Synthesis and Properties of Trifluoromethyl Groups Containing Epoxy Resins Cured with Amine for Low D_k Materials

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Received 7 May 2011; accepted 9 July 2011
DOI 10.1002/app.35300
Published online 2 November 2011 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The study synthesized a trifluoromethyl (CF_3) groups with a modified epoxy resin, diglycidyl ether of bisphenol F (DGEBF), using environmental friendly methods. The epoxy resin was cured with 4,4′-diaminodiphenyl-methane (DDM). For comparison, this study also investigated curing of commercially available diglycidyl ether of bisphenol A (DGEBA) with the same curing agent by varying the ratios of DGEBF. The structure and physical properties of the epoxy resins were characterized to investigate the effect of injecting fluorinated groups into epoxy resin structures. Regarding the thermal behaviors of the specimens, the glass transition temperatures (T_g) of 50–160°C and the thermal decomposition temperatures of 200–350 °C at 5% weight loss ($T_{d5\%}$) in nitrogen decreased as amount of DGEBF increased. The different ratios of cured epoxy resins showed reduced dielectric constants (D_k) (2.03–3.80 at 1 MHz) that were lower than those of pure DGEBA epoxy resins. Reduced dielectric constant is related to high electrronegativity and large free volume of fluorine atoms. In the presence of hydrophobic CF_3 groups, the epoxy resins exhibited low moisture absorption and higher contact angles. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2615–2624, 2012

Key words: epoxy resins; thermal behaviors; dielectric constants; free volume

INTRODUCTION

Epoxy resins have a wide range of applications, including paints, coatings, die attach adhesives, industrial composites, and electronic packaging.[1,2] In many high-tech structural applications, epoxy resins are viewed as the minimum standard of performance for the matrix of the composite. Epoxy resins form multifunctional materials of generally amorphous thermosetting resins known for their excellent adhesive properties, superior mechanical properties, improved resistance to fatigue and micro cracking, reduced degradation from water ingress, and increased resistance to osmosis.[3,4] Emergent applications of epoxy resins include lithographic ink, electronic packing, low dielectric constant materials, and photoresists for the electronic industry. Electronic circuit development has been accomplished with the downscaling of component size. Increases in circuit speed are mainly due to reduction in transistor gate lengths, resulting in shorter transistor switching times. As dimensions are scaled down to the submicro range, the signal runtime delays caused by the higher resistance capacitance (RC) of the metallization may outweigh the benefits of a reduced gate length. Introducing materials with a lower dielectric constant for insulators is necessary.[5,6]

The carbon-fluorine (C-F) bond has larger molecular-free volume, small dipole, and low polarizability properties, which results in low dielectric constant for many materials.[7–12] The fluorine atoms also have low refractive index and moisture adsorption.[13,14] Thus, fluorine-containing polymers have been widely investigated in the fields of optical communication and microelectronics. Sasaki and Nakamura found that among fluorinated polymers, the epoxy resins with incorporated perfluorobutenyloxy groups had low dielectric constant and 75% reduced water adsorption.[15,16] Maruno et al. synthesized a novel fluorinated epoxy resin, which exhibited high optical transparency and low refractive index properties.[17] Many studies demonstrate the synthesis of fluorine-containing epoxy resins by different steps to reduce dielectric constant (D_k) and lower their moisture adsorption. The main objective of this research was to synthesize of novel F-containing epoxy resins compound by a one-step reaction without using any NaOH or KOH as basic catalyst. This study

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Component	Abbreviation	Chemical structure
Monomer	BHHP	
	ECH	CH_2–CH–CH_2Cl (epoxide)
Epoxy	DGEBA	
	DGEBF	
Curing agent	DDM	H_2N–Ph–CH_2–Ph–NH_2
Catalyst	BTAC	Ph–$CH_2\dot{N}(C_2H_5)_3Cl^-$

Scheme 1 Chemical structures of the used materials.

synthesized and explored the properties of new fluorine-containing epoxy resins, including thermal stability, electrical, and mechanical properties.

In this study, a novel material with low dielectric constant (D_k), the CF_3 groups with modified epoxy resin (DGEBF), was synthesized and characterized. The fluorinated epoxy resin and different ratios of DGEBA were thermally cured with diaminodiphenyl methane (DDM). This study examined the activation energy (E_a) of the cured epoxy resins' decomposition. The thermal stability, electrical and dielectric properties, and water adsorption of different ratios of the fully cured fluorine-containing epoxy resins were investigated.

