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Synthesis and Properties of Methyl Hexahydrophthalic Anhydride-Cured Fluorinated Epoxy Resin 2,2-Bisphenol Hexafluoropropane Diglycidyl Ether

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ABSTRACT: The fluorinated epoxy resin, 2,2-bisphenol hexafluoropropane diglycidyl ether (DGEBHF) was synthesized through a two-step procedure, and the chemical structure was confirmed by ^{1}H n***uclear magnetic resonance*** (NMR), ^{13}C NMR, and Fourier transform infrared (FTIR) spectra. Moreover, DGEBHF was thermally cured with methyl hexahydrophthalic anhydride (MHHPA). The results clearly indicated that the cured DGEBHF/MHHPA exhibited higher glass transition temperature (T_g 147°C) and thermal decomposition temperature at 5% weight loss (T_5 372°C) than those (T_g 131.2°C; T_5 362°C) of diglycidyl ether of bisphenol A (DGEBA)/MHHPA. In addition, the incorporation of bis-trifluoromethyl groups led to enhanced dielectric properties with lower dielectric constant (D_k 2.93) of DGEBHF/MHHPA compared with cured DGEBA resins (D_k 3.25). The cured fluorinated epoxy resin also gave lower water absorption measured in two methods relative to its nonfluorinated counterparts. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

KEYWORDS: thermosets; synthesis and processing; dielectric properties; thermal properties; structure-property relations

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INTRODUCTION

Epoxy resins are one of the most important thermoset materials and have been extensively used in many industrial fields such as adhesives, coatings, packaging, and insulating materials for electronic and electric devices because of their excellent chemical resistance, low-moisture adsorption, good mechanical and electrical properties, high adhesion, as well as ease and low-cost of processing.[1–6] At present the trends toward denser and faster microelectronic circuits and toward high reliability for power equipments lead to increasing demands on the advanced electronic packaging and insulating materials, for instance, lower dielectric constant, higher thermal resistance, lower coefficient of thermal expansion (CTE), high-mechanical strength, and so on.[7,8] Therefore, considerable attentions have been devoted to developing novel epoxy resins with superior electrical insulating properties and enhanced thermal properties recently.

It has been shown by previous researches that modification of the backbone or side chain of the polymers by fluorination has become one of the most promising methods to endow the new materials with improved electrical insulation performance because of the low polarizability and large molecular-free volume of the carbon–fluorine (C–F) bond.[9,10] Especially, fluorine-containing group is usually an effective candidate to modify polymer materials with enhanced moisture resistance and thermal properties owing to its excellent hydrophobicity and thermal stability.[11,12] Recently, property enhancement of epoxy resin with the incorporation of fluorine-containing groups has attracted great interest. For example, Sasaki and co-workers has successfully synthesized perfluorobutenyloxyphthalic anhydride and cured with bisphenol A type epoxy, of which the dielectric constants decreased to 2.7–2.8, and the water absorption was reduced by 75%.[13,14] Lee et al.[15] has reported a novel fluorinated epoxy resin, 2-diglycidylether of benzotrifluoride (DGEBTF) cured with diaminodiphenyl methane (DDM) bearing the reduced dielectric constant by 15%. Liu et al. has reported several fluorinated epoxy resins containing trifluoromethyl segments with good thermal stabilities and moisture absorption.[16] However, there are only few reports describing fluorinated epoxy resins with excellent dielectric properties best combination of reliable thermal stabilities.[17,18] Hence, it remains an important challenge to prepare fluorinated epoxy resins with

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good electrical and thermal properties for advanced insulating materials.

In this article, we have successfully synthesized a low-molecular-weight fluorinated epoxy compound 2,2-bisphenol hexafluoropropane diglycidyl ether (DGEBHF) through epichlorohydrin reacting with 4,4′-(hexafluoroisopropylidene) diphenol (BPAF) by phase-transfer catalysis and the desired structure was then characterized by ^{1}H n***uclear magnetic resonance*** (NMR), ^{13}C NMR, and Fourier transform infrared (FTIR). Moreover, DGEBHF was thermal cured with methyl hexahydrophthalic anhydride (MHHPA) to give cured fluorinated epoxy resins material because we found in the common curing agents anhydride-cured epoxy resins exhibited lower dielectric constants than other curing agents such as the amine-cured epoxy resins. We have also done some experiments on the DDM, DDS, and MHHPA-cured diglycidyl ether of bisphenol A (DGEBA) in our preliminary work. Their dielectric constants are 4.4, 4.0, and 3.25 (50 Hz), respectively. The thermal stability, mechanical properties, and moisture absorption as well as the dielectric properties were studied in detail. It is found that the fluorinated epoxy exhibited improved combined properties compared with the corresponding commercial bisphenol A epoxy resins. In addition, the relationship between the structure and the integrated properties of the cured resins by incorporating two symmetric trifluoromethyl groups into the epoxy backbone was also investigated. This study provides a way to obtain a better epoxy resin as promising candidates in potential electronic packaging and insulating materials.

