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Synthesis and properties of novel fluorinated epoxy resins based on 1,1-bis(4-glycidylesterphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane

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Abstract

A novel fluorinated epoxy resin, 1,1-bis(4-glycidylesterphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane (BGTF), was synthesized through a four-step procedure, which was then cured with hexahydro-4-methylphthalic anhydride (HMPA) and 4,4′-diaminodiphenyl-methane (DDM). As comparison, a commercial available epoxy resin, bisphenol A diglycidyl ether (BADGE), cured with the same curing agents was also investigated. We found that the BGTF gave the exothermic starting temperature lower than BADGE no mater what kind of curing agents applied, implying the reactivity of the former is higher than the latter. The fully cured fluorinated BGTF epoxy resins have good thermal stability with glass transition temperature of 170–175 °C and thermal decomposition temperature at 5% weight loss of 370–382 °C in nitrogen. The fluorinated BGTF epoxy resins also showed the mechanical properties as good as the commercial BADGE epoxy resins. The cured BGTF epoxy resins exhibited improved dielectric properties as compared with the BADGE epoxy resins with the dielectric constants and the dissipation factors lower than 3.3 and dissipation 2.8×10^{-3}, respectively, which is related to the low polarizability of the C–F bond and the large free volume of CF_3 groups in the polymer. The BGTF epoxy resins also gave low water absorption because of the existence of hydrophobic fluorine atom.

Keywords: Fluorinated epoxy resin; Reactivity; Dielectric properties; Water absorption

1. Introduction

The epoxy resins have been extensively used in many industrial fields as adhesives, constructions, coating and insulation materials for electric devices [1,2] due to their good balance of properties such as excellent moisture, solvent and chemical resistance; low shrinkage after cure; superior electrical and mechanical properties; good adhesion to many substrates [3]. In recent years, epoxy resins have been found wide applications in electronic packaging as epoxy molding compound, electrically conductive silver paste, die attach adhesives, etc. [4–6]. With the rapid development of advanced microelectronic packaging technology, the epoxy resins should have improved combined physical, mechanical, thermal

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properties, including: (1) good thermal stability; (2) low dielectric constant and dissipation factor with low water absorption; (3) low coefficient of thermal expansion (CTE) and low internal stress; (4) high mechanical strength and low modulus [7–10]. For meet the requirements of advanced electronic packaging, many efforts have been made on developing novel epoxy resins with enhanced thermal properties as well as improved electrical insulating properties.

It is well known that incorporation of fluorinated substituents into polymer structure is an effective method to improve the electrical insulation performance of polymer. The dielectric constant of polymers could be decreased as fluorinated groups incorporated because of their small dipole and the low polarizability of the C–F bond as well as the large free volume [11]. An additional positive effect of fluorinated substituents is reduced moisture absorption due to the non-polar character of fluorocarbon groups, which further reduces the dielectric constant [12]. The incorporation of fluorinated substituents in the network structure of epoxies will improve the resins durability in moist environments and lower their moisture absorption [13]. Recently, some researches have been concentrated on the investigation of fluorinated epoxy resins. Sasaki and Nakamura [14] reported that perfluorobutenyloxyphthalic anhydride cured bisphenol A type epoxy could reduce the water absorption by 75%. Sasaki [15] also studied the dielectric properties of cured epoxy resins containing perfluorobutenyloxy group and found that dielectric constants of the fluorinated epoxy resins decreased to 2.7–2.8. Maruno et al. [16] described a novel fluorinated epoxy resin bearing alicyclic segments, which had improved optical transparency and low refractive index.

Aiming at improving the dielectric properties and the moisture resistance of epoxy resins, in the present research, a novel fluorinated epoxy compound, 1,1-bis(4-glycidylesterphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane (BGTF), was synthesized and characterized. The fluorinated epoxy was thermally cured with two different kind of curing agents, *i.e.*, alicyclic anhydride HMPA and aromatic diamine DDM, respectively. The reactivity of the fluorinated epoxy towards the curing agents was studied. The thermal stability, mechanical properties, electrical and dielectric properties, as well as the water absorption of the fully cured fluorinated epoxy resins were investigated. Furthermore, the epoxy resins based on the commercial available epoxy bisphenol A diglycidyl ether (BADGE) cured with the same curing agents were also prepared and their properties were discussed in comparison with the corresponding fluorinated epoxies.

2. Experimental

2.1. Materials

Toluene, triethylamine and benzene were purchased from Beijing Chemical Reagents Co., China, which were dried and distilled prior to use. Pyridine, potassium permanganate, ethanol, hydrochloric acid were purchased from Beijing Chemical Reagents Co., China and used as received. Bisphenol A diglycidyl ether (BADGE, EEW = 189) was purchased from Shell Chemicals and used as received. Glycidol trifluoromethanesulfonic acid, hexahydro-4-methylphthalic anhydride (HMPA) and 4,4′-diaminodiphenylmethane (DDM) were purchased from Aldrich and used as received. 1-Cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN) was purchased from Shikoku Chemicals Corp. and used as received. 3′-Trifluoromethyl-2,2,2-trifluroacetophenone was prepared from anhydrous lithium trifluoroacetate and 3-bromobenzotrifluoride by Grignard reaction in our laboratory [17].