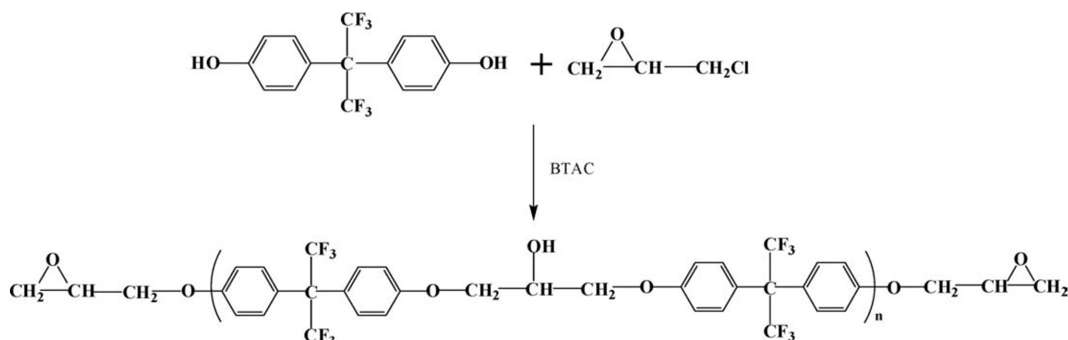
EXPERIMENTAL

Materials

The 2,2-bis(4-hydroxyphenyl)-hexafluoropropane (BHHP) was purchased from TCI America. The DGEBA epoxy resin was obtained from Aldrich Chem, which has an epoxide equivalent weight of 185–190 g eq^{-1} and a density of $\sim$ 1.16 g cm^{-3} at 25°C. Benzyltrimethyl ammonium chloride (BTAC) and DDM were purchased from ACROS. Epichlorohydrin was obtained from TEDIA Company. The chemical structures of the used materials are shown in Scheme 1.

Synthesis of DGEBF

The synthetic route of DGEBF was shown in Scheme 2. BHHP (6.72 g, 0.68 mol), BTAC (4 g) and epichlorohydrin (ECH; 80 mL) were placed in a magnetically stirred 250-mL three-necked round flask and well mixed. The solution was then reacted in an oil bath at 70°C for 72 h. After BHHP was completely reacted with epichlorohydrin (ECH), the solution was washed with distilled water repeatedly to remove BTAC catalysts. The DGEBF solution was dried by added enough amount of anhydrous magnesium sulfate into the solution and filtrated. Finally, the extra solvent of epichlorohydrin (ECH)



Scheme 2 Synthesis of DGEBF.

TABLE I
Glass Transition Temperatures and Dynamic DSC Scans of DGEBF/DGEBA/DDM System Under an N2 Atmosphere

DGEBF/DGEBA Blend						
Sample code	DGEBF ratio (%)	DGEBA ratio(%)	T_g° (C)	T_{on}° (C)	T_p° (C)	Δ (J/g)
10F0D	100	0	64.59	89.53	134.48	76.3
9F1D	90	10	52.43	92.73	138.32	108.1
8F2D	80	20	58.15	93.42	139.64	171.9
7F3D	70	30	66.36	96.41	143.07	264.5
6F4D	60	40	98.34	97.66	145.38	318.5
5F5D	50	50	108.72	112.22	153.65	365.8
4F6D	40	60	119.90	110.42	152.54	370.5
3F7D	30	70	122.53	114.25	154.47	390.4
2F8D	20	80	138.72	123.15	160.62	396.7
1F9D	10	90	141.25	129.65	164.44	407.1
0F10D	0	100	158.93	132.78	167.27	484.6

*T_g: glass transition temperature.
T_{on}: the onset temperature of curing reaction.
T_p: the exothermic peak temperature of curing reaction.
ΔH: the total heat of reaction for the cured samples.

in the DGEBF solution was removed under reduced pressure. The yield of the DGEBF epoxy resin was 80%.

