Synthesis and Characterization of Novel Trifunctional Fluorine Containing Epoxy Resins Based on 1,1,1-Tris(2,3-epoxypropoxyphenyl)-2,2,2-trifluoroethane

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ABSTRACT: A novel trifunctional fluorine containing epoxy compound, 1,1,1-Tris(2,3-epoxypropoxyphenyl)-2,2,2-trifluoroethane (TEF) synthesized starting from 4-bromoanisole was cured with alicyclic anhydride or aromatic diamines to produce the epoxy resins. As comparison, commercial available Biphenol A 828 epoxy (BPA) was cured under the same conditions. Experimental results indicated that the cured TEF epoxy resins showed good thermal stability with onset thermal decomposition temperature (T_d) of 363–388 °C in nitrogen, glass transition temperature (T_g) of 210–287 °C (determined by DMA) and coefficient of thermal expansion (CTE) ranged in 46.7–59.6 ppm/°C. The fluorine containing epoxy resins possessed outstanding mechanical properties with flexural strengths of 64–115 MPa, flexural moduli of 2.29–2.65 GPa. The epoxy resins also exhibited excellent electric insulating properties with volume resistivity of $1.19\text{--}8.15 \times 10^{16} \Omega\cdot\text{cm}$ and the dielectric constants at 1 MHz of 3.2–3.5 as well as low moisture absorption of 0.31–0.87%. As comparison with BPA resins, the trifunctional fluorine containing TEF resins exhibit higher T_g and improved dielectric properties as well as low CTE, which are promising candidates for advanced microelectronic packaging. [doi:10.1295/polymj.PJ2007096]

KEY WORDS Trifunctional Epoxy Resins / Fluorine Containing Polymer / Glass Transition Temperature / Coefficient of Thermal Expansion /

Advanced epoxy resins have been widely used as coatings, adhesive, composites, laminates and encapsulation owing to their excellent combined properties such as chemical resistance, good electric insulation, high adhesion and excellent processability.^{1–5} In the field of microelectronic packaging they were extensively employed as epoxy molding compounds, electrically conductive silver paste, and die attach adhesives etc. With the rapid progress of advanced microelectronic packaging technology, the integrated circuits (ICs) have been developing toward larger size, higher density, smaller and thinner chip size, which demands the epoxy encapsulation materials possessing low thermal stress, high T_g , and low dielectric constant as well as low moisture adsorption.^{6–9} The thermal stress will give rise to package cracking, passivation layer cracking, aluminium pattern deformation and delamination. In general, it is caused by the differences in coefficient of thermal expansion (CTE) between the silicon chip and the organic moulding materials, which is described by the following simplified equation:¹⁰

$$S = K \int_{T_1}^{T_2} \alpha_{r1} E_{r1} dT$$

where S is thermal stress, K is a constant, α_{r1} is CTE of the resin. E_{r1} is the young's modulus of the resin.

Clearly, low CTE is required to decrease the stress while conventional epoxy resins possess relative high CTE of 60–80 ppm/°C, extensively higher than that of silicon chip (2.3–2.8 ppm/°C). Although the CTE of epoxy resins can be reduced to 10–20 ppm/°C by the method of blending silicon beads, the mismatch with that of silicon ICs chips is still critical.

Recently, the novel IC packaging technology such as Surface Mount Technology (SMT) need to expose the devices to a soldering temperature of 220–250 °C, which demands the encapsulation materials possessing high T_g , low thermal stress and high T_d . Further, moisture diffusion in epoxy networks will corrode the metal wiring of ICs leading to packaging failure.¹¹ Considering above-mentioned factors, it is necessary to develop novel epoxy resins with high T_g , low CTE and low moisture adsorption to meet the requirements of electronic packaging.

Thus, many efforts have been made to develop novel epoxy resins, such as incorporating multifunctional groups to increase the crosslink density and enhance the heat resistance,^{12–14} introducing high rigid moieties to increase the T_g ,^{15,16} or hydrophobic fluorine containing groups to reduce the moisture adsorption.^{17,18} For example, Lin *et al.*¹⁹ prepared a series of novel trifunctional epoxy resins with high T_g of 238–268 °C. Maier *et al.*²⁰ reported several fluorine con-

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taining epoxy resins with low dielectric constant for microelectronic packaging applications.