EXPERIMENTAL

Materials

4,4′-(Hexafluoroisopropylidene) diphenol (BPAF) was purchased from Aladdin Chemistry Co. Ltd. DGEBA with a quoted epoxide equivalent weight of 185–210 and MHHPA used as the curing agent were both purchased from Sichuan EM Technology Co. Ltd., China. The other chemical reagents including epichlorohydrin (ECH), tetraethylammonium chloride (TEAC), tris(dimethylaminomethyl) phenol (DMP-30), benzene, magnesium sulfate anhydrous, and sodium hydroxide were obtained from Chengdu Kelong Chemical Co., China.

Synthesis of DGEBHF

The synthetic route of DGEBHF was shown in Scheme 1. BPAF (10.08 g, 0.03 mol), TEAC (0.1 g, 0.6 mmol), and ECH (24 mL, 0.3 mol) were placed and mixed in a 250-mL three-necked round flask equipped with a magnetic stirrer. The solution was etherified for 1 h at 75°C. Then, lower the temperature to 60°C and sodium hydroxide solution (30 wt %) was slowly dripped into the mixture in one portion and stirring was continued for 2 h at 75°C. The excessive ECH was removed under reduced pressure. Benzene (60 mL) and the rest of sodium hydroxide solution (30 wt %) were both added into the residue and the mixture was stirred for 2 h at 75°C. After the reaction was completed, the solution was washed with distilled water repeatedly to remove TEAC, sodium hydroxide, and sodium chloride. Finally, the solvent was concentrated *in vacuo* and the fluorinated epoxy resin, a viscous liquid, was obtained. Yield was 48.8%. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.68–2.85 (*t*, *J* = 4.0 Hz, 2H), 3.29 (*m*, 1H), 3.87–4.19 (*d*, *J* = 8.0 Hz, 2H), 6.81–6.83 (*d*, *J* = 8.0 Hz, 4H), 7.22–7.28 (*m*, 4H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 131.8, 128.3, 126.4, 114.3, 69.3, 63.8, 50.3, and 44.9 ppm.

Measurement of Epoxide Value

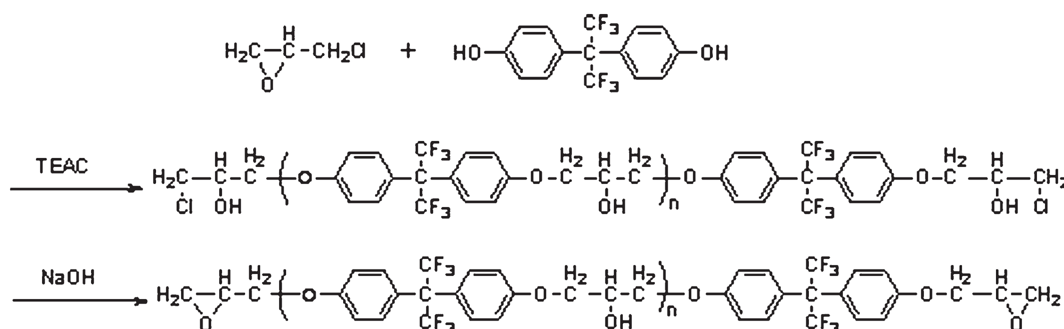
Epoxide value is the equivalent number of epoxide group per 100 g epoxy resin, this is equal to 100/(equivalent weight).

Principle: Hydrochloric acid–acetone method was applied to measure the epoxide value of DGEBHF in this study. In acetone solvent, an excess of the hydrochloric acid was used to react with epoxy group, generating chlorohydrin. Then alkali was used to titrate the excess hydrochloric acid.