Sample preparation

The mixed weight ratios of DGEBF/DGEBA were summarized in Table I. The equivalent amount of DDM was added to the epoxy resin and degassed in a vacuum oven to eliminate air bubbles before forming film. The degassed mixture was poured into an aluminum plate and cured. The curing condition was 80°C for 1.5 h/120°C for 2 h/150°C for 2 h.

Characterizations

FT-IR spectra were recorded with a Perkin–Elmer RX-I by using KBr pellet. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were obtained by a Varian Unity Inova 500 NMR operated at 500 MHz in *d*-chloroform. Differential scanning calorimetric (DSC) analyses were performed with TA Instrument TA2010 analyzer from 30 to 200°C at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. Thermogravimetric analyses were performed with a Du Pont TGA 2900 analyzer from 30 to 900°C. The activation energy (E_a) for the cured epoxy resins' decomposition at a heating rate of 20°C min^{-1} in a nitrogen atmosphere was calculated from the TGA thermogram analysis by using the Horowitz–Metzger Equation.[18,19]

$$\ln\{ \ln(1-\alpha)^{-1}\} = E_a\theta/RT_{\max}{}^2 \quad (1)$$

where α is the decomposition ratio, θ the difference between T and $T_{\max}$, $T_{\max}$ the temperature of maximum rate of weight loss, and R the ideal gas constant. The activation energy was received by the straight line corresponding to the plot of $\ln\{\ln(1-\alpha)^{-1}\}$ versus θ.

The surface morphologies and fluorine content of cured DGEBF/DGEBA epoxies were obtained by using a scanning probe microscope (Digital Instrument NS3a controller with D3100 stage) and time-of-flight secondary ion mass spectrometer, TOF-SIMS (TOF.SIMS IV, ION-TOF, Germany), respectively. The water adsorption of cured epoxy was determined by immersion in water at 25°C for 24 h and soaking in boiling water for 6 h. The dielectric constants of cured epoxies were measured over a frequency range from 1 MHz to 1.6 GHz at room temperature using a dielectric spectrometer (HP/Agilent 4291B RF impedance/material analyzer).

RESULTS AND DISCUSSION

Structural characterization of the DGEBF

Figure 1 shows the FT-IR spectra of BHHP and DGEBF. In Figure 1(a), the characteristic absorption bands of the aromatic ring were found to appear at 3058, 1585, and 1172 cm^{-1}. Figure 1(b) shows the adsorption spectra from 600 to 1100 cm^{-1}, the absorption attributed to the epoxide group was observed at 916 cm^{-1} in the FT-IR spectrum of DGEBF.[20]

In the ^{1}H-NMR spectra of DGEBF [Fig. 2(a)], the signals assigned to the protons in aromatic rings appeared in the region of 7.0–7.21 ppm. The signal of the OH group appeared at 3.78 ppm. The signals of protons in the epoxide group were observed in the range of 2.72–3.34 ppm. For the ^{13}C NMR spectra (chloroform-d_6) [Fig. 2(b)], the chemical shift of the epoxide group appeared at 42.0 and 48.2 ppm. The chemical shift of the aromatic rings was observed at 116.4–129.2 ppm. The chemical shift at 119.0–126.0 ppm belonged to the CF_3 group. For the ^{19}F NMR spectra, Figure 2(c) shows the chemical shift of the CF_3 group at −64.56 ppm.[21]

Thermal properties of fluorine-containing epoxy resins

Figure 3 illustrates the dynamic DSC thermograms of DGEBA and DGEBF cured with DDM at a heating rate of 10°C min^{-1}. The exothermal peak of DGEBA/DDM ranged from 105 to 220°C with a reaction enthalpy of 482 J g^{-1}. The curing of DGEBF/DDM showed two exothermal peaks of 75–180°C and 180–240°C, with a total reaction enthalpy of 82 J g^{-1}. The introduction of CF_3 groups into the main-chain of epoxy resins increases steric hindrance, resulting in reduction of the reactivity of the