With the purpose to develop new epoxy resins with high T_g and low CTE as well as good dielectric properties, we try to incorporate trifunctional moieties to increase the thermal properties, and fluorine containing CF_3 group to improve the dielectric performance simultaneously. Thus, in this study, a novel trifunctional fluorine containing epoxy compound, 1,1,1-tris(2,3-epoxypropoxyphenyl)-2,2,2-trifluoroethane (TEF) was designed and synthesized starting from 4-bromoanisole with four steps. TEF was then cured with two different kinds of curing agent, an alicyclic anhydride of hexahydro-4-methylphthalic anhydride (HMPA) and two aromatic diamines of 4,4'-diaminodiphenylmethane (DDM) and 4,4'-diaminodiphenylsulfone (DDS). As comparison, a commercial available Bisphenol-A epoxy 828 (BPA) resin was cured with HMPA under the same conditions. Experimental results demonstrated that the cured trifunctional epoxy resins possessed extensively high T_g of 210–287 °C (determined by DMA), low CTE ranged in 46.7–59.6 ppm/°C and low moisture absorptions of 0.31–0.87%. TEF resins exhibits enhanced T_g and improved dielectric properties as well as low CTE while keeping the good mechanical properties simultaneously, as comparison with corresponding BPA resins.

EXPERIMENTAL

Measurement

Differential scanning calorimeter (DSC), thermogravimetric analysis (TGA) and dynamic mechanical analysis (DMA) and Thermal mechanical analysis (TMA) were recorded on a Perkin-Elmer 7 series thermal analysis system at a heating rate of 10 °C/min. FT-IR 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. Moisture adsorptions were determined by immersing the cured epoxy samples ($\varnothing$ 50 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.

Materials

4-bromoanisole, DDM, DDS, Phenol, $ZnCl_2$, epichlorohydrin, hydrochloride and ethanol were purchased from Beijing Chemical Reagents Corp., China,

and used without purification. BPA (Shell Corp.), HMPA (Acros) and 2-ethyl-4-methylimidazole (Acros) were used as received.

Monomer synthesis

1-(4-Methoxyphenyl)-2,2,2-trifluoroethanone (3FPO). A mixture of anhydrous lithium trifluoroacetate (96.0 g, 0.80 mol), magnesium (19.2 g, 0.80 mol), iodine (0.5 g) and freshly distilled tetrahydrofuran (500 mL) was placed into a 1000 mL three-necked round-bottom flask fitted with a dropping funnel, a drying tube, and a reflux condenser. After the anhydrous lithium trifluoroacetate was completely dissolved by stirring, 4-bromoanisole (140.3 g, 0.75 mol) was added dropwise, followed by refluxed for 3 h. The solution was cooled down to room temperature, then a mixture of concentrated hydrochloric acid (36%, 80 mL) and distilled water (100 mL) was slowly added with agitation. The aqueous phase was separated and the organic phase was washed with 5% aqueous sodium bicarbonate and distilled water. The organic solution was dried with anhydrous magnesium sulfate and distilled to remove the solvent. The crude product was purified by distillation to give a liquid of 3FPO (99.5 g, 65%). B.p.: 80 °C (1 mmHg). FT-IR (cm^{-1}): 3014, 2845, 708, 1602, 1273, 1167. 1H -NMR ($CDCl_3$, 300 MHz, δ ppm): 6.76–7.02 (d, 2H); 8.04–8.07 (d, 2H). MS (EI, m/e, % relative intensity): 204 (M^+ , 28), 135 (M-69, 100). Elemental analysis: Calcd. for $C_9H_7F_3O_2$: C, 52.95%; H, 3.46%. Found: C, 52.78%; H, 3.43%.

