Synthesis and Properties of Novel Fluorinated Epoxy Resins

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ABSTRACT: A novel fluorinated epoxy compound, 4,4′-bis(2,3-epoxypropoxy-phenyl)-1-(3-trifluoromethylphenyl)-2,2,2-trifluoroethane (BEF), was synthesized starting from the coupling of phenol with 3′-trifluoromethyl-2,2,2-triflur-oacetophenone catalyzed by Lewis acid to yield an intermediate compound, which was then converted to the fluorinated epoxy by epoxidation with epichlorohydrin. BEF could be thermally cured with organic anhydride or aromatic amine as curing agents to produce thermally cured epoxy resins. Experimental results demonstrated that the thermally cured fluorinated epoxy resins showed good thermal stability with decomposition temperature at 5% weight loss of 342–364°C in nitrogen, high glass transition temperature (T_g) of 165–171°C (determined by DMA), and outstanding mechanical properties with flexural strengths of 79–119 MPa, flexural moduli of 2085–2130 MPa. The thermally cured fluorinated epoxy resins also exhibited excellent electric insulating properties with volume resistivity of $1.59–9.23 \times 10^{16}$ Ω cm and surface resistivity of $4.81 \times 10^{15}–7.70 \times 10^{16}$ Ω. The dielectric constants at 1 MHz were measured in the range of 3.1–3.4 and the dielectric dissipation factor (tan δ) in the range of $1.38–2.48 \times 10^{-3}$. It was found that the fluorinated epoxy resins have improved electric insulating and dielectric properties as well as lower moisture adsorption compared with the corresponding commercial Bisphenol A type epoxy resins.
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Key words: fluorinated epoxy resins; dielectric properties; thermal stability

INTRODUCTION

Advanced epoxy resin materials have been extensively used in electronic packaging as epoxy molding compound, electrically conductive silver paste and die attach adhesives etc. owing to their excellent chemical resistance, good electrical insulating properties, high adhesion, and good processability.[1–5] With the rapid development of advanced microelectronic packaging technology, the epoxy resin materials should be improved their combined properties to satisfy the higher and higher requirements, including: (1) better thermal stability; (2) lower dielectric constant and dissipation factor with low moisture adsorption; (3) lower coefficient of thermal expansion (CTE) and lower internal stress; (4) high mechanical strength and low modulus.[6–9] Thus, a lot of efforts have been made in recent years to develop novel epoxy resin materials with unique chemical structures. For instance, Lin et al.[10] have reported a novel 2,6-dimethyl phenoldipentene epoxy resin, which showed low dielectric constant (3.1) and low dissipation factor (0.065), low modulus and low moisture adsorption (1.21–2.18%).

Of many efforts to improve the properties of conventional epoxy resins, the introduction of fluorine-containing groups in backbone or side chain of the polymers leading to great benefits such as chemical stability, low dielectric constant, low dissipation factor and low moisture adsorption, is one of the most efficient methods to meet the above-mentioned demands. That arises from the special characteristics of fluorine, such as low polarizability, small dipole, hydrophobicity and oxidization-resistance as well as relative larger free volume.[11,12] Hence, considerable efforts have been made recently to prepare novel fluorinated epoxy resins. Cassidy et al.[13] has reported a series of fluorinated epoxy resins derived from 2-phenyl-1,1,1,3,3,3-hexafluoropropan-2-ol and its derivatives. Maruno et al.[14] has synthesized a novel fluorinated epoxy resin bearing alicyclic segments. Maier[15] has reported several fluorinated epoxy resins with low dielectric constants for the potential microelectronic packaging applications.

In this study, a novel fluorinated epoxy compound, 4,4′-bis(2,3-epoxypropoxy-phenyl)-1-(3-trifluoromethyl-phenyl)-2,2,2-trifluoroethane (BEF), was synthesized, which was then characterized by thermal-curing with two different types of curing agents, liquid organic anhydride and solid aromatic diamines.

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Experimental results demonstrated that the fluorinated epoxy could be completely thermally cured to give thermal-cured epoxy resins, which exhibited improved combined properties compared with the corresponding commercial Bisphenol A epoxy resins.

EXPERIMENTAL

Materials

Phenol, $ZnCl_2$, epichlorohydrin, hydrochloride and ethanol were purchased from Beijing Chemical Reagents Corp., China, and used as received. Bisphenol-A epoxy 828 (DGEBA) was purchased from Shell and used as received. Hexahydro-4-methylphthalic anhydride (HMPA) was purchased from Acros and used as received. 3′-Trifluoromethyl-2,2,2-trifluroacetophenone[16] and 1,4-bis(4-amino-2-trifluoromethyl-phenoxy)benzene (6FAPB)[17] were synthesized in this laboratory according to the method previously reported. α,α-Bis(4-amino-3,5-dimethylphenyl)diphenylmethane (TMDA) was prepared according to the literature.[18]

Measurements

Differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) were recorded on a Perkin–Elmer 7 series thermal analysis system at a heating rate of 10°C/min. FTIR spectra were obtained with a Perkin–Elmer 782 Fourier transform spectrophotometer. Mass spectra were obtained on an AEI MS-50 mass spectrometer. Mechanical properties were performed with 60 mm × 15 mm × 3 mm specimens in accordance with GB 1449-87. Water adsorptions were determined by immersing the thermal-cured epoxy resin samples (φ50 mm × 3 mm) in water at 25°C for 24 h or in boiling water for 6 h, followed by weighing. 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 and 25°C.