2.2. Monomer synthesis

*2.2.1. 1,1-Bis(4-tolyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane (**1**)*

3′-Trifluoromethyl-2,2,2-trifluroacetophenone (60.53 g, 0.25 mol) and anhydrous toluene (184.30 g, 2.00 mol) were added into a 500 ml three-necked flask. Then, trifluoromethane sulfonic acid (30.00 g, 0.20 mol) was added dropwise at room temperature under stirring. The mixture was stirred at room temperature for 72 h and then poured into ice water. The organic phase was separated from the aqueous phase and washed with 5% of sodium bicarbonate aqueous solution and distilled water. The product was obtained by water vapor distillation to remove the excess toluene, which was then purified by recrystallization from petroleum ether to yield white crystal. Yield: 82.70 g (81%). m.p.: 80 °C (determined by DSC). ^{1}H NMR (DMSO-d_6, δ, ppm): 2.32 (s, 6H); 6.91–6.93 (d, 4H); 7.23–7.25 (d, 4H); 7.27 (s, 1H); 7.39–7.41 (d, 1H); 7.67–7.71 (t, 1H); 7.80–7.82 (d, 1H).

FT-IR (cm^{-1}): 3033, 2926, 1514, 1151. MS: (EI, *m*/*e*, % relative intensity): 408 (M^+, 6); 339 (M−69, 100). Elem. Anal. Calcd. for $C_{23}H_{18}F_6$: C, 67.64%; H, 4.44%. Found: C, 67.63%; H, 4.61%.

*2.2.2. 1,1-Bis(4-carboxyphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane (**2**)*

A mixture of compound **1** (61.22 g, 0.15 mol), pyridine (600 ml) and distilled water (300 ml) was placed in a 2000 ml three-necked flask equipped with mechanical stirrer and a reflux condenser and then heated to reflux. To which, $KMnO_4$ (142.20 g, 0.90 mol) was added in portions during 4 h followed by refluxing with stirring for another 3 h. After that, the mixture was hot filtered to remove MnO_2, and the gained solution was concentrated to 400 ml. The solution was added to a 2000 ml three-necked flask, to which 85 g of sodium hydroxide and 500 ml of water were placed. The mixture was heated to reflux and then $KMnO_4$ (118.50 g, 0.75 mol) was added again in portions in 4 h. The mixture was refluxed for another 3 h and then cooled to 70 °C. Then, 60 ml of ethanol was added dropwise to eliminate the unreacted $KMnO_4$. After refluxed for 1 h, the mixture was hot filtered to remove the MnO_2 to afford a pale green solution. The solution was acidized with diluted hydrochloride acid to pH = 1–2, then filtrated, washed with diluted hydrochloride and water respectively, and then dried at 120 °C in vacuum to give a white powder. Yield: 63.25 g (90%). m.p.: 244 °C (determined by DSC). ^1H NMR (DMSO-d_6, δ, ppm): 7.20–7.22 (d, 4H); 7.23 (s, 1H); 7.40–7.42 (d, 1H); 7.70–7.74 (t, 1H); 7.99–8.01 (d, 1H). FT-IR (cm^{-1}): 3009, 1696, 1157. MS: (EI, *m*/*e*, % relative intensity): 468 (M^+, 6); 399 (M−69, 100). Elem. Anal. Calcd. for $C_{23}H_{14}F_6O_4$: C, 58.98%; H, 3.01%. Found C, 58.79%; H, 2.92%.

2.2.3. 1,1-Bis(4-glycidylesterphenyl)-1-(3′-trifluoromethylphenyl)-2,2,2-trifluoroethane (BGTF)

The compound **2** (30.00 g, 0.06 mol) and thionyl chloride (200 ml) were added in a 500 ml flask equipped with a reflux condenser and then two drops of *N*,*N*-dimethylformamide (DMF) were added. The mixture was refluxed for 6 h under stirring followed by vacuum distillation to remove the residue thionyl chloride. After cooled to room temperature, the white precipitate was afforded and collected by filtration. The crude product was purified by recrystallization from anhydrous petroleum ether. The yellowish powder of compound **3** was obtained after dried in vacuum. m.p.: 108 °C (determined by DSC).

Glycidol (7.84 g, 0.11 mol) was stirred with 50 ml of anhydrous benzene in a 250 ml three-necked flask. Distilled anhydrous triethylamine (10.69 g, 0.11 mol) was added and then the solution was cooled to 0 °C with an ice bath. The compound **3** (26.45 g, 0.05 mol) dissolved in 50 ml of anhydrous benzene was added to the reaction solution dropwise over a period of 2 h the solution became viscous due to the precipitation (formation) of the triethylamine hydrochloride with the reaction process. After stirring at 0 °C for 4 h, the reaction mixture was kept at room temperature for another 20 h. The precipitate of triethylamine hydrochloride was removed by filtration and the filtrate was concentrated, washed with ice-cold aqueous solution of 5% of sodium bicarbonate and distilled water repeatedly. After dehydrate over $MgSO_4$, the organic phase was concentrated with a vacuum evaporator to afford a viscous brown yellow liquid. The final product was stored in a refrigerator. Yield: 25.50 g (88%). ^1H NMR ($CDCl_3$, δ, ppm): 2.75 (s, 1H); 2.92 (s, 1H); 3.36 (s, 1H); 4.20 (s, 1H); 4.70 (s, 1H); 7.20–7.22 (d, 4H); 7.29–7.31 (d, 4H); 7.38(s, 1H); 7.47–7.51 (t, 1H); 7.65–7.67 (d, 1H); 8.04–8.06 (d, 1H). FT-IR (cm^{-1}): 3433, 3066, 2980, 1725, 1155, 907. MS: (EI, *m*/*e*, % relative intensity): 580 (M^+, 13); 511 (M−69, 100); 507 (M–73, 40). Elem. Anal. Calcd. for $C_{29}H_{22}F_6O_6$: C, 60.00%; H, 3.82%. Found: C, 60.23%; H, 4.00%.