1-(4-Methoxyphenyl)-1,1-bis(4-hydroxyphenyl)-2,2,2-trifluoroethane (3FMO). In a 250 mL three-necked flask equipped with a reflux condenser and a gas inlet tube, 3FPO (40.8 g, 0.20 mol) was mixed with phenol (75.0 g, 0.80 mol) and 2.50 g of anhydrous $ZnCl_2$. The mixture was heated at 100 °C with stirring while dry hydrogenchloride gas was bubbled into the flask. With the reaction processing, the reaction mixture gradually became a pale salmon solution. After 8 h, the mixture was poured into excess of hot water with agitation. The precipitate was collected and washed with hot water and hexane. The crude product was purified by recrystallization in ethanol/water (40/40 mL) to give a white crystal. Yield: 63.6 g (85%), m.p.: 185 °C (determined by DSC). FT-IR (cm^{-1}): 3358, 2845, 1608, 1513, 1236.3, 1157, 832. 1H -NMR (300 MHz, $DMSO-d_6$, δ ppm): 3.74 (s, 3H), 6.71–6.74 (d, 4H), 6.79–6.83 (d, 4H), 6.88–6.95 (m, 4H), 9.61 (s, 2H). Mass spectrometry (MS): [electron ionization (EI), m/e, percentage of relative intensity]: 374 (M^+ , 100), 359 (M-15, 25). Elemental Analysis: Calcd. for $C_{21}H_{17}F_3O_3$: C, 67.38%; H, 4.58%. Found: C, 67.18%; H, 4.43%.

1,1,1-Tri(4-hydroxyphenyl)-2,2,2-trifluoroethane (3FTO). In a 1000 mL three-necked flask equipped

Scheme 1. Synthesis of TEF.

with a stirrer and a gas inlet tube was charged 6FMO (34.0 g, 0.09 mol), HBr (47%, 200 mL) and acetic acid (100 mL). The mixture was heated to reflux for 8 h and distilled to remove most of the solvent. The residue was poured into water and the precipitate was filtered and then recrystallized in mixture of methanol and water (1:1, v/v) to give a white solid of 3FTO (29.8 g, 92%). M.p.: 289.8 °C. FT-IR (KBr, cm^{-1}): 3377, 1614, 1598, 1515, 1435, 1223, 1149, 834. $^1\text{H-NMR}$ (300 MHz, DMSO-d_6 , δ ppm): 6.70–7.73 (d, 6H); 6.79–6.82 (d, 6H), 9.56 (s, 3H). $^{13}\text{C-NMR}$ (300 MHz, DMSO-d_6 , δ ppm): 62.7, 62.9, 63.2, 63.4, 115.2, 124.5, 127.3, 130.2, 130.9, 133.1, 156.8, 157.1. Mass spectrometry (MS): [electron ionization (EI), m/e , percentage of relative intensity]: 360 (M^+ , 25), 291 (M-69, 100), 197 (M-163, 15). Elemental Analysis: Calcd. for $\text{C}_{20}\text{H}_{15}\text{F}_3\text{O}_3$: C, 66.67%; H, 4.20%. Found: C, 66.60%; H, 4.29%.

1,1,1-Tri(2,3-epoxypropoxyphenyl)-2,2,2-trifluoroethane (TEF). A 1000 mL three-necked flask equipped with a stirrer, a Dean-Stark trap with a reflux condenser and a thermometer, was placed 36.0 g (0.10 mol) of 3FTO and 277.0 g (3.00 mol) of epichlorohydrin. The mixture was heated at 65 °C, to which 25.0 g of 48% aqueous NaOH was added dropwise in 3 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 was extracted with ethyl ether, washed with water for three times, and dried by MgSO_4 . The organic phase was distilled to remove the epichlorohydrin to give a white solid. (47.0 g, 89%). M.p.: 30 °C. IR (KBr, cm^{-1}): 3053, 2929, 1609, 1511, 1457, 1255, 1149, 916, 830. $^1\text{H-NMR}$ (300 MHz, CDCl_3 , δ ppm): 2.76–2.78 (m, 6H); 3.91–3.93 (m, 3H), 3.97–4.39 (m, 6H), 6.83–6.86 (d, 6H), 7.02–7.05 (d, 6H). Mass spectrometry (MS): [electron ionization (EI), m/e , percentage of relative intensity]: 528 (M^+ , 15); 459 (M-69, 100); 403 (M-125, 18); 347 (M-181, 8).