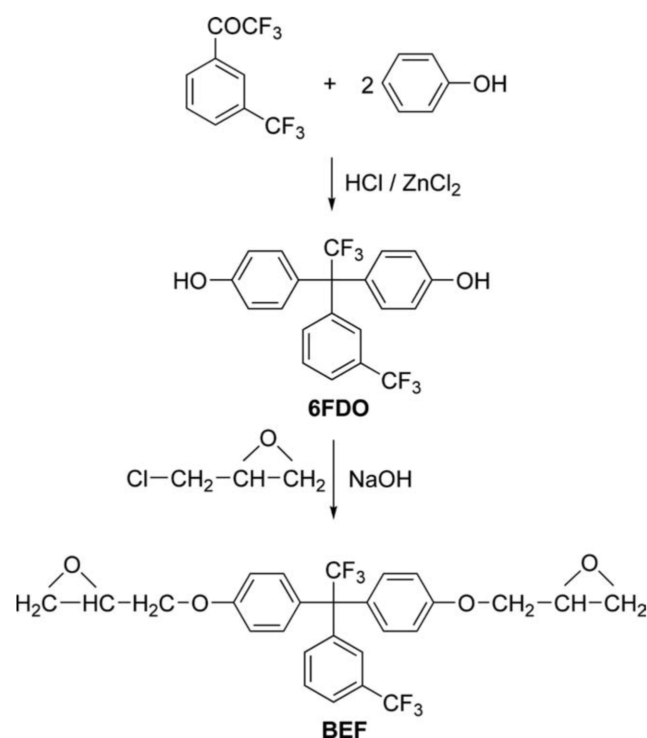
Synthesis of the fluorinated epoxy resin

1,1′-Bis(4-hydroxyphenyl)-1-(3-trifluoromethylphenyl)-2,2,2-trifluoroethane (6FDO)

In a 250-mL three-necked flask equipped with a reflux condenser and a gas inlet tube, 3′-trifluoromethyl-2,2,2-trifluroacetophenone (36.30 g, 0.15mol) was mixed with phenol (56.50 g, 0.60 mol) and 1.50 g of anhydrous $ZnCl_2$. The mixture was heated at 100°C with stirring while dry hydrogen chloride gas was bubbled into the flask. With the reaction processing, the reaction mixture gradually became a pale salmon solution. After 6 h, the mixture was poured into excess of hot water with agitation. The precipitate was collected and washed with hot water for three times. The crude product was purified by recrystallization in ethanol/water (80/20 mL) to give a white crystal. Yield: 48.20g (78%), m.p.: 200–201°C (determined by DSC). FTIR (cm^{-1}): 3269, 1516, 1226, 1151. ^1H NMR (300MHz, DMSO-d_6, ppm): 6.67-6.69 (d, 4H), 6.71-6.74 (d, 4H), 7.15 (s, 1H), 7.31-7.34 (d, 1H), 7.54-7.59 (t, 1H), 7.67-7.69 (d, 1H). Mass spectrometry (MS): [electron ionization (EI), *m/e*, percentage of relative intensity]: 412 (M+, 18), 343 (M-69, 100), 249 (M-163, 8), 197. 213,7 Elemental analysis: Calcd. for $C_{21}H_{14}F_6O_2$: C, 61.17%; H, 3.42%. Found: C, 61.08%; H, 3.43%.

4,4′-Bis(2,3-epoxypropoxyphenyl)-1-(3-trifluoromethylphenyl)-2,2,2-trifluoroethane

A 500-mL three-necked flask equipped with a stirrer, a Dean-Stark trap with a reflux condenser and a thermometer, was placed 27.20 g (0.06 mol) of 6FDO and 122.00 g (1.32 mol) of epichlorohydrin. The mixture was heated at 65°C, to which 11.00 g of 48% aqueous NaOH was added dropwise in 1 h. The reaction was processed at 65°C for 2 h, during which the water was removed by azeotrope with epichlorohydrin. After cooling to room temperature, the precipitate was removed by filtration and the filtrate



Scheme 1 Synthesis pathway of the fluorinated epoxy resin (BEF).