2.3. Curing procedure of epoxy resins

The BGTF and BADGE epoxies were cured with anhydride HMPA and diamine DDM, respectively. The chemical structures of epoxies and curing agents are showed in Table 1. The reactant compositions were mixed homogeneously in a 1:0.8 molar ratio for epoxy/anhydride system and in a 1:1 molar ratio for epoxy/diamine system according to the EEW values, respectively. DDM curing system did not require a curing accelerator, but for HMPA curing system, 1 wt.% of 2E4MZ-CN was added as an accelerator and stirred until a homogeneous solution was obtained. The curing cycles are listed in Table 2, which were determined by DSC tracing of the respective epoxy/curing agent compositions. After curing, samples were allowed to cool slowly to room temperature in order to prevent cracking.

Table 1
Chemical structures of the epoxies and curing agents

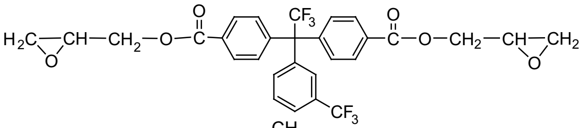
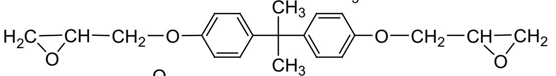
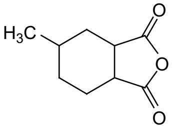
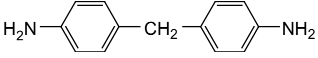
Component	Abbreviation	Chemical structure
Epoxy	BGTF	
	BADGE	
Curing agent	HMPA	
	DDM	

Table 2
Curing cycles of epoxy resins

Sample	Curing temperature (°C)	Curing time (h)	Postcure temperature (°C)	Postcure time (h)
BGTF/HMPA	120	1	150	2
BGTF/DDM	150	1	190	2
BADGE/HMPA	130	1	160	2
BADGE/DDM	160	1	200	2

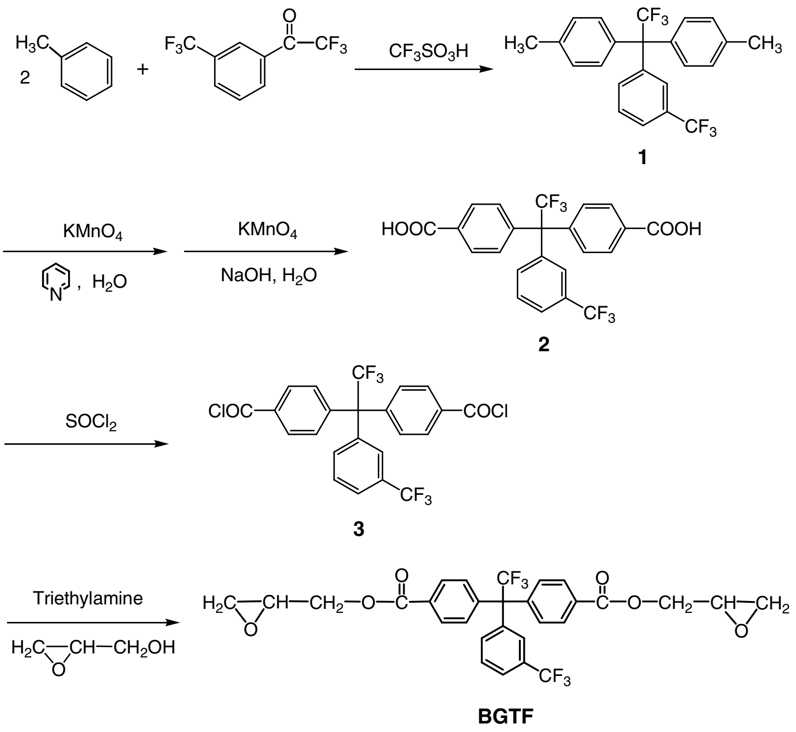
2.4. Characterization

^{1}H NMR spectra was record with a Bruker MSL-300 spectrometer using $CDCl_3$ and DMSO-d_6 as solvents. FT-IR spectra were obtained using a Perkin–Elmer 782 Fourier transfer infrared spectrophotometer. Mass spectra were recorded on an AEI MS-50 mass spectroscopy. The EEWs of epoxy resins were determined by the HCl/acetone titration method. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed on a Perkin–Elmer 7 series thermal analysis system in nitrogen at a heating rate of 20 °C min^{-1}. Dynamic mechanical analysis (DMA) was carried out a Perkin–Elmer 7 series thermal analysis system in nitrogen using at a heating rate of 5 °C min^{-1}. Mechanical properties were performed with 60 × 15 × 3 mm specimens in accordance with GB 1449-87 using an Instron 3365 Tensile Apparatus. Water absorptions were determined by weighing the changes of cured epoxy samples (Φ 50 mm × 3 mm) before and after immersion in water at 25 °C for 24 h (I) and in boiling water for 6 h (II). The electrical properties were measured on a Hewlett–Packard 4284A Presion LCR meter. The dielectric constant and dissipation factor were determined by the bridge method with an LKI-1 capacitance meter at a frequency of 1 MHz at 25 °C. Rheological measurements were conducted on an AR2000 rheometer of TA Instruments. The measurements for the compacted resin discs were performed using a parallel-plate fixture (diameter: 25 mm, gap: 1.0 mm) by flow mode with a shear rate of 1.5 s^{-1} and a heating rate of 5 °C min^{-1}.