Preparation of Samples

For HMPA curing system, 8.0 g TEF or BPA epoxy was placed in a 5 mL flask and heated at 80 °C for 30 min. The mixture of 6.1 g HMPA (equivalent ratio of anhydride/epoxy $R = 0.80$) and 0.4 g 2-ethyl-4-methylimidazole (0.5 wt %) was heated at 60 °C for 30 min, then blended with melted TEF or BPA and agitated to a homogeneous solution. The mixture was placed in a plate and heated at 80 °C/1 h, 120 °C/1 h, 150 °C/2 h and 170 °C/1 h to give the cured epoxy resin TEF-HMPA and BPA-HMPA. For the aromatic diamines curing systems of DDM and DDS, the diamines powders and TEF were mixed homogeneously in 1:1 equivalent ratio, without catalyst, respectively, and cured at 120 °C/1 h, 150 °C/2 h, 220 °C/2 h to give TEF-DDM, BPA-DDM and TEF-DDS.

RESULTS AND DISCUSSION

Synthesis of TEF

TEF was synthesized by a four-step procedure (Scheme 1). First, compound 3FPO was prepared by the Grignard reaction between anhydrous lithium trifluoroacetate and 4-bromoanisole in the presence of magnesium in THF. Then, the diphenol intermediate compound 3FMO was synthesized by the coupling of 1 equiv of 3FPO with 2 equiv of phenol catalyzed by HCl gas and ZnCl_2 at 100 °C. 3FMO was refluxed in the mixture of HOAc and HBr to remove the methyl protective group to give triphenol compound (3FTO) in good yield. TEF was prepared by the reaction of 3FTO with epichlorohydrin catalyzed by NaOH (48 wt % in water) at 65 °C. The chemical structures of 3FPO, 3FMO, 3FTO and TEF were confirmed by FT-IR, MS, NMR spectra and elemental analysis. Figure 1 showed the $^1\text{H-NMR}$ spectrum of TEF, in which all of the absorptions were assigned with the corresponding protons in the expected chemical structures. The absorptions at δ 2.76–2.78 and

Figure 1. ^1H -NMR spectra of TEF (CDCl_3 , 300 MHz).

Figure 2. MS spectra of TEF.

3.91–3.93 ppm were assigned to the protons H_1 and H_2 in oxirane ring, respectively. The peaks at δ 3.97–4.39 were attributed to the proton H_3 of methylene in TEF. The absorptions at δ 6.83–7.05 were assigned to the protons H_4 – H_5 of aromatic rings. Figure 2 outlined the mass spectrum of TEF, in which the characteristic peak at 529 (M^+ , base), 459 ($\text{M}-\text{CF}_3$), 403 ($\text{M}-\text{CF}_3-\text{CH}_2\text{CHOCH}_2$) and 347 [$\text{M}-\text{CF}_3-2(\text{CH}_2-\text{CHOCH}_2)$] were observed. Clearly, no MS peaks of byproduct were found implying that the TEF has good purity. TEF was determined with equivalent weight in the range of 188–191 g/equiv, which was close to the theoretical value of 176 g/equiv. The impurities were measured with the value of Na^+ : 1.8 ppm; Cl^- : 2.1 ppm.