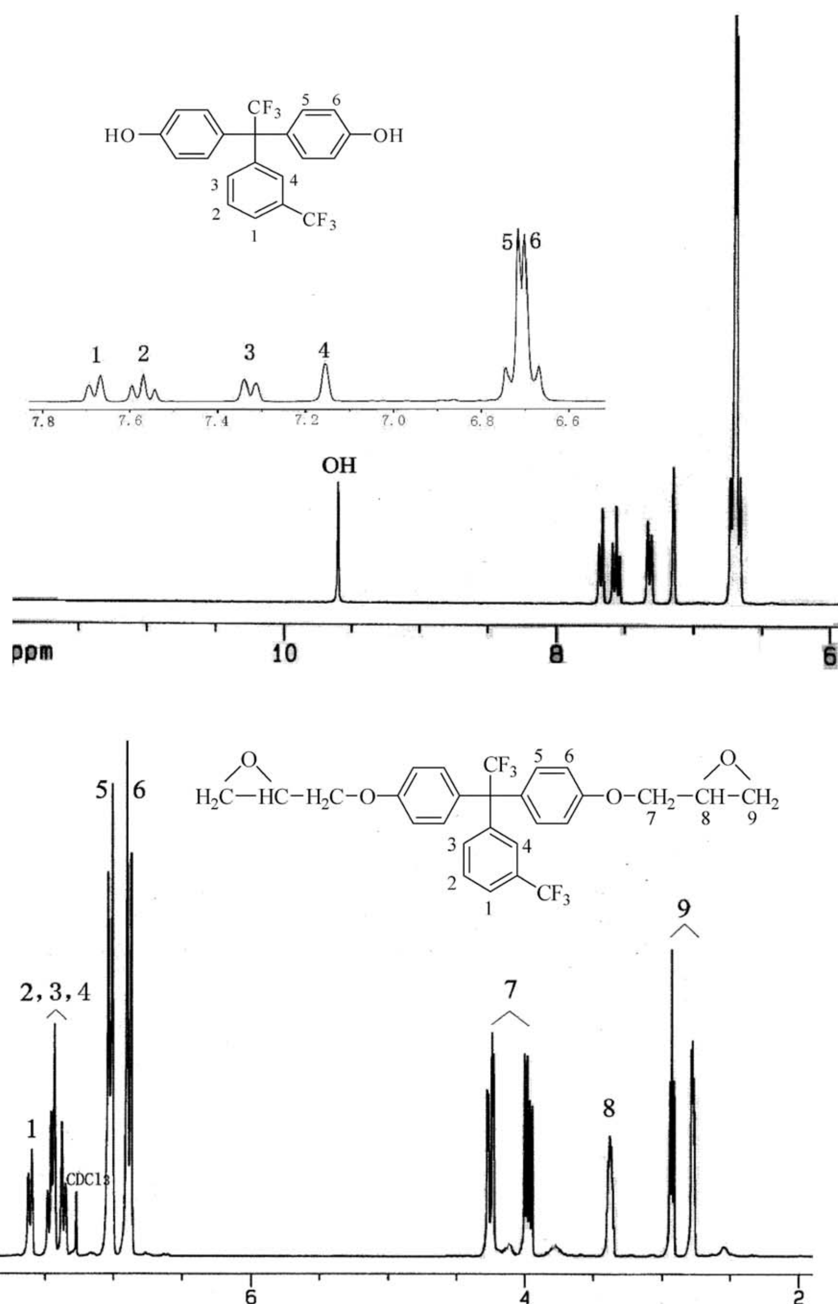


Figure 1 ^{1}H NMR Spectra of the fluorinated epoxy resin (BEF) in $CDCl_3$ and its intermediate compound (6FDO) in DMSO-d_6 (300 MHz).

was washed with water for three times, and dried by $MgSO_4$. The organic phase was distilled to remove the excess of epichlorohydrin to afford a clear and viscous liquid. FTIR (cm^{-1}): 2930, 1610, 1513, 1328, 1255, 1151, 916. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 2.68-2.90 (m, 4H); 3.29-3.31 (m, 2H), 3.81-4.21 (m, 4H), 6.79-6.82 (d, 4H), 6.93-6.96 (d, 4H), 7.27-7.40 (m, 3H), 7.52-7.54 (d, 1H). Mass spectrometry (MS): [electron ionization (EI), *m/e*, percentage of relative intensity]: 524 (M^{+}, 50), 455 (M-CF_3, 100), 399 (M-CF_3-CH_2CHOCH_2, 38) and 343 [M-CF3-2(CH_2CHOCH_2), 18].

Thermal-curing of the fluorinated epoxy resin

The fluorinated epoxy compound (BEF) was first tested for thermally curing with an organic anhydride, i.e., HMPA, as the curing agent. BEF was mixed with HMPA at room temperature in equivalent ratios of anhydride/epoxy in the range of 0.70–0.90, then 2-ethyl-4-methylimidazole (0.5 wt %) as curing catalyst was added. The mixture was placed in a plate and then heated to 120°C for 1 h, and 150°C for 3 h to yield the anhydride-cured resin, EP-1(BEF-HMPA).