3. Results and discussion

3.1. Synthesis of BGTF

The fluorinated epoxy BGTF was synthesized through a four-step procedure as shown in Scheme 1. Firstly, 3′-trifluoromethyl-2,2,2-trifluroacetophenone was reacted with toluene catalyzed by CF_3SO_3H to yield compound **1** in good yield. Then, the dimethyl intermediate compound **1** was oxidized by $KMnO_4$ in base condition to give a diacid compound **2**, which was reacted with $SOCl_2$ to give a diacyl chloride compound **3**. Finally, the fluorinated epoxy BGTF was obtained by the reaction of compound **3** with glycidol. The chemical structures of these compounds were confirmed by ^{1}H NMR, FT-IR, elemental analysis and MS. Fig. 1 shows the ^{1}H NMR spectra of compounds **1** and **2** in DMSO-d_6, respectively, as well as that of BGTF in $CDCl_3$. All the signals corresponding to the proposed structures were observed. The resonance



Scheme 1. Synthesis of the fluorinated epoxy compound BGTF.

signals of aromatic protons in compound **1** appeared in the region of 6.91–7.82 ppm and the signal of methyl protons showed at 2.32 ppm (Fig. 1a). In ^{1}H NMR spectrum of compound **2** (Fig. 1b), the signal assigned to the protons H_2 in aromatic ring adjacent to the carboxyl group shifted to the downfield in the range of 7.99–8.01 ppm because of the effect of electron drawing carboxyl group. In ^{1}H NMR spectrum of BGTF (Fig. 1c), the signals assigned to the protons in aromatic rings appeared in the region of 7.20–8.06 ppm. The signals of protons H_8 and H_9 in oxirane ring were observed in the range of 3.34–3.38 and 2.74–2.93 ppm, respectively. The signal of methylene proton H_7 showed at 4.18–4.72 ppm. Fig. 2 shows the FT-IR spectra of these monomers. The absorption due to the C–F linkage was observed in the range of 1150–1157 cm^{-1} for all the monomers. As comparing the FT-IR spectra of compounds **1** and **2**, we found that the absorption at 2926 cm^{-1} due to the methyl C–H vibration disappeared in the latter and the absorption of carboxyl C=O was observed at 1696 cm^{-1}, which then shifted to 1725 cm^{-1} because of the formation of ester in BGTF. The absorption attributed to the oxirane ring was observed at 907 cm^{-1} in the FT-IR spectrum of BGTF. The elemental analysis results are listed in Table 3, which were in good agreement with the calculated values. In the mass spectrum of BGTF, the characteristic peaks at 580 (M^+, base), 511 ($M-CF_3$) and 507 ($M-OCH_2CHOCH_2$) were observed. The EEW of BGTF was measured according to the titration procedure. The measured EEW value is 292 g/equiv, which was close to the theoretical value of 290 g/equiv. These results confirmed that pure BGTF compound was obtained.

3.2. Rheological properties of epoxy resins

The viscosities of epoxies BGTF and BADGE as a function of temperature were evaluated by rheological measurement under parallel plate flow mode with a heating rate of 5 °C min^{-1} from room temperature to 200 °C, respectively. The rheological curves are shown in Fig. 3. It is found that the fluorinated epoxy BGTF exhibited the viscosity higher than that of BADGE. A decreasing in viscosity along with the increasing of temperature was observed for both of epoxies. Then, a balance was reached as the temperature higher than 70 °C for BADGE and 130 °C for BGFT, respectively. As the temperature enhanced to