Thermal Curing of Epoxy Resins

The curing behavior of the epoxy and curing agent compositions were studied by DSC. TEF were cured

Scheme 2. Chemical structures of BPA and curing agents.

at programmed thermal curing procedures with two different kinds of curing agents, anhydride (HMPA) and aromatic diamines (DDM and DDS) as shown in Scheme 2. HMPA was a liquid curing agent at

Figure 3. DSC scans for the curing procedure of the epoxy resins.

room temperature, which was easily to mix with the epoxy. The mixtures with uncured state were scanned directly with the heating rate of $10^{\circ}\text{C min}^{-1}$. The reactivities of the epoxies could 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.²¹ Figure 3 compared the DSC scans for the curing procedures of TEF with HMPA, DDM and DDS, respectively. The exothermic starting temperatures of TEF-HMPA, TEF-DDM and TEF-DDS exhibited at 113, 122 and 164 $^{\circ}\text{C}$, individually. It is well known that HMPA is a reactive curing agent. As comparing the reactivities of DDM and DDS, the lower reactivity of DDS toward TEF might be attributed to the electronic effects and physical properties. DDS has the electron-withdrawing sulfone linkage ($\text{O}=\text{S}=\text{O}$) in the main chain, which decreases the electron density of the amine nitrogen and subsequently reduced the nucleophilic attack on the oxirane ring of the epoxy resin. Further, the melting point of DDS was 175 $^{\circ}\text{C}$ extensively higher than that of DDM (90 $^{\circ}\text{C}$), which has negative effect on reactivity.

Thermal Properties of the Cured Resins

Figure 4 compared TGA curves of the cured epoxy resins in nitrogen, it was found that TEF epoxy resins did not loss any original weight before the scanned temperature reached up to 350 $^{\circ}\text{C}$, implying that no thermal decomposition occurred below 350 $^{\circ}\text{C}$. T_d were measured at 385 $^{\circ}\text{C}$ for TEF-HMPA, 363 $^{\circ}\text{C}$ for TEF-DDM, and 388 $^{\circ}\text{C}$ for TEF-DDS, respectively (Table I), which is similar with the relative commercial BPA resins. The thermal decomposition temperature at 5% weight loss (T_5) of TEF resins were in the range of 348–380 $^{\circ}\text{C}$, and the temperature at 10% weight loss (T_{10}) in the range of 373–398 $^{\circ}\text{C}$, in which TEF-DDS exhibited the best thermal stability with T_5

Figure 4. TGA curves of the epoxy resins.

Table I. Thermal properties of the epoxy resins

Sample ID	T_g , DSC	T_d	T_5	T_{10}	R_w
TEF-HMPA	185	385	348	398	19.8
BPA-HMPA	142	414	387	402	3.0
TEF-DDM	270	363	353	373	43.0
BPA-DDM	161	370	374	395	19.0
TEF-DDS	282	388	380	394	42.1

T_d : Onset decomposition temperature ($^{\circ}\text{C}$); T_5 , T_{10} : Temperatures at 5% and 10% weight loss, respectively ($^{\circ}\text{C}$, in N_2); R_w : Residual weight retention at 700 $^{\circ}\text{C}$ (%).

of 380 $^{\circ}\text{C}$, 30 $^{\circ}\text{C}$ higher than that of TEF-HMPA and TEF-DDM. As the scanning temperature rose to 400 $^{\circ}\text{C}$, these epoxy resins exhibit a rapid thermal decomposition. The residual weight retentions (R_w) at 700 $^{\circ}\text{C}$ of TEF-DDM and TEF-DDS cured with aromatic diamines were 43.0% and 42.1%, respectively, obviously higher than that of TEF-HMPA (19.8%) cured with alicyclic anhydride implying that the epoxy resins cured with aromatic diamines possessed better thermal stability than that with alicyclic anhydrides.

Figure 5 depicted DMA curves of the cured TEF epoxy resins. Table II summarized all the DMA data of cured TEF and BPA epoxy resins, in which the TEF resins exhibit the glass transition temperature (T_g , the peak temperature of the loss tangent) of 210–287 $^{\circ}\text{C}$, and the heights of tangent are in the range of 0.128–0.323, individually. The storage moduli ranged in 1.24–1.52 GPa at 60 $^{\circ}\text{C}$ and 1.10–1.32 GPa at 120 $^{\circ}\text{C}$, respectively.