Measurement: 0.5000–1.0000 g epoxy resin was put into a 100 mL conical flask. Then 20 mL hydrochloric acid–acetone solution (concentrated hydrochloric acid 1 mL, dissolved in 50 mL acetone) was added in the conical flask. The bottle was plugged and shaken up until the sample was completely dissolved. After the sample was located in a shade place for 1 h, two or three drops of methyl red indicator were added into it, then the titration was carried out by using 0.1 mol/L NaOH standard solution until the color turned from red to yellow in the end. The blank experiment was also carried out in the same way. The epoxide value can be deduced using a simple formula and is given as

$$E = \frac{(V_0 - V_1) \times N_{\mathrm{NaOH}}}{1000 \times W} \times 100 \quad (1)$$

where E is epoxide value; V_0 is the NaOH solution volume (mL) consumed by blank; V_1 is the NaOH solution volume (mL) consumed by sample; N_{NaOH} is the NaOH solution



Scheme 1. Synthesis of the DGEBHF.

Table I. The Composition of DGEBA and DGEBHF Formulations

Epoxy resin (wt %)	MHHPA (wt %)	DMP-30 (wt %)
DGEBA (100)	68.6	1
DGEBHF (100)	53.8	1

DGEBA, diglycidyl ether of bisphenol A; DGEBHF, 2,2-bisphenol hexafluoropropane diglycidyl ether; DMP-30, tris(dimethylaminomethyl) phenol; MHHPA, methyl hexahydrophthalic anhydride.

concentration (mol/L); and *W* is the quality of the sample (g).[19] The measured epoxide value of DGEBHF is 0.40 eq/100 g and the epoxide value of DGEBA is 0.51 eq/100 g.

Sample Preparation

The epoxy resin (DGEBHF or DGEBA) and MHHPA were mixed homogeneously; then the accelerator DMP-30 (1 wt % based on epoxy resin) was added. The composition of DGEBA and DGEBHF formulations was shown in Table I and the anhydride–epoxy equivalent ratio is 0.8 for both formulations. The mixture was fully stirred and degassed in a vacuum oven to eliminate air bubbles. The bubble-free mixture was poured into a stainless mold and cured at 120°C for 1 h, 140°C for 1 h, 160°C for 1 h, 180°C for 1 h, and 200°C for 2 h in a convection oven. The chemical structures of the compounds used in this study were depicted in Table II.

Characterization and Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded with a Bruker AV-400 spectrometer (400 Hz) at 25°C. The samples were dissolved with $CDCl_3$. Tetramethyl silane (TMS) was used as the internal standard. The FTIR measurements were conducted on a Nicolet 6700 FTIR instrument at room temperature. The specimens were ground with KBr and pressed into pellets for measurement. Thermogravimetric analysis (TGA) was performed on a TA Q500 in nitrogen at a heating rate of 10°C·min^{-1} from 30°C to 650°C. Dynamic mechanical analysis (DMA) was carried out on a TA Q800 instrument with a heating rate of 5°C·min^{-1} at a constant frequency of 1 Hz in single cantilever bending under a nitrogen atmosphere. Rectangular specimens of 35 mm length, 15 mm width, and 1.5 mm thickness were used. Differential scanning calorimetric (DSC) analyses were performed with TA Q200 analyzer from 25°C to 300°C at a heating rate of 10°C·min^{-1} in a nitrogen atmosphere. Dielectric analysis (DEA) experiments were performed using an SF2801 (TETTEX AG Instrument, Switzerland) Dielectric Analyzer and the frequency used for the DEA experiments was 50 Hz. Circular specimens of 100 mm diameter and 1.2 mm thickness were used. Tensile strength and flexural strength were measured using Universal Testing Machine (WSM-20KB). The crosshead speed was maintained at 5 mm/min and 2 mm/min, respectively. The specimens were used for measurement according to the GB/T 2567-2008. Impact strength was studied using Impact Testing Machine (JJ-20). The samples were used for measurement according to the GB/T 2567-2008. Water absorptions were carried out by weighing the changes of cured epoxy samples with a size of 50 mm length, 50 mm width, and 4 mm thickness before and after immersion in water at 25°C for 24 h (1 day), 10 days, 15 days, and 30 days (method I) and in boiling water for 6 h (method II).