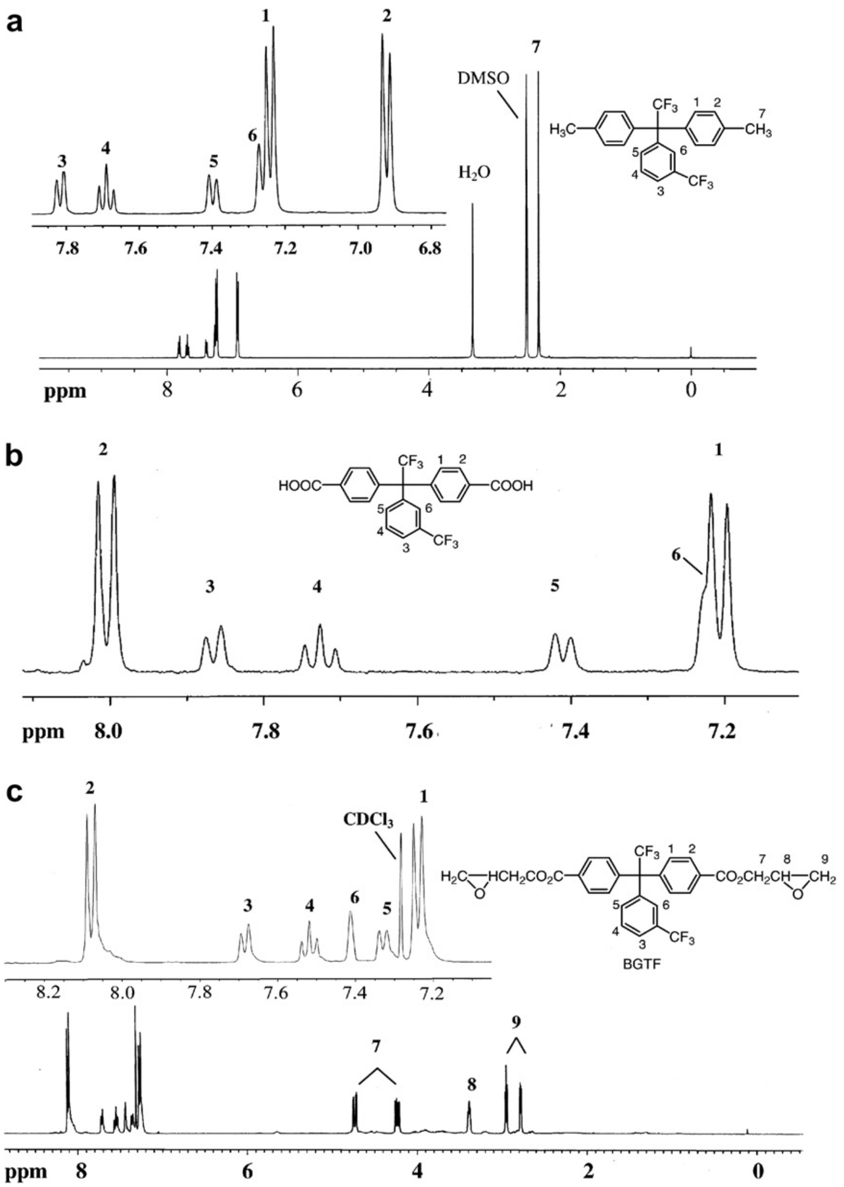


Fig. 1. ^{1}H NMR spectra of compound 1 (a), compound 2 (b) in DMSO-d_6 and BGTF (c) in $CDCl_3$.

140 °C, the viscosities of both closed to 0.2 Pa s. The rheological behavior of epoxy resin systems BGTF/HMPA, BGTF/DDM, BADGE/HMPA and BADGE/DDM were characterized and shown in Fig. 4. The viscosities of these epoxy resin systems dropped with the temperature increasing due to the molecular movement. However, as the temperature increased higher than a definite degree, the viscosities increased dramatically because of the gelation occurred during this stage [18]. It revealed that the gel temperature of BGTF system occurred earlier than that of BADGE system. Fig. 5 shows the viscosities as a function of time for epoxy resins holding at 120 °C. It is found that BGTF/HMPA, BGTF/DDM, BADGE/HMPA and BADGE/DDM gave the gel times at about 11, 17, 7 and 12 min, respectively. Moreover, the gel time for BGTF system occurred later than that for BADGE system as the epoxies cured at the same temperature. It may be related to the relatively moderate curing reaction of BGTF system, which also can be confirmed by their DSC thermograms.

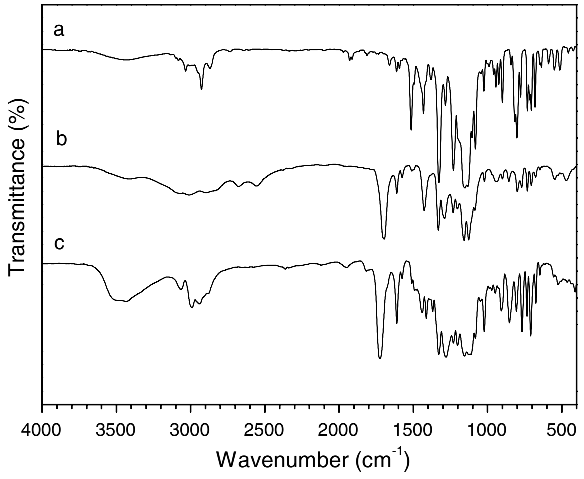


Fig. 2. FT-IR spectra of compound **1** (a), compound **2** (b) and BGTF (c).

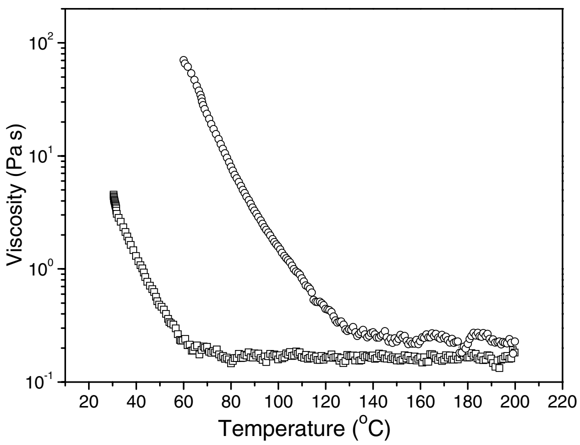


Fig. 3. Viscosity as a function of temperature for epoxy BADGE (□) and BGTF (○).

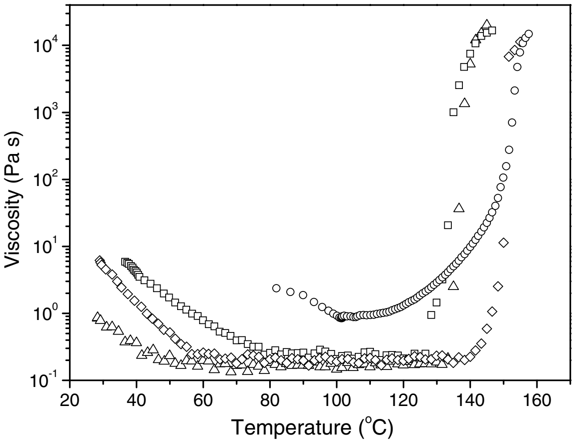


Fig. 4. Viscosity as a function of temperature for epoxy resins: (□) BGTF/HMPA; (○) BGTF/DDM; (△) BADGE/HMPA; (◇) BADGE/DDM.