As comparing TEF resins with BPA ones, it is important to note that TEF exhibits much higher T_g s than commercial BPA resins. The T_g of TEF-HMPA (185 $^{\circ}\text{C}$ from DSC and 210 $^{\circ}\text{C}$ from DMA) is 40–50 $^{\circ}\text{C}$ higher than BPA-HMPA (142 $^{\circ}\text{C}$ from DSC and 162 $^{\circ}\text{C}$ from DMA). TEF-DDM exhibits the high T_g value of 270 $^{\circ}\text{C}$ from DSC and 275 $^{\circ}\text{C}$ from DMA, which is about 100 $^{\circ}\text{C}$ higher than that of BPA-DDM.

Figure 5. DMA curves of the epoxy resins.

Figure 6. TMA curves of the epoxy resins.

Table II. DMA analysis of the epoxy resins

Sample ID	T_g , DMA (°C)	$\tan \delta$	Storage Moduli (GPa)		
			60 °C	120 °C	$T_g + 40$ °C
TEF-HMPA	210	0.323	1.52	1.32	0.0588
BPA-HMPA	162	0.615	1.81	1.63	0.0380
TEF-DDM	275	0.128	1.44	1.19	0.0627
BPA-DDM	187	0.412	1.58	1.63	0.0390
TEF-DDS	287	0.218	1.24	1.10	0.0889

The T_g s of TEF resins are near or even higher than the soldering temperature of 220–250 °C in SMT, indicating that they are suitable to be used in this advanced packaging technology. According to rubber elasticity theory,²² the crosslink density is proportional to the storage modulus at $T_g + 40$ °C. Hence, the ratio of crosslink density of TEF-HMPA:BPA-HMPA:TEF-DDM:BPA-DDM:TEF-DDS is 1.0:0.6:1.1:0.7:1.5. Clearly, the trifunctional TEF resins showed higher crosslink density compared with relative BPA ones, which can also be confirmed by their higher T_g values. BPA resins also exhibited much dramatically degradation behavior at high temperature and the R_w values at 700 °C of BPA-HMPA and BPA-DDM are 3% and 19%, 16% and 24% lower than relative TEF ones respectively, implying the trifunctional TEF epoxy possess better thermal resistance due to their higher crosslink density attributed to the trifunctional group and the presence of thermal-resistant CF_3 groups in the polymer backbone.

The CTEs of TEF epoxy resins were determined from TMA curves (Figure 6) for TEF-HMPA of 59.6 ppm/°C, TEF-DDM of 54.2 ppm/°C and TEF-DDS of 46.7 ppm/°C, respectively, which were lower than those of conventional epoxy resins (60–80 ppm/°C). Low CTE is desirable to decrease the thermal stress and decrease packaging failure in ICs.

Mechanical Properties

The cured TEF resins exhibited good mechanical

Table III. Mechanical properties of the epoxy resins

Sample ID	Flexural Strength (MPa)	Flexural Moduli (GPa)
TEF-HMPA	115	2.65
BPA-HMPA	126	1.95
TEF-DDM	66	2.29
BPA-DDM	101	2.17
TEF-DDS	64	2.49

properties (Table III), in which TEF-HMPA had the highest flexural strength of 115 MPa, compared with TEF-DDM (66 MPa) and TBEF-DDS (64 MPa), respectively. The flexural moduli were measured in the range of 2.29–2.65 GPa. The resins cured with HMPA performed better mechanical properties than that with DDM and DDS owing to more efficient curing procedure and its flexible structure. Moreover, as comparing with the commercial epoxy BPA system, it was found that the TEF system exhibited the mechanical properties as good as the cured BPA system no matter what kind of curing agents employed.