RESULTS AND DISCUSSION

Synthesis of DGEBHF

The fluorinated epoxy resin DGEBHF was synthesized through a two-step procedure as depicted in Scheme 1. First, etherification reaction has happened on the ECH and BPAF with the catalyst TEAC. Then, sodium hydroxide solution was added into the mixture and reacted for 4 h, and gave rise to ring-closure reaction with dehydrochlorination. The chemical structure was confirmed by FTIR, ^{1}H NMR, and ^{13}C NMR. As shown in Figure 1, the characteristic absorption band of the C–F was observed at 1213 cm^{-1}. The absorption peaks at 3049, 1616, and 1510 cm^{-1} were attributed to the aromatic ring. In contrast to BPAF, the characteristic absorption peak of the oxirane ring

Table II. Chemical Structure of Used Materials

Component	Abbreviation	Chemical structure
Epoxy	DGEBA	
	DGEBHF	
Curing agent	MHHPA	
Accelerator	DMP-30	

DGEBA, diglycidyl ether of bisphenol A; DGEBHF, 2,2-bisphenol hexafluoropropane diglycidyl ether; DMP-30, tris(dimethylaminomethyl) phenol; MHHPA, methyl hexahydrophthalic anhydride.

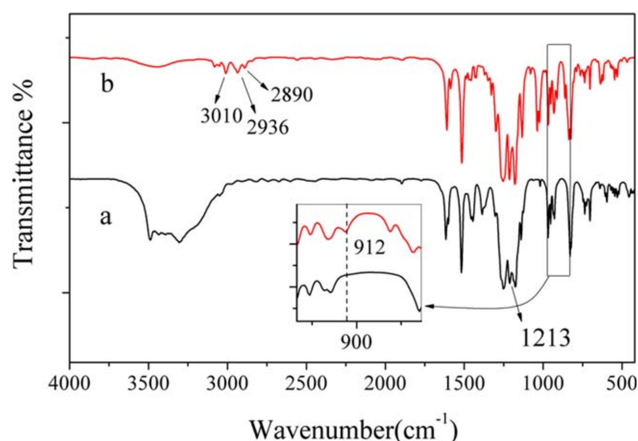


Figure 1. FTIR Spectra of BPAF (a) and DGEBHF (b). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

vibration appeared at 912 cm^{-1} and the absorption at 2936 and 2890 cm^{-1} because of the methylene and methine C–H vibration appeared in the spectra of DGEBHF. Figure 2(a) shows the ^{1}H NMR spectra of the DGEBHF in $CDCl_3$. All the signals of the proposed structure were observed, in which signals in the range of 6.81–7.28 ppm were ascribed to the protons of the aromatic rings, and the signals in the range of 2.83–3.29 ppm were the protons of epoxides. The ^{13}C NMR spectra [Figure 2(b)] also gave the corresponding carbon shifts of the compound. In terms of the FTIR and NMR results, it is judged that DGEBHF was obtained.

Thermal Properties of the Cured Resins

TGA was carried out to evaluate the thermal stability of cured resins. The TGA and DTG thermograms of cured epoxy resins under N_2 atmosphere in the temperature range 30°C–650°C were presented in Figure 3 and the data were summarized in Table III. It was found that the initial decomposition temperature of weight loss at 5% (T_5) for DGEBA/MHHPA and DGEBHF/MHHPA were at 362.1°C and 372.4°C, respectively. The decomposition temperature of maximum weight loss rate (T_{max}) were both at 426°C, while the maximum weight loss rate was significantly lower of DGEBHF/MHHPA in comparison with cured DGEBA resins. The residual weight retention at 650°C of fluorinated epoxy resins was 10.5%, which was higher than that of DGEBA/MHHPA (4.9%). The results clearly revealed that fluorine-containing epoxy resins exhibited higher thermal stability than DGEBA resins, which might be attributed to the incorporation of two symmetric trifluoromethyl groups in the epoxy backbone. The strong electron negativity of C–F bond might enhance the polarity of cured epoxy resins, restricting the movement of the polymer link, and resulting in better thermal stability.[20] Moreover, the bond enthalpy of C–F (116 kcal/mol) was larger than that of C–H (99 kcal/mol), meaning that the breakage of C–F bond needed more thermal energy. The results also contributed to improved thermal stability of DGEBHF/MHHPA. This is in contrast to the results of J. Y. Wang[21] who found a decreasing trend of the initial decomposition temperature and glass-transition temperature. Moreover, the T_5 of DGEBHF/MHHPA was obviously higher than the T_5 (324°C) of DGEBS/anhydride/DMBA systems, so was the T_{max}.[22]