3.3. Reactivity of epoxy resins and curing agents

The curing behavior of the epoxy and curing agent compositions were studied by DSC. Significant caution was taken during the DSC study of the polymerization reactions to obtain homogenous mixture of the epoxy resins and curing agents. The reactivity of the epoxies can be directly read from the exothermic starting temperature. A curing agent that exhibits a lower exothermic starting temperature under the same set of curing conditions is more reactive towards the epoxy resins [19,20]. Fig. 6 shows the DSC thermograms for the curing procedure of BGTF and BADGE with HMPA and DDM, respectively. The exothermic starting temperatures of BGTF/HMPA, BGTF/DDM, BADGE/HMPA and BADGE/DDM exhibited at 99, 93, 138 and 132 °C, respectively. As comparing with the reactivities of these epoxy resins, we found that the BGTF gave the exothermic starting temperature lower than that of BADGE both in anhydride and in aromatic diamine curing systems. Therefore, we can cure BGTF in lower temperature than that of BADGE. However, it is also found that the BGTF exhibited weak and broad exothermic peaks, which indicated that the curing reaction of BGTF is a moderate process.

3.4. Thermal properties of the cured resins

TGA is the most favored technique for rapid evaluation in comparing and ranking the thermal

Table 3
Elemental analysis of monomers

Monomer	Molecular formula	C (%)		H (%)	
		Found	Calculated	Found	Calculated
Compound **1**	$C_{23}H_{18}F_6$	67.63	67.64	4.61	4.44
Compound **2**	$C_{23}H_{14}F_6O_4$	58.79	58.98	2.92	3.01
BGTF	$C_{29}H_{22}F_6O_6$	60.23	60.00	4.00	3.82

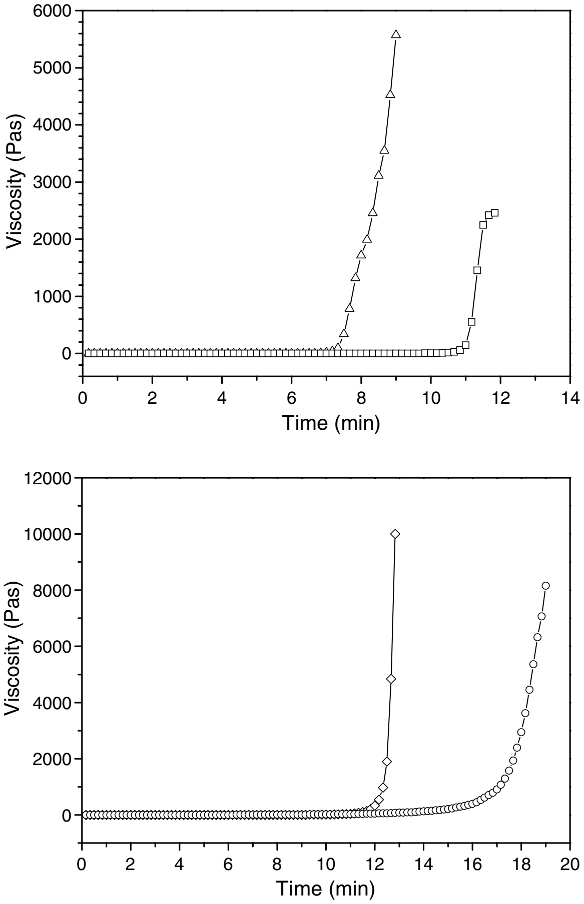


Fig. 5. Viscosities as a function of time for epoxy resins holding at 120 °C: (□) BGTF/HMPA; (△) BADGE/HMPA; (○) BGTF/DDM; (◇) BADGE/DDM.

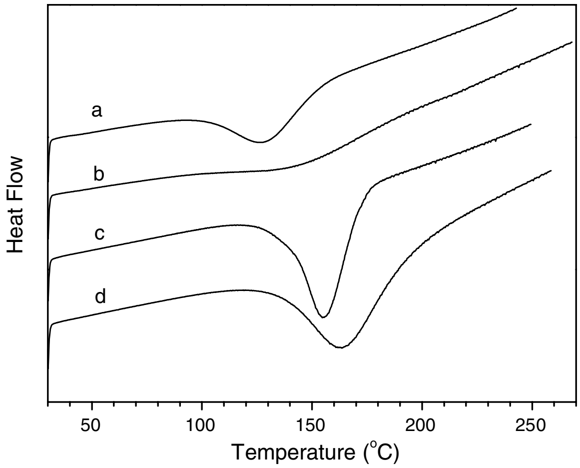


Fig. 6. DSC thermograms of the curing procedure of epoxy resins: (a) BGTF/HMPA; (b) BGTF/DDM; (c) BADGE/HMPA; (d) BADGE/DDM.

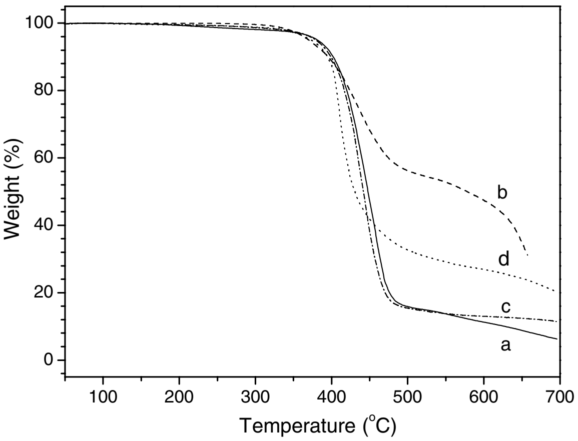


Fig. 7. TGA thermograms of cured epoxy resins: (a) BGTF/HMPA; (b) BGTF/DDM; (c) BADGE/HMPA; (d) BADGE/DDM.