Then, two aromatic diamines (6FAPB and TMDA) were used as the curing agents to thermally cure BEF resin in the diamine/epoxy equivalent ratio of 1:1. The thermal-curing was carried out by heating the resin mixture to 150°C for 2 h, and 200°C for 2 h to give the amine-cured resins, EP-2 (BEF-6FAPB) and EP-3 (BEF-TMDA), respectively.

In comparison, the commercial Bisphenol-A epoxy resin 828 (DGEBA) was also cured with HMPA, 6FAPB or TMDA at the same conditions as described above to give the cured resins EP-4 (DGEBA-HMPA), EP-5 (DGEBA-6FAPB), and EP-6 (DGEBA-TMDA), respectively.

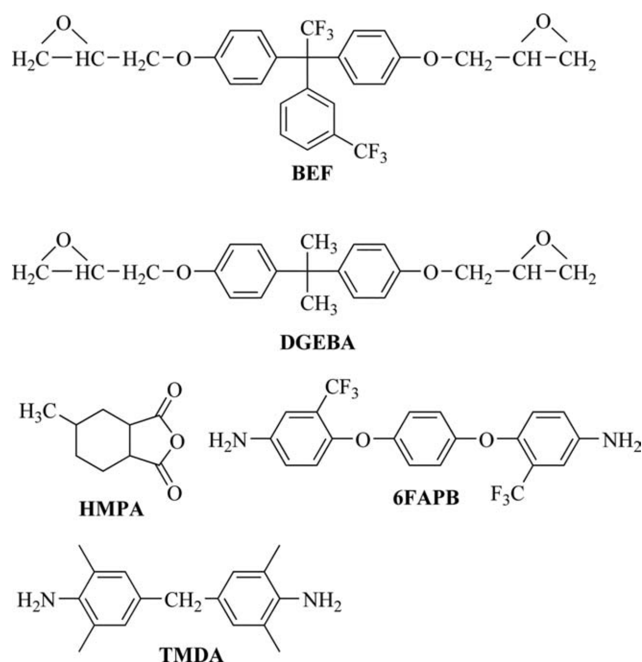
RESULTS AND DISCUSSION

Synthesis of the fluorinated epoxy resin

The fluorinated epoxy resin was synthesized by a two-step synthesis procedure as showed in Scheme 1. First, 3′-trifluoromethyl-2,2,2-trifluroacetophenone was reacted with phenol catalyzed by a Lewis acid, $HCl/ZnCl_2$, to yield a fluorinated diphenol intermediate compound (6FDO) in good yield, which was purified by recrystallization in the mixture of ethanol and water. The fluorinated epoxy resin (BEF) was prepared by the reaction of 6FDO with excess of epichlorohydrin catalyzed by NaOH (48 wt %) at 65°C. The chemical structures of 6FDO and BEF were confirmed by elemental analysis, MS, ^{1}H NMR, and FTIR spectra. Figure 1 shows the ^{1}H NMR spectra of 6FDO and BEF, in which all of the absorptions were assigned with the corresponding protons in the expected chemical structures. In ^{1}H NMR spectrum of BEF, the absorptions at δ2.68–2.90 (m, 4H) and 3.29–3.31 (m, 2H) were assigned to the protons H_8 and H_9 in oxirane ring, respectively. The peaks at δ3.81 and 4.21 (m, 4H) were attributed to the proton H_7 of methylene in BEF. The absorptions at δ6.79–6.82 (d, 4H), 6.93–6.96 (d, 4H), 7.27–7.40 (m, 3H), and 7.52–7.54 (d, 1H) were assigned to the protons H_1-H_6 of aromatic rings. Comparing the FTIR spectra of BEF and 6FDO, the absorption at 3270 cm^{-1} of 6FDO was completely disappeared in BEF, while the characteristic absorptions at 915 cm^{-1} for oxirane were observed. The measured EEW value is 274-276 g/equiv, which was close to the theoretical value of 262 g/equiv, and its absolute viscosity measured at room temperature was 3.20×10^5 mPa s. The impurities were measured with Na^+ of 1.9 ppm, Cl^- of 2.2 ppm.

Thermal curing of the fluorinated epoxy resin

The fluorinated epoxy resin BEF was cured at programmed thermal curing procedures with two different kinds of curing agents in Scheme 2, one is aliphatic anhydride (HMPA) and another are two solid aromatic diamines (6FAPB and TMDA). HMPA was a liquid aliphatic anhydride at room temperature, which was easy to mix with BEF. The BEF/HMPA mixtures in different equivalent ratios were thermally cured to produce the amine-cured epoxy resins. Figure 2 compares the dynamic DSC curves of the BEF/HMPA mixtures with HMPA to BEF ratios (*R*) in the range of 0.70–0.90. It can be seen that exothermic peak temperatures of the BEF/HMPA mixtures were observed in the range of 148–152°C, indicating that the anhydride/epoxy ratios did not have obvious effect on the exothermic reaction in the thermal curing. However, the glass transition temperatures (T_g) of the thermal-cured epoxy resins depended greatly on the ratios of HMPA to BEF(R) (Table I). The T_g values of the anhydride-cured epoxy resins increased gradually with increasing of *R* values. For instance, the HMPA-cured resin with $R = 0.85$ has the T_g of 151.2°C, 28.8°C higher than that (132.4°C) with $R = 0.70$ and 23.1°C higher than that (138.1°C) with $R = 0.75$, respectively. Further higher *R* value (0.90) result in the T_g value of 167.9°C, indicating that high *R* values would benefit in improving the thermal properties of the thermal-cured fluorinated epoxy resin. The anhydride-cured resins with different *R* values exhibited similar mechanical properties with flexural strengths of 86–120 MPa and flexural modulus of 1.90–2.20 GPa.