DMA and DSC

The glass-transition temperature (T_g) was achieved as the maximum peak value of tanδ curve by DMA. Figure 4 shows the storage modulus and the temperature dependence of tanδ of cured samples and the corresponding data obtained from tanδ curves were given in Table IV. It can be seen that cured DGEBA exhibits higher storage modulus (E') than that of DGEBHF/MHHPA in glassy region because of the higher packing density. Packing density increases with the concentration of hydrogen bonds and DGEBA has a smaller molecular weight meaning that DGEBA network contains more hydroxyls than DGEBHF.[23] But the DGEBHF resins have higher E' at elevated temperature because of the steric hindrance of bulky CF_3 groups, which limit the chain mobility and increase chain stiffness. The T_g values of DGEBA/MHHPA and DGEBHF/MHHPA were 131.2°C and 147°C, respectively.

DSC also provides a useful technique to obtain the T_g values of cured thermosets, but it is less sensitive than DMA. The DSC curves of cured epoxy resins were shown in Figure 5 and the T_g values were summarized in Table IV. For both the two curves, there were no exothermal peaks, indicating that the networks have been cured completely and the DGEBHF/MHHPA system performs higher T_g (151.5°C) than the cured DGEBA resins (132.6°C). Furthermore, the T_g of DGEBHF/MHHPA was also higher than the anhydride-cured DGEBF epoxy[22] and the cured 3F-PQE (fluorine-containing epoxy resin) systems.[16]

From the results of T_g values, it can be seen that T_g values of DGEBHF/MHHPA were 16°C (or 19°C) higher than that of DGEBA/MHHPA. The DSC results were in good agreement with the results from DMA analysis. It has been disclosed that molecular packing state and chain rigidity were the two factors affecting T_g values of polymers.[24] The higher T_g of cured fluorinated epoxy resin could be interpreted that the presence of large bulky trifluoromethyl groups enhanced the rigidity of polymer chain by inhibiting its free rotation.[25,26]

Mechanical Properties Analysis

The mechanical properties of the cured epoxy resins were evaluated, including tensile strength, flexural strength, impact strength, and flexural modulus and the corresponding results are tabulated in Table V. The tensile strength of DGEBHF/MHHPA showed 29.1% decrease, and the flexural and impact strength were also decreased by 20.2% and 28.6%, respectively. The flexural modulus of DGEBA/MHHPA and DGEBHF/MHHPA were 1.97 and 1.87 GPa, respectively. We inferred that the incorporation of CF_3 groups had slightly decreased the mechanical properties of the cured epoxy resins. This phenomenon could be interpreted by the pendant CF_3 groups which reduced the conformational freedom and retarded free rotation, bringing about increase of chain rigidity and brittleness of cured resins.

Dielectric Analysis

The electrical properties of cured epoxy resins were studied by measuring dielectric constant (D_k) and dielectric loss (D_f) at