stability. The TGA thermograms of cured epoxy resins BGTF/HMPA, BGTF/DDM, BADGE/HMPA and BADGE/DDM in nitrogen are shown in Fig. 7. It is found that the cured epoxy resins did not loss any original weight before the scanning temperature reached up to 300 °C, implying that they have good thermal stability below 300 °C. As the scanning temperature rose to 370 °C, the epoxy resins exhibited a slight weight loss. The decomposition temperature at 5% of weight loss (T_5) for BGTF/HMPA and BGTF/DDM epoxy resins were at 382 and 370 °C, respectively, and that for BADGE/HMPA and BADGE/DDM epoxy resins were at 380 and 374 °C, respectively (Table 4). However, as the scanning temperature over 400 °C, these epoxy resins showed a rapid thermal decomposition. The BGTF/DDM resin revealed higher thermal stability as comparing with BADGE/DDM resin, the residual weight retention at 600 °C for the former was 47.3%, which was much higher than that of BADGE/DDM (26.9%). The improved thermal stability of BGTF/DDM is probably attributed

Table 4
Thermal properties of the epoxy resins[a]

Sample	T_5 (°C)	T_{10} (°C)	R_w (%)
BGTF/HMPA	382	402	11.3
BGTF/DDM	370	395	47.3
BADGE/HMPA	380	399	13.0
BADGE/DDM	374	395	26.9

[a] T_5: Decomposition temperatures at 5% of weight loss; T_{10}: decomposition temperatures at 10% of weight loss, respectively; R_w: residual weight retention at 600 °C.

to the presence of CF_3 groups in the polymer backbone. As comparing with the epoxy resins cured with DDM, the resins cured with HMPA exhibited much dramatically degradation behavior at high temperature. The relatively low thermal stability of the epoxy resins cured with HMPA can be explained by the presence of alicyclic structure in the polymer, which has low thermal stability as compared with aromatic structure. Moreover, the TGA trace of BGTF/HMPA is similar to that of BADGE/HMPA despite the former derived from the fluorinated epoxy BGTF. We suspect that the effect of CF_3 groups on improvement of the thermal stability may be concealed in HMPA curing system because of their low thermal stability at high temperature.

DMA curves of the cured epoxy resins are shown in Fig. 8 and the data are summarized in Table 5. Their glass transition temperatures (the peak temperature of the loss tangent) are in the range of 164–187 °C. The heights of loss tangent are in the range of 0.41–0.65. The storage modulus ranged in 1.63–2.23 GPa at 50 °C and 0.024–0.039 GPa at $T_g + 40$ °C, respectively. According to rubber elasticity theory [21]: the crosslink density is proportionate to the storage modulus at $T_g + 40$ °C, therefore, the ratio of crosslink density for BGTF/HMPA:BGTF/DDM: BADGE/HMPA:BADGE/DDM is 1:1.1:1.2:1.6. The crosslink densities of these resins have no significant difference, which also can be confirmed by their similar T_g values.

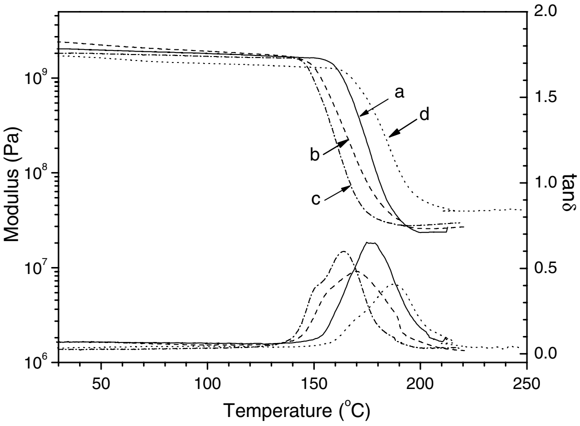


Fig. 8. DMA curves of the cured epoxy resins: (a) BGTF/HMPA; (b) BGTF/DDM; (c) BADGE/HMPA; (d) BADGE/DDM.

Table 5
DMA analysis of the epoxy resins

Sample	T_g (°C) peak of tan δ	Storage modulus (GPa)	
		50 °C	$T_g + 40$ °C
BGTF/HMPA	175	1.97	0.024
BGTF/DDM	170	2.23	0.026
BADGE/HMPA	164	1.81	0.028
BADGE/DDM	187	1.63	0.039

3.5. Mechanical properties

The mechanical properties of cured epoxy resins were investigated and the results are listed in Table 6. The BGTF/HMPA and BADGE/HMPA had the similar flexural strengths of 123 and 128 MPa, respectively, which were 35 and 27 MPa higher than the corresponding epoxy resins cured with DDM, respectively. The BGTF and BADGE cured with HMPA showed the flexural moduli in the range of 2.67–2.88 GPa, which were also relatively higher than that for epoxy resins cured with diamine. The epoxy resins with anhydride curing system exhibited the enhanced tensile strengths as compared with the corresponding epoxy resins cured with diamine. The tensile moduli of these epoxy resins were measured in the range of 1.55–1.92 GPa. The results suggested that the epoxies cured with anhydride have the improved mechanical properties than those cured with aromatic diamine. Moreover, as comparing with the commercial epoxy BADGE system, we found that the fluorinated epoxy BGTF system exhibited the mechanical properties as good as the cured BADGE system no matter what kind of curing agents applied.