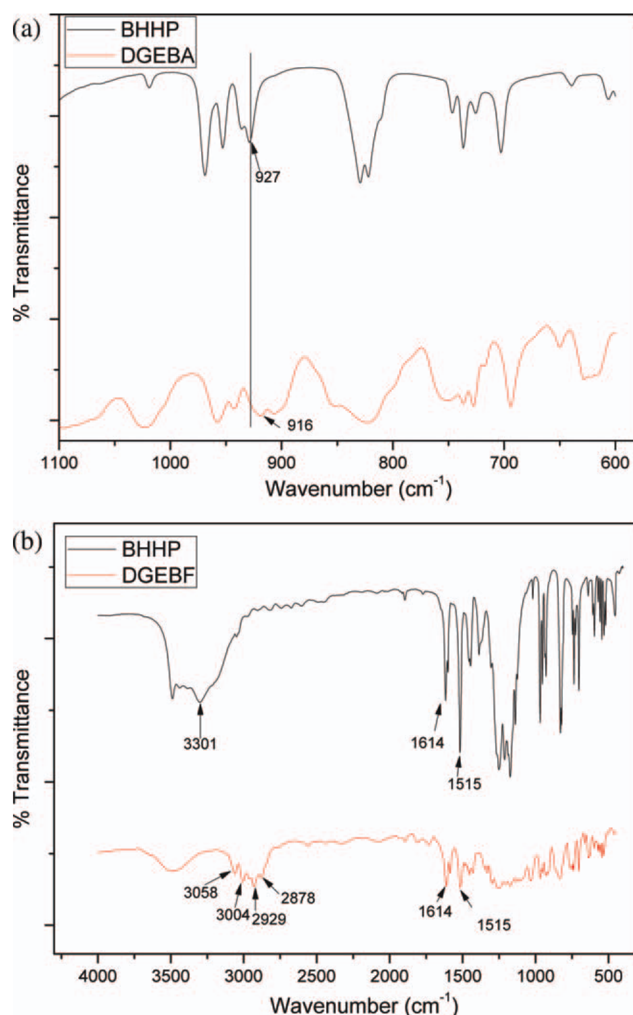


Figure 1 FT-IR spectrum of BHHP and DGEBF epoxy resin. (a) 400–4000 cm^{-1} (b) 600–1100 cm^{-1}. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

oxirane ring and DDM in the curing reaction.[22] In the following experiment, the same curing conditions were used to cure the mixture of DGEBA/DGEBF resins: 80°C, 120°C, 150°C for 2 h.

The thermal properties of cured DGEBA/DGEBF mixtures were characterized by DSC and TGA. Figure 4 shows the DSC trace in a nitrogen atmosphere. The results are summarized in Table I. The table clearly illustrates that the glass transition temperatures of epoxy resins containing various amounts of DGEBF were lower than those of pure DGEBA epoxy resins. The presence of CF_3 groups increased steric hindrance, resulting in lower crosslinking density and thus lower T_g. Additionally, the results demonstrated that the introduction of CF_3 groups can create more free volume, which can act as a plasticizer to decrease the glass transition temperature of the epoxy resins.[23,24] From Table I, it is clear that DGEBF facilitated the curing initially by lowering the onset temperature of curing (T_{on}). The DGEBF has higher reactivity for DDM attributed to the high nucleophilic ability of CF_3 group introduced into the chain of the epoxy resin.[25] It is obvious that for the epoxy resin with higher contents of DGEBF, the exothermic peaks were smaller and the onset of temperatures of curing were lower than those of the pure DGEBA system, implying the inclusion of DGEBF decreased the curing degree of the epoxies, possibly due to the physical hindrance of the DGEBF oligomer to the mobility of the monomers.[26–28] The steric effect of the DGEBF prepolymer implies that the new carbamate crosslinking within the network is not structurally and chemically identical to the normally cured neat DGEBA network. Therefore, the higher contents of DGEBF experienced less degree of curing to result in low crosslinking density. On the other hand, Figure 3 showed the DSC thermograms for the curing procedure of DGEBA and BGEBF with DDM. As comparing with the reactivities of these epoxy resins, we found that the DGEBF give the exothermic starting temperature lower than that of DGEBA in DDM curing systems. During solvent evaporation, the DGEBF chains will pack increasingly closer together as a consequent of a concentration effect. Because DGEBA and DGEBF are thermodynamically immiscible, microphase separation gradually occurred as amount of DGEBF increased in the epoxy resins. Therefore, we believe that large free volume of CF_3 groups and microphase separation of thermodynamically immiscible process decrease the crosslinking density of the polymer network structure.