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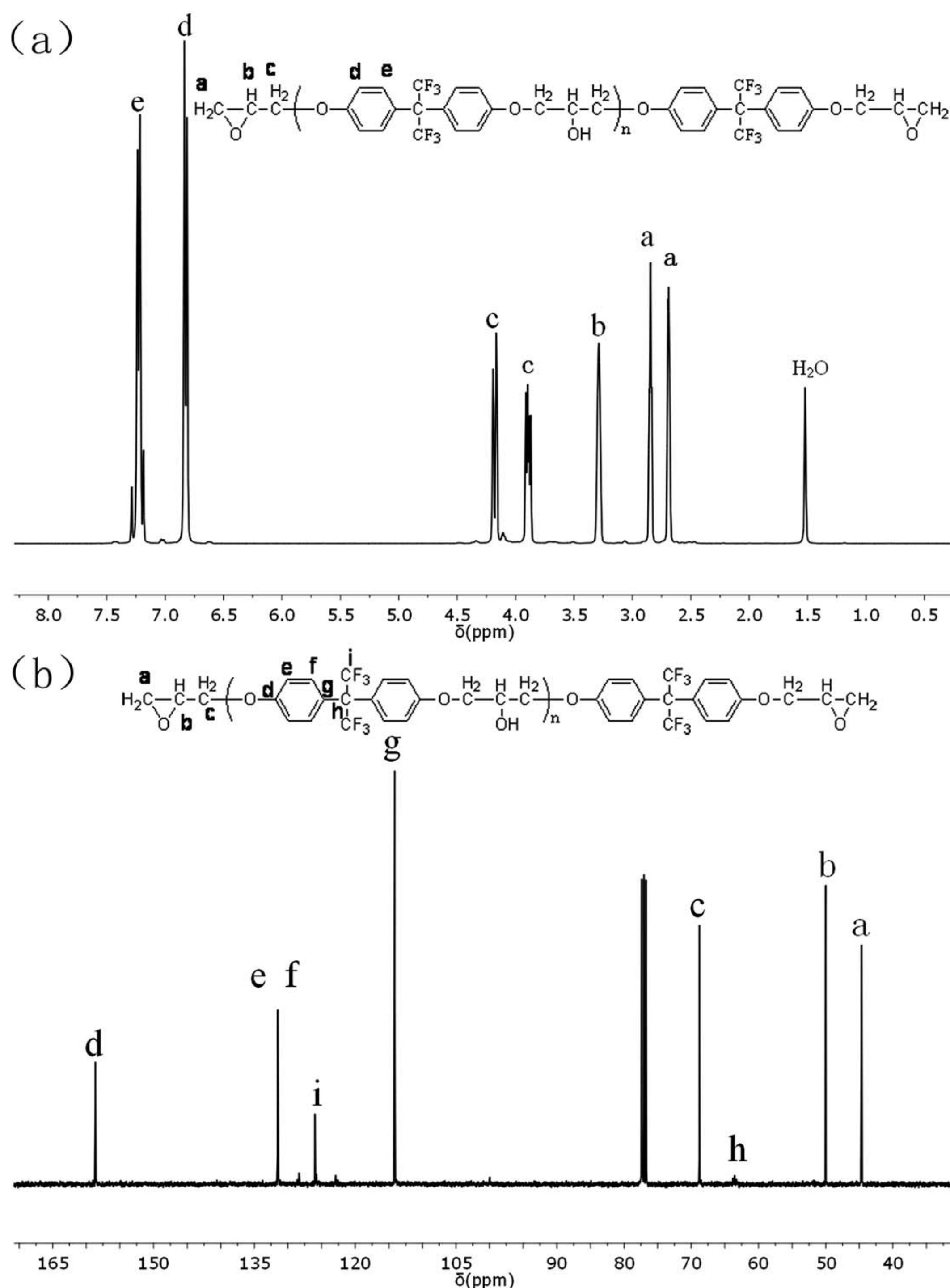

Figure 2. ^{1}H NMR (a) and ^{13}C NMR (b) Spectra of DGEBHF.

50 Hz at room temperature (25°C). The dielectric data were shown in Table VI. The dielectric constants of DGEBA/MHHPA and DGEBHF/MHHPA were 3.25 and 2.93, and the dielectric losses were 0.0060 and 0.0065, respectively. The lower dielectric constant of DGEBHF/MHHPA than that of DGEBA/MHHPA could be explained by the small dipole and low polarizability of the C–F bond as well as the increase in free volume, which accompanied the replacement of methyl groups by trifluoromethyl groups. What's more, the large electron negativity of fluorine atoms led to tight binding of electrons which reduced the electronic polarization in the polymer.[20,27,28] These results suggested that CF_3 groups in the network structure of epoxy resins played an important role in their dielectric performance. The development of epoxy resin with a low dielectric constant (D_k) is an important research direction, which enables them to have great potential application in microelectric field.