Electrical and Dielectric Properties

The electric insulating and dielectric properties of the cured TEF and BPA epoxy resins were investigated and shown in Table IV. The epoxy resins showed good dielectric properties, including the volume resistivity of $1.19\text{--}8.15 \times 10^{16} \Omega\cdot\text{cm}$ and surface resistivity of $4.51 \times 10^{15}\text{--}1.65 \times 10^{16} \Omega$, in which TEF-HMPA exhibited better electrical insulating properties than that of TEF-DDM and TEF-DDS. The dielectric constants (ϵ_r) at 1 MHz were measured in the range of 3.2–3.5 and the dielectric dissipation factor ($\tan \delta$) of $1.52\text{--}3.14 \times 10^{-3}$, which are the same or lower than respective BPA ones. TEF-HMPA ($\epsilon_r = 3.2$, $\tan \delta = 1.52 \times 10^{-3}$) had lower dielectric constants and dissipation factor than TEF-DDM ($\epsilon_r = 3.4$, $\tan \delta = 2.09 \times 10^{-3}$) and TEF-DDS ($\epsilon_r = 3.5$,

Table IV. Moisture adsorption and dielectric properties of the epoxy resins

Sample ID	Moisture adsorption (%)		ρ_v (Ω -cm)	ρ_s (Ω)	ϵ_r (1 MHz)	tan δ
	I	II				
TEF-HMPA	0.31	1.25	8.15×10^{16}	1.65×10^{16}	3.2	1.52×10^{-3}
BPA-HMPA	0.48	0.99	2.29×10^{16}	1.71×10^{16}	3.2	1.45×10^{-3}
TEF-DDM	0.37	1.45	2.31×10^{16}	6.93×10^{15}	3.4	2.09×10^{-3}
BPA-DDM	0.49	0.92	1.90×10^{16}	4.90×10^{15}	3.5	7.30×10^{-3}
TEF-DDS	0.87	2.86	1.19×10^{16}	4.51×10^{15}	3.5	3.14×10^{-3}

Moisture adsorption, 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.

tan $\delta = 3.14 \times 10^{-3}$). Obviously, the fluorine containing epoxy resins cured with liquid alicyclic anhydride (HMPA) exhibited better electrical insulating and dielectric properties than those cured with aromatic diamines (DDM and DDS), which might be attributed to the combined effects of higher curing efficiency of HMPA and the lower polarization of the anhydride-cured resins than that of DDM and DDS, respectively.

Moisture has negative influence on the electric insulating and dielectric performance of the cured epoxy resins, which will erode the wiring of ICs causing packaging failure. Table IV summarized the moisture adsorption of the cured epoxy resins, which were determined by immersing the dried cured epoxy resin samples ($\varnothing 50 \text{ mm} \times 3 \text{ mm}$) 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 moisture adsorptions of TEF-HMPA and TEF-DDM resins measured by Method I ranged in 0.31–0.37%, lower than those of BPA ones (0.48–0.49%). It is strange to note that the moisture adsorption of TEF-HMPA and TEF-DDM by Method II were 1.25–1.45%, higher than relative BPA ones (0.92–0.99%). The difference and contrast in the moisture absorptions by two different methods could be explained by the fact that a high temperature could increase the diffusion of H₂O molecules into the epoxy resin networks. Furthermore, trifunctional TEF resins possess larger free volume facile to water sorption than BPA resins, leading to the higher moisture adsorption at high temperature. The lower moisture absorption (at 25 °C) and improved dielectric properties of the TEF epoxy resins can be interpreted by the low polarizability of the C-F bond and hydrophobic features of fluorine atoms. These results suggested that the CF₃ groups in the network structure of the epoxy resins play a significant role in their electrical and dielectric performance.

CONCLUSION

A novel trifunctional fluorine containing epoxy compound was successfully synthesized by a four-step

procedure starting from 4-bromoanisole, which was then cured by alicyclic anhydride HMPA and aromatic diamines DDM and DDS. Commercial available BPA epoxy was cured under the same conditions. Experimental results indicated that the cured fluorine containing epoxy resins showed high T_g of 210–287 °C (determined by DMA), low CTE of 46.7–59.6 ppm/°C and low moisture adsorption of 0.31–0.87%. Clearly, compared with commercial BPA resins, the novel TEF epoxy resins have enhanced thermal resistance and electric properties due to the introduction of multifunctional and fluorine containing groups. The novel trifunctional fluorine containing TEF epoxy resins exhibit promising potentials in microelectronic packaging for their good integrated properties.

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