Scheme 2 Chemical structures of the epoxy resins and curing agents.

Figure 3 shows the impact of curing temperatures on the T_g values and the flexural strength of the anhydride-cured resin (EP-1). It can be seen that the BEF/HMPA system could be completely cured at

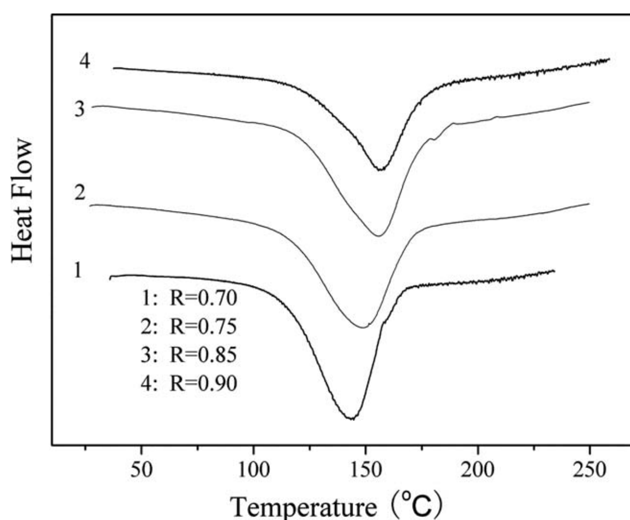


Figure 2 DSC curves of the fluorinated epoxy resin (BEF) cured with HMPA in different HMPA/BEF equivalent ratios (R).

150°C for 3 h to yield an anhydride-cured resin with T_g of 168°C and flexural strength of 120*M* Pa. However, lower curing temperatures (<140°C) could not ensure the thermal-curing being completed, resulting in the cured resins with low T_gs and low flexural strengths, and higher temperature (>170°C) would result in the thermal-cured resin with deteriorated flexural strength and reduced T_g value, probably due to the thermal oxidative damage of the epoxy chemical structures. Clearly, the curing temperatures have strong impact on the mechanical and thermal properties of the thermal-cured epoxy resins.

Figure 4 compares the exothermal behaviors of BEF cured with three different curing agents, including HMPA, 6FAPB and TMDA, in which it can be seen that the exothermic peak temperatures increased in the order of HMPA(150°C) < 6FAPB(200°C) < TMDA(210°C), demonstrating that the aliphatic anhydride (HMPA) is more reactive than the aromatic diamines (6FAPB and TMDA). TMDA, probably due to the bulky steric hindrance of the multimethyl groups in the α-positions of amine groups, exhibited lower reactivity toward BEF than 6FAPB. The electron-donating ability of the ether linkage (-O-) in 6FAPB molecular structure

TABLE I
Thermal and Mechanical Properties of the Thermal-Cured BEF Resins with HMPA in Different HMPA/BEF Equivalent Ratios (R)

No	R	T_g (°C, DMA)	Flexural strength (MPa)	Flexural modulus (GPa)
1	0.70	132.4	86	1.94
2	0.75	138.1	101	2.02
3	0.85	151.2	116	2.18
4	0.90	167.9	120	2.03

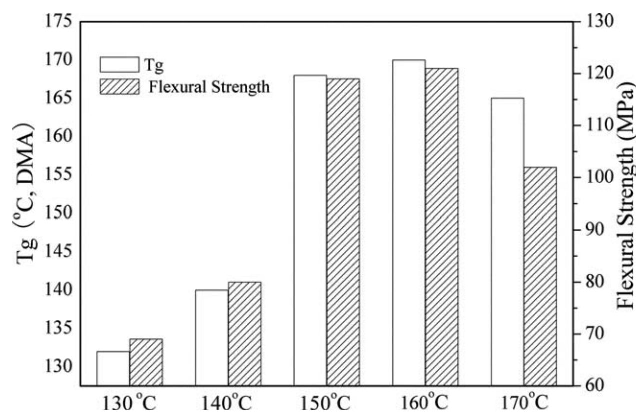


Figure 3 Dependence of the flexural strengths and T_gs of the thermal-cured BEF resins with HMPA on curing temperatures.

could enhance the electron density of the nitrogen atom in the amine groups, resulting in 6FAPB with higher nucleophilic attackability into the oxirane rings of epoxy resin.