3.6. Electrical and dielectric properties

The electrical and dielectric properties of the cured epoxy resins are shown in Table 7. The volume resistivities (ρ_v) and surface resistivities (ρ_s) of the epoxy resins were at the level of $1.2–3.6 \times 10^{16}\ \Omega$ cm and $2.2–4.9 \times 10^{16}\ \Omega$, respectively. The dielectric constants (ε_r) and the dielectric dissipation factors (tan δ) at 1 MHz were measured in the range of 3.2–3.6 and $2.1–7.3 \times 10^{-3}$, respectively. In comparison, the cured fluorinated epoxy resins exhibited improved dielectric properties than the commercial BADGE epoxy resins cured with the corresponding curing agents. The decreased dielectric constants of the fluorinated epoxy resins can be interpreted by the low polarizability of the C–F bond and the large free volume of CF_3 groups. These results suggested

Table 6
Mechanical properties of the epoxy resins

Sample	Flexural strength (MPa)	Flexural modulus (GPa)	Tensile strength (MPa)	Tensile modulus (GPa)
BGTF/HMPA	123	2.88	76	1.70
BGTF/DDM	88	2.79	56	1.55
BADGE/HMPA	128	2.67	65	1.82
BADGE/DDM	101	2.17	53	1.92

Table 7
Electrical and dielectric properties of the cured epoxy resins and their water absorption[a]

Sample	ρ_v (Ω cm)	ρ_s (Ω)	ε_r (1 MHz)	$\tan\delta$	Water absorption (%)	
					I	II
BGTF/HMPA	3.6×10^{16}	2.2×10^{16}	3.3	2.8×10^{-3}	0.38	0.85
BGTF/DDM	1.2×10^{16}	2.8×10^{16}	3.2	2.1×10^{-3}	0.40	0.90
BADGE/HMPA	1.9×10^{16}	4.9×10^{16}	3.5	7.3×10^{-3}	0.49	0.92
BADGE/DDM	2.7×10^{16}	4.5×10^{16}	3.6	6.9×10^{-3}	0.41	0.98

[a] ρ_v: volume resistivity; ρ_s: surface resistivity; ε_r: dielectric constant at 1 MHz at 25 °C; $\tan\delta$: dissipation factor; water absorption, I: immersion in water at 25 °C for 24 h; II: immersion in boiling water for 6 h.

that the CF_3 groups in the network structure of epoxy resins play an important role in their electrical and dielectric performance.

3.7. Water absorption

In actual service, epoxy composites are subject to varying conditions of humidity and temperature. Unfortunately, moisture has a detrimental effect, especially at elevated temperature, on the mechanical properties of epoxy composites [22,23]. Low water absorption is an important factor for the advanced microelectronic packaging materials because the absorbed H_2O molecules have obvious influence on their electrical insulating and dielectric performance. Table 7 summaries the water absorption of the cured epoxy resins, in which the water absorption was determined by immersing the dried cured epoxy resin samples (Φ 50 mm×3 mm) in water at room temperature for 24 h (method I), or in boiling water at 100 °C for 6 h (method II), followed by weighing the changes of samples. The water absorptions of cured BGTF/HMPA and BGTF/DDM determined by method I were 0.38% and 0.40%, respectively, and those measured by method II gave the higher values, which were 0.85% and 0.90%, respectively. The absorption of water by epoxy resin has been described by simple Fickian diffusion [24]. The relatively high water absorptions gained in method II may be related to the revealed experimental temperature, which could accelerate the diffusion of H_2O molecules into the polymer. No matter what kind of curing agents were employed, the cured fluorinated BGTF epoxy resins exhibited lower water absorption than those derived from the commercial BADGE epoxy resins. Fig. 9 depicts the changes of water absorption of these epoxy resins according to the time. We found that these epoxy resins showed the water absorptions increased with the time prolongation. Moreover, the results also clearly indicated that the fluorinated epoxy resins exhibited lower water absorption than that of non-fluorinated epoxy resins, which is

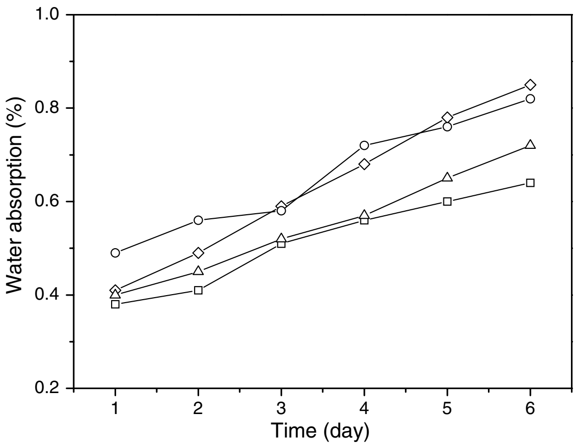


Fig. 9. Water absorption of the cured epoxy resins: (□) BGTF/HMPA; (△) BADGE/HMPA; (○) BGTF/DDM; (◇) BADGE/DDM.

attributed to the existence of strong hydrophobic fluorine atom.

4. Conclusions

A novel fluorinated epoxy compound BGTF was successfully synthesized by a four-step procedure, which was then thermally cured with alicyclic anhydride HMPA or aromatic diamine DDM. The reactivity and the properties of the fully cured BGTF epoxy resins were investigated and compared with the cured commercial BADGE epoxy resins. The experimental results indicated that the BGTF gave the exothermic starting temperature lower than BADGE no mater what kind of curing agents applied, implying the reactivity of the former is higher than the latter. The fully cured BGTF have good thermal stability with glass transition temperature of 170–175 °C and thermal decomposition temperature at 5% weight loss of 370–382 °C in nitrogen. The fluorinated BGTF epoxy resins exhibited the mechanical properties as good as the commercial BADGE epoxy resins, the flexural strengths were in the range of 88–123 MPa and tensile strengths were around 56–76 MPa. As comparing with BADGE epoxy resins, the cured BGTF epoxy resins exhibited lower dielectric constants and water absorptions, which attributed to the incorporation of CF_3 groups in the network structure of epoxy resins.

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