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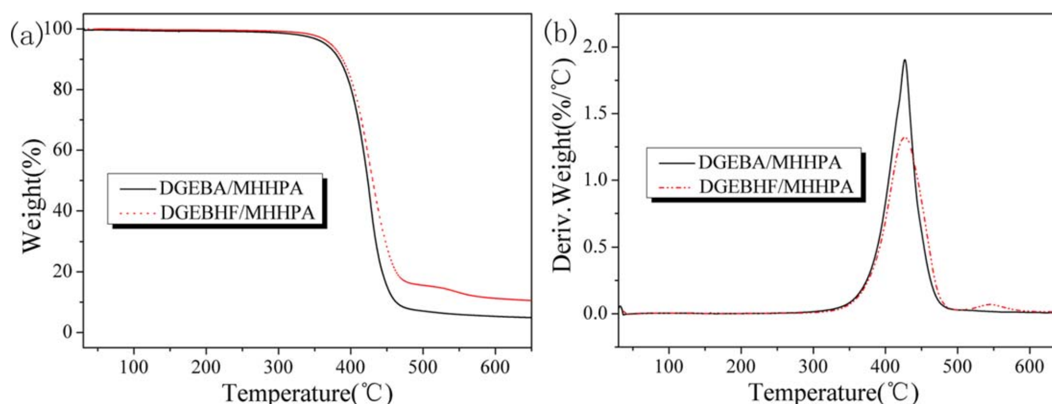

Figure 3. TGA (a) and DTG (b) Thermograms of DGEBA/MHHPA and DGEBHF/MHHPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Water Absorption

In practical application, materials had to suffer from varying conditions of temperature and humidity. However, the moisture adsorption had a great effect, especially at high temperature, on the thermal stability and mechanical properties of materials. Low-water absorption was an important factor for the advanced microelectronic packing materials because a small amount of moisture could substantially affect the electrical insulating and dielectric performance obviously by enhancing total polarizability of the resin system.

The water absorption could be ascribed largely to the moisture affinity of specific functional groups of a highly polar nature in the cured resin.[30] Table VI shows the water absorptions of the cured epoxy resins. The water absorptions of cured DGEBA/

Table III. Thermal Properties of Cured Epoxy Resins

Sample	T_5 (°C)	T_{10} (°C)	T_{max} (°C)	R_w (%)
DGEBA/MHHPA	362.1	383.9	426.8	10.5
DGEBHF/MHHPA	372.4	388.5	426.6	4.9

DGEBA, diglycidyl ether of bisphenol A; DGEBHF, 2,2-bisphenol hexafluoropropane diglycidyl ether; MHHPA, methyl hexahydrophthalic anhydride; T_5, the decomposition temperature of weight loss at 5%; T_{10}, the decomposition temperature of weight loss at 10%; T_{max}, the temperature at the maximum weight loss rate; R_w, residual weight retention at 650°C.

Table IV. T_g Values and Storage Modulus of Cured Epoxy Resins

Sample	E' (MPa) (50°C)	E' (MPa) (150°C)	$T_{g\ DMA}$ (°C)	$T_{g\ DSC}$ (°C)
DGEBA/MHHPA	3044	21	131.2	132.6
DGEBHF/MHHPA	2566	80	147.0	151.5

DGEBA, diglycidyl ether of bisphenol A; DGEBHF, 2,2-bisphenol hexafluoropropane diglycidyl ether; E′, higher storage modulus; MHHPA, methyl hexahydrophthalic anhydride.

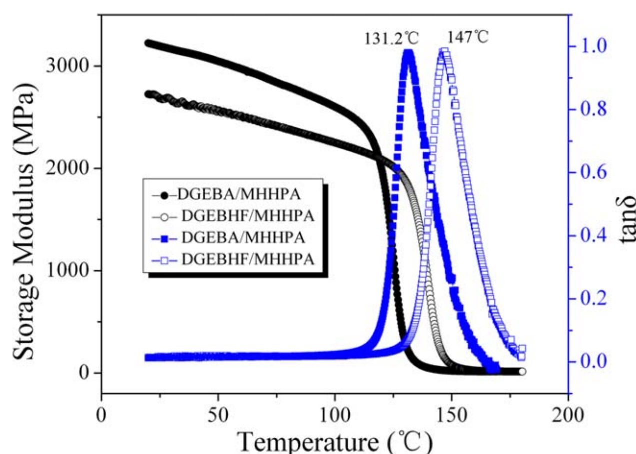

Figure 4. DMA Curves of DGEBA/MHHPA and DGEBHF/MHHPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

