88 | 6.90 |

6.90%, 72 h) polymers, DGEBA/DDS (2.50%, 72 h), naphthalene epoxy resins/DDS (2.21–2.44%, 72 h) [44], BPA-epoxy/DDM (1.98%, 48 h), tetramethyl bisphenol (TMBP) epoxy system/DDM (2.40%, 48 h), and TMBP/DDS (2.90%, 48 h) [45]. The hydrophobic fluorene moieties might be responsible for the lower moisture absorption. During the curing process, hydroxyl groups were generated via ring opening of epoxy groups [44,46]. The average volume of fluorene ring is deduced to be larger than those of methylene or cyclohexyl groups, and it might cause a reduced crosslink density in the network of cured polymers to produce less hydroxyl groups, and finally leads to an improved hydrophobicity of the system. In addition, compared with that of DDS and DDM, more contents of phenyl group in the fluorenyl diamines further decrease the polarity of cured polymers, and inhibit water to invade. The cured TDE-85/fluorenyl diamine polymers have relatively poor moisture resistance compared with the other two kinds of thermosets, which could be the result of abundant strong hydrophilic ester groups and more hydroxyl groups generated via ring opening of epoxy groups in crosslink network. Free volume of the cured polymers might be further reduced by the introduction of moisture repulsive methyl group into side groups. As a result, the cured epoxy/BMAPF polymers display a lower moisture uptake relative to the cured epoxy/BPF polymers.

According to the aforementioned results, if DGEBF, DGEBA, and TDE-85 blended at an advisable proportion, these fluorenyl diamine/epoxy blend polymers are expected to be with improved properties, such as heat resistance, moisture resistance and ease of processing, and would be widely used in composite circuit boards, encapsulant for semiconductor, insulating material for electric devices, laminate materials, etc.

## 4. Conclusions

Several different epoxy/fluorenyl diamine systems were prepared and the curing kinetics of these epoxy systems was studied by Kissinger, Ozawa and Crane methods. Fluorene-based epoxy monomer has a lower reactivity towards fluorenyl diamine than bisphenol A epoxide. The introduction of methyl in the side groups decreased curing reactivity and thermal stability of the fluorenyl diamines. With the introduction of massive fluorene moieties, the cured polymers exhibit higher glass transition temperature, better thermal stability and lower moisture absorption compared to bisphenol A epoxide and cycloaliphatic triepoxide. The fluorene-containing curing systems may be used as potential candidates for electronic encapsulation materials, laminate materials and high performance composite matrices.

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