Thermal properties of the thermal-cured resins

TGA curves of the thermally cured epoxy resins in nitrogen were outlined in Figure 5, in which the all of the cured epoxy resins started to loss original weight at about 200°C. For the fully-cured BEF resins with different curing agents, the onset thermal decomposition temperatures (T_d) were measured at 391°C for EP-1 (BEF/HMPA), 365°C for EP-2 (BEF/6FAPB), and 416°C for EP-3 (BEF/TMDA), successively (Table II). The thermal decomposition temperature at 5% of original weight loss (T_5) were measured in the range of 342–364°C, and the temperature at 10% weight loss (T_{10}) in the range of 374–397°C, in which EP-3 exhibited the best thermal stability with T_5 of 364°C and T_{10} of 397°C, respectively. In

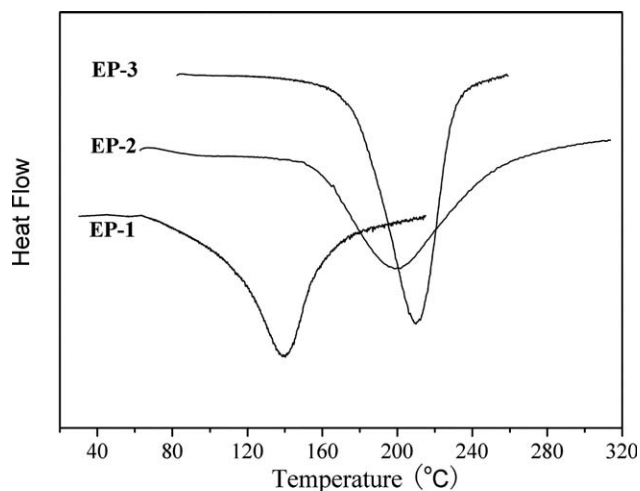


Figure 4 DSC curves of the thermal-cured BEF resins with different curing agents.

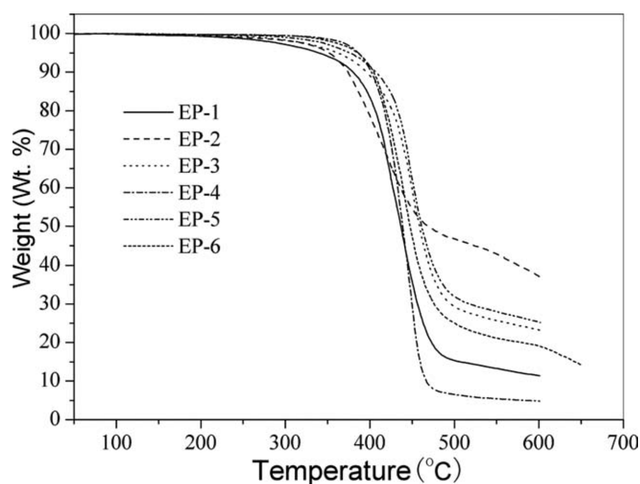


Figure 5 TGA curves of the thermal-cured BEF and DGEBA resins with different curing agents.

comparison, the fully cured DGEBA resins exhibited the thermal properties slightly better than the corresponding fully cured BEF resins. Moreover, all of the cured epoxy resins showed rapid thermal decompositions beginning from about 400°C, and the residual weight retentions at 600°C (R_w) were only 11.4–37.2%. In addition, the fully cured EP-2 (BEF/6FAPB) showed the highest value of R_w (37.2%) at 600°C, implying that the fluorinated groups in the epoxy resins might have contributed to the improved thermal stability due to the outstanding thermal oxidative resistance of the CF_3 groups.

Figure 6 depicts the DMA curves of the thermal-cured BEF resins with three different curing agents, including HMPA, 6FAPB, and TMDA and Table III compares the DMA data of the thermal-cured BEF resins with the corresponding commercial DGEBA resins. The thermal-cured BEF resins showed glass transition temperatures determined as the peak temperatures of the loss tangent curves in the range of 165–171°C, compared with the thermal-cured DGEBA resins (162–174°C). The storage modulus started to drop down when the temperature was

TABLE II
Thermal Properties of the Thermal-Cured BEF and DGEBA Resins with Different Curing Agents

Samples	$T_{g,\ DSC}$	T_d	T_5	T_{10}	R_w
EP-1	148	391	342	380	11.4
EP-2	142	365	352	374	37.2
EP-3	150	416	364	397	23.3
EP-4	142	414	387	402	4.8
EP-5	144	422	378	408	25.3
EP-6	155	409	386	405	19.1

T_d, onset decomposition temperature (°C); $T5$, $T10$, temperatures at 5 and 10% weight loss, respectively (°C, in N2); R_w, residual weight retention at 600°C (%).