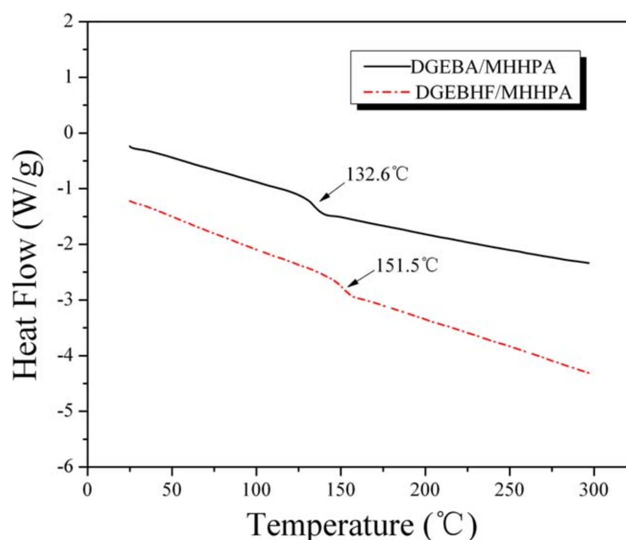

Figure 5. DSC Curves of DGEBA/MHHPA and DGEBHF/MHHPA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table V. Mechanical Properties of Cured Epoxy Resins

Sample	Tensile strength (MPa)	Flexural strength (MPa)	Impact strength (kJ/m^2)	Flexural modulus (GPa)
DGEBA/MHHPA	72.4	118.3	14.7	1.97
DGEBHF/MHHPA	51.3	94.4	11.5	1.87

DGEBA, diglycidyl ether of bisphenol A; DGEBHF, 2,2-bisphenol hexafluoropropane diglycidyl ether; MHHPA, methyl hexahydrophthalic anhydride.

Table VI. Dielectric Properties of Cured Epoxy Resins and Their Water Absorptions

			Water absorption (%)				
			I				
Sample	D_k	D_f	1 day	10 days	15 days	30 days	II
DGEBA/MHHPA	3.25	0.0060	0.1098	0.3517	0.3811	0.4548	0.4187
DGEBHF/MHHPA	2.93	0.0065	0.0876	0.2838	0.3023	0.3648	0.2989

D_f, dielectric loss at 50 Hz at 25°C; DGEBA, diglycidyl ether of bisphenol A; DGEBHF, 2,2-bisphenol hexafluoropropane diglycidyl ether; D_k, dielectric constant at 50 Hz at 25°C; E′, higher storage modulus; I, immersion in water at 25°C for 1 day, 10 days, 15 days, and 30 days; II, immersion in boiling water for 6 h; MHHPA, methyl hexahydrophthalic anhydride.

MHHPA and DGEBHF/MHHPA determined by method I were 0.1098–0.4548% (1–30 days) and 0.0876–0.3648% (1–30 days), respectively, and those measured by method II were 0.4187% and 0.2989%, respectively, smaller than those of a fluorinated epoxy resin BGTF/HMPA[17] in the same testing condition. According to Fickian diffusion,[31] the relatively high-water absorption obtained by method II was related to the high experimental temperature which could accelerate the diffusion of H_2O molecules into the polymer. The cured DGEBHF/MHHPA exhibited lower water absorption in both methods I and II than that of DGEBA/MHHPA. The increase of water absorption of DGEBHF/MHHPA is smaller than that of DGEBA/MHHPA with the increasing immersion time in method I. The results made clear that incorporation of fluorine atom into polymer structure could obviously reduce the water absorption because of the low polarity and strong hydrophobicity of fluorine atom.

CONCLUSIONS

The fluorinated epoxy resin DGEBHF has been successfully synthesized via a two-step reaction based on epichlorohydrin and BPAF by phase-transfer catalysis, and further thermally cured with MHHPA. The obtained DGEBHF/MHHPA exhibited higher glass-transition temperature (T_g) and initial decomposition temperature (T_5 and T_{10}) than that of pure DGEBA resins. The water absorption and the dielectric constant were also lower than those of DGEBA/MHHPA. The cured fluorinated epoxy resin also displayed good mechanical properties including tensile strength, flexural strength, and impact strength. The experimental results demonstrated that incorporation of fluorine into the epoxy backbone apparently improved the integrated performance of the cured resins. Therefore, epoxy resins containing bis-trifluoromethyl groups have been looked upon to be one of the most promising matrix materials f or applications in microelectronics.

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