The TGA trace of epoxy resins with different degrees of DGEBF in a nitrogen atmosphere is shown in Figure 5. The figure clearly shows that the decomposition temperature at 5 wt % of weight loss ($T_{d5\%}$) of epoxy resins with various degrees of DGEBF was lower than that of pure DGEBA epoxy resins. These results show that low epoxy crosslinking density functions to reduce decomposition temperature. The trend of the decomposition temperature is equivalent to that of glass transition temperature.[29,30]

Thermal stability of epoxy resins

According to eq. (1), the activation energy (E_a) at every stage of the weigh loss of the cured epoxy resins was obtained from the straight line corresponding to the $\ln\{(1 - \alpha)^{-1}\}$ versus θ.[18,19] All of the slope data attained strong correlation exceeding 0.99. The activation energy, the temperature of maximum weight loss rate (T_{max}), and the char yield are summarized in Tables II and III. The temperature of maximum weight loss rate (T_{max}) and the activation energy (E_a) decreased as amount of DGEBF increased in the epoxy resins. The novel epoxy resins maintained elementary thermal stability with glass transition

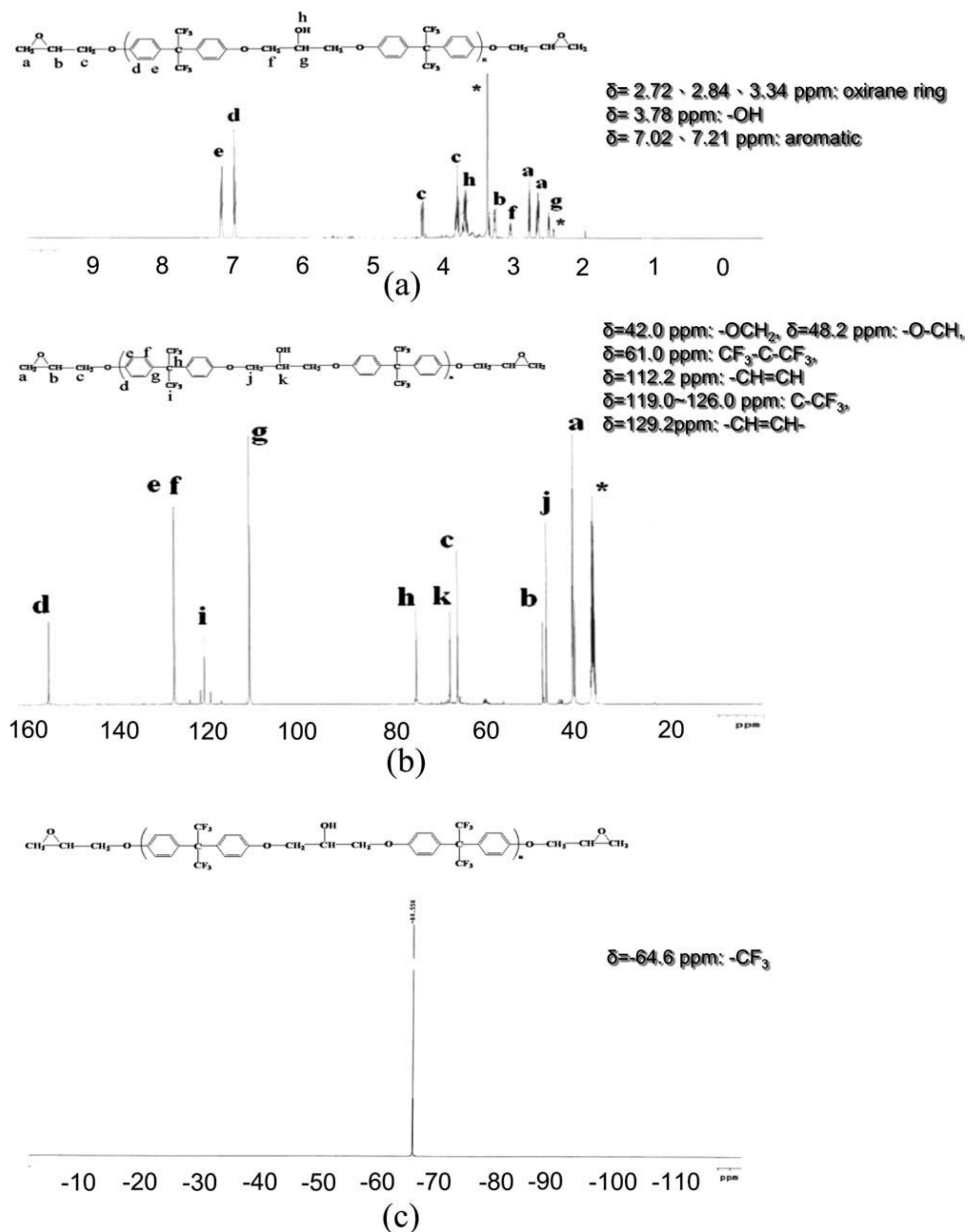


Figure 2 NMR spectra of DGEBF epoxy resin. (a) ^{1}H NMR, (b) ^{13}C NMR, (c) ^{19}F NMR.

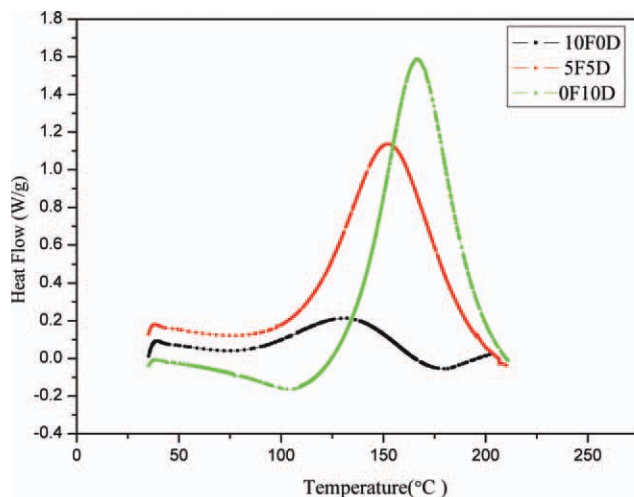


Figure 3 Dynamic DSC thermograms of DGEBF/DGEBA/DDM system under an N_2 atmosphere (heating rate: 10°C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

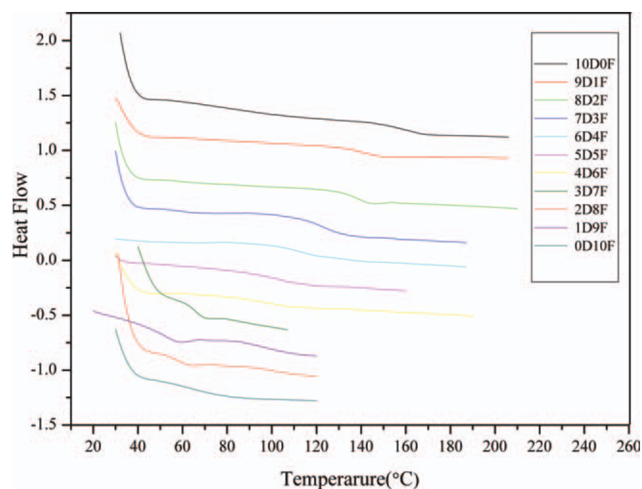


Figure 4 DSC trace of DGEBF/DGEBA/DDM system under an N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

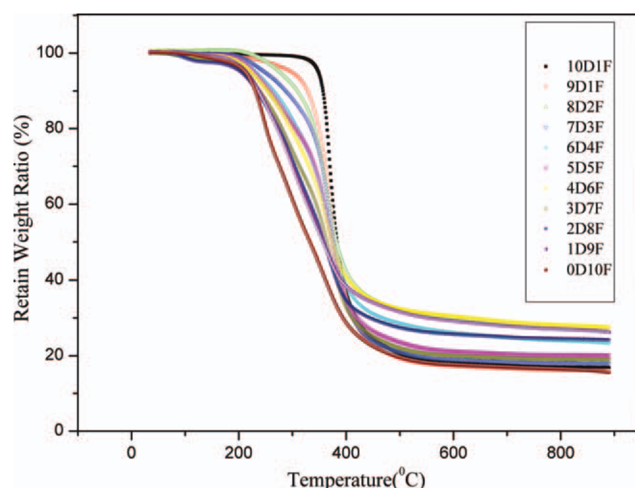


Figure 5 TGA trace of DGEBF/DGEBA/DDM system under an N_2 atmosphere. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