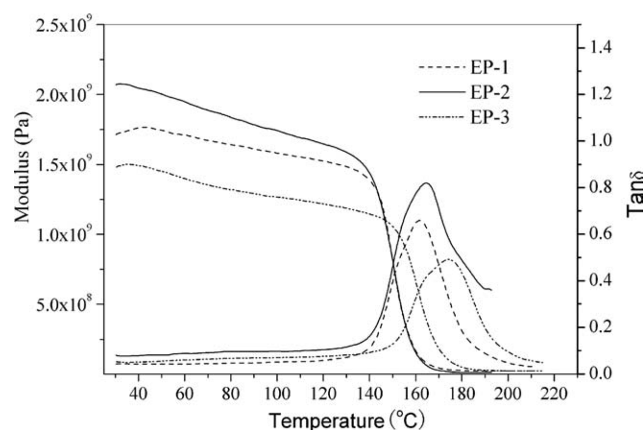


Figure 6 DMA curves of the thermal-cured BEF resins with different curing agents.

scanned up to 140°C. The storage moduli of the BEF cured with different curing agents were determined in the range of 1.40–1.95 GPa at 60°C and 1.21–1.65 GPa at 120°C, respectively, implying that the thermal-cured BEF resins could withstand the thermal impact at 120°C.

Mechanical properties

The thermal-cured BEF resins with different curing agents exhibited good mechanical properties as shown in Table IV, in which EP-1 (BEF-HMPA) has the highest flexural strength of 119 MPa, compared with EP-2 (BEF-6FAPB) (79 MPa) and EP-3 (BEF-TMDA) (92 MPa), respectively. The flexural modulus was measured in the range of 2.09–2.13 GPa. In comparison, Table IV also shows the flexural strengths and moduli of the thermal-cured epoxy resins derived from the commercial epoxy resin (DGEBA). It can be seen that the thermal-cured fluorinated epoxy resins have mechanical properties as good as the commercial epoxy resins.

Electric and dielectric properties

The electric insulating and dielectric properties of the thermal-cured BEF resins were showed in Table V.

TABLE III
DMA Data of the Thermal-Cured BEF and DGEBA Resins with Different Curing Agents

			Storage modulus (GPa)	
Samples	T_g (°C)	tan δ	60°C	120°C
EP-1	168	0.62	1.71	1.52
EP-2	165	0.79	1.95	1.65
EP-3	171	0.48	1.40	1.21
EP-4	162	0.61	1.81	1.63
EP-5	166	0.71	2.01	1.64
EP-6	174	0.52	1.80	1.41

TABLE IV
Mechanical Properties of the Thermal-Cured BEF and DGEBA Resins with Different Curing Agents

Samples	Flexural strength (MPa)	Flexural modulus (GPa)
EP-1	119	2.09
EP-2	79	2.13
EP-3	92	2.09
EP-4	126	1.95
EP-5	82	2.23
EP-6	105	1.86

The volume resistivity (ρ_v) were measured in the range of 1.93–9.23 × 10^{16} Ω cm and the surface resistivity (ρ_s) in the range of 4.81 × 10^{15}–7.70 × 10^{16} Ω. It seems that the EP-1 ($\rho_v = 9.23 \times 10^{16}$ Ω cm, $\rho_s = 7.70 \times 10^{16}$ Ω), using anhydride as the curing agent, exhibited better electrical insulating properties than EP-2 ($\rho_v = 1.93 \times 10^{16}$ Ω cm, $\rho_s = 1.46 \times 10^{16}$ Ω) and EP-3 ($\rho_v = 1.59 \times 10^{16}$ Ω cm, $\rho_s = 4.81 \times 10^{15}$ Ω) which were cured with aromatic diamines. The dielectric constants (ε_r) at 1 MHz were measured in the range of 3.1–3.4 and the dielectric dissipation factor (tan δ) in the range of 1.38–2.48 × 10^{-3}. It can be seen the fluorinated epoxy resin cured with HMPA showed lower dielectric constant and dissipation factor ($\varepsilon_r = 3.1$, tan $\delta = 1.38 \times 10^{-3}$) than that cured with aromatic diamines, such as EP-2 ($\varepsilon_r = 3.3$, tan $\delta = 2.01 \times 10^{-3}$) and EP-3 ($\varepsilon_r = 3.4$, tan $\delta = 2.48 \times 10^{-3}$). It can be concluded that the fluorinated epoxy resins cured with liquid alicyclic anhydride (HMPA) exhibited better electrical insulating and dielectric properties than that cured with aromatic diamines (6FAPB and TMDA), probably due to the curing efficiency of the liquid anhydride and the low polarization of the anhydride-cured resins. In comparison, the thermal-cured BEF resins exhibited improved dielectric properties than the thermal-cured DGEBA resins, probably due to the contribution of the fluorinated groups in the epoxy resin backbone which resulted in the increase in free volume and hydrophobicity as well as the decrease in polymer polarization.

Moisture adsorption

Low moisture adsorption was an important factor for the advanced microelectronic packaging materials because the adsorbed H_2O molecules have negative impact on the electric insulating and dielectric performance of the thermal-cured epoxy resins. Table V also summaries the water uptakes of the thermal-cured epoxy resins, in which the water uptake was determined by immersing the dried cured-epoxy resin samples (φ50 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. For the thermal-cured BEF resins, the water uptakes determined by Method I were measured in the range of 0.36–0.38%, compared that by Method II which were in the range of 0.94–1.23%. The difference in the moisture adsorptions by two different methods might be interpreted by the different testing temperature, which resulted in the increase of H_2O diffusion into the cured resins. No matter what curing agents employed, the thermal-cured fluorinated epoxy resins always exhibited lower moisture adsorptions than the corresponding commercial DGEBA resins, implying the introduction of fluorinated groups into epoxy resins is an efficient way to decrease the water uptakes. For instance, EP-1 cured by anhydride, showed lower moisture adsorption (0.36% by Method 1) than EP-4 (0.48%).

Figure 7 depicts the dependence of the moisture adsorptions and volume resistivities on the exposure time at 52% relative humidity and room temperature. (The relative humidity was obtained from aqueous salt solution of $Mg(NO_3)_2 \cdot 6H_2O$ according to the literature.[19]). It could be seen that EP-1 adsorb moisture to reach a saturated state after the sample was exposed for 5 h, compared with EP-2 and EP-3

TABLE V
Water Adsorptions and Dielectric Properties of the Thermal-Cured BEF and DGEBA Resins with Different Curing Agents

Samples	Water uptake (%)					
	I	II	ρ_v (Ω cm)	ρ_s (Ω)	ε_r (1MHz)	tan δ
EP-1	0.36	0.94	9.23×10^{16}	7.70×10^{16}	3.1	1.38×10^{-3}
EP-2	0.36	1.12	1.93×10^{16}	1.46×10^{16}	3.3	2.01×10^{-3}
EP-3	0.38	1.23	1.59×10^{16}	4.81×10^{15}	3.4	2.48×10^{-3}
EP-4	0.48	0.99	2.29×10^{16}	1.71×10^{16}	3.2	1.45×10^{-3}
EP-5	0.37	1.35	1.23×10^{16}	3.95×10^{15}	3.4	2.71×10^{-3}
EP-6	0.41	1.42	7.01×10^{15}	2.95×10^{14}	3.6	3.56×10^{-3}

Water uptakes, I, Immersion in water at 25°C for 24 h; II, immersion in boiling water for 6 h. ρ_v, volume resistivity; ρ_s, surface resistivity; ε_r, dielectric constant at 1 MHz at 25°C; tan δ, dissipation factor.

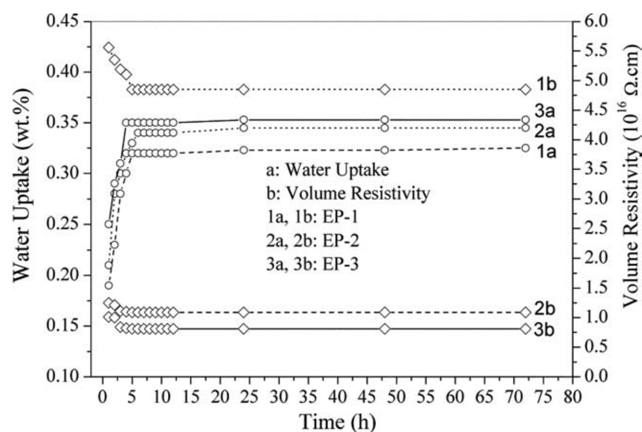


Figure 7 Dependence of moisture adsorption and volume resistivity of the thermal-cured BEF resins on exposuring time in 52% relative humidity and room temperature.

which required 8–10 h to get the saturated state. The volume resistivities were reduced with the increase of exposure time, implying the water adsorption has negative effect on the electric properties of the epoxy resins.

CONCLUSIONS

A novel fluorinated epoxy compound, 4,4′-bis(2,3-epoxypropoxyphenyl)-1-(3-trifluoromethylphenyl)-2, 2,2-trifluoroethane (BEF), has been synthesized by the coupling of phenol and 3′-trifluoromethyl-2,2,2-trifluroacetophenone catalyzed by Lewis acid, followed by epoxidation with epichlorohydrin. The fluorinated epoxy could be thermally cured with organic anhydride or aromatic amine as curing agents to produce the thermal-cured epoxy resins. Experimental results demonstrated that the thermal-cured fluorinated epoxy resins showed good thermal stability and outstanding mechanical properties. The thermal-cured fluorinated epoxy resins also exhibited good electric insulating properties and surface resistivity, as well as dielectric constants and the dielectric dissipation factor (tan δ). It was found that the fluorinated epoxy resins showed better electric insulating and dielectric properties as well as lower moisture adsorption than the corresponding commercial epoxy resins due to the special characteristics of fluorinated groups.

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