temperature of 65–159°C and thermal decomposition temperature at 5% weight loss of 213–348°C in nitrogen compared with other fluorinated polymers.[15–17] The relatively low thermal stability of the epoxy resins can be explained by the presence of CF_3 group structure in the polymer, which had low thermal stability as compared with pure DGEBA system. This result can be also understood through epoxy crosslinking density. As more CF_3 groups are incorporated into the epoxy resin chains, more free volume is introduced. Therefore, the decomposition of epoxy resin decreases as DGEBF content increases.[31–34] The char yield ratio was 16.2–28.1 wt %.

Water adsorption and surface analysis

Epoxy resins exhibit hydrophobic properties and low water adsorption. Low water adsorption is an important factor for the advanced microelectronic materials because H_2O molecules in the materials will affect electrical insulation and dielectric performance. Table IV summarizes the contact angles and the water adsorption of the cured epoxy resins. The water contact angle could be increased gradually as fluorinated groups incorporated because of their small dipole and the low polarizability of the C—F bond for hydrophobicity between water and epoxy resin surface. The dried cured epoxy resin samples (50.8 mm in diameter and 3.2 mm in thickness) were immersed in water at room temperature for 24 h (MethodI-ASTM D570-98) or in boiling water at 100°C for 2 h (MethodII-ASTM D570-98). The weight differences were then determined. The water adsorptions of epoxy resins with different ratios of DGEBF as determined by Method I was 1.69–2.66%; water adsorption as determined by Method II was 2.2–3.2%. According to Fickian diffusion,[35] higher temperature could accelerate the diffusion of H_2O molecules into the polymer. Experimental data indicated that the fluorine containing

TABLE II
Thernal Stability and Degradation Data of the Epoxy Resins from Thermogravimetric Analysis in Nitrogen

Sample	T_{d5}	T_{d10}	T_{max}	800°C Char Yield	850°C Char Yield
10F0D	213	231	300	16.45	16.07
9F1D	214	237	347	27.03	26.69
8F2D	205	234	360	24.48	24.27
7F3D	227	252	364	20.09	19.97
6F4D	224	253	361	28.13	27.86
5F5D	228	257	370	20.18	20.15
4F6D	232	265	371	24.04	23.8
3F7D	255	291	371	19.37	19.28
2F8D	276	310	365	27.37	27.02
1F9D	299	329	371	16.21	16.13
0F10D	348	357	370	17.02	16.99

*T_{d5}: Decomposition temperature at 5% of weight loss.
T_{d10}: Decomposition temperature at 10% of weight loss.
T_{max}: the temperature of maximum rate of weight loss.

TABLE III
Degradation Data from Horowitz-Metzger Equation

Sample	Slope	T_{max}	E_a(kJ/mol)	R
10F0D	0.0128	573.15	34.96	0.9932
9F1D	0.0106	620.15	33.89	0.9961
8F2D	0.0119	633.15	39.66	0.9988
7F3D	0.016	637.15	54.00	0.9978
6F4D	0.0148	634.15	49.48	0.9967
5F5D	0.0196	643.15	67.40	0.9974
4F6D	0.0179	644.15	61.75	0.9982
3F7D	0.0262	644.15	90.38	0.9956
2F8D	0.0276	638.15	93.45	0.9951
1F9D	0.0349	644.15	120.40	0.9966
0F10D	0.0746	643.15	256.55	0.9905

*E_a: activation energy of the decomposition.

TABLE IV
Moisture Absorption and Contact Angle of Cured Epoxy Resins

Sample	Contact Angle (°)	Water absorption(%)	
		I	II
10F0D	79.83	1.69	2.2
9F1D	76.35	1.70	2.6
8F2D	75.11	1.66	2.4
7F3D	74.78	1.66	2.9
6F4D	73.93	2.56	3.0
5F5D	75.16	2.58	3.2
4F6D	77.65	2.56	3.2
3F7D	73.72	2.57	3.1
2F8D	74.74	2.56	3.2
1F9D	76.08	2.60	3.0
0F10D	70.00	2.66	3.1

*Water absorption, I: immersion in water at 25°C for 24 h; II:immersion in boiling water for 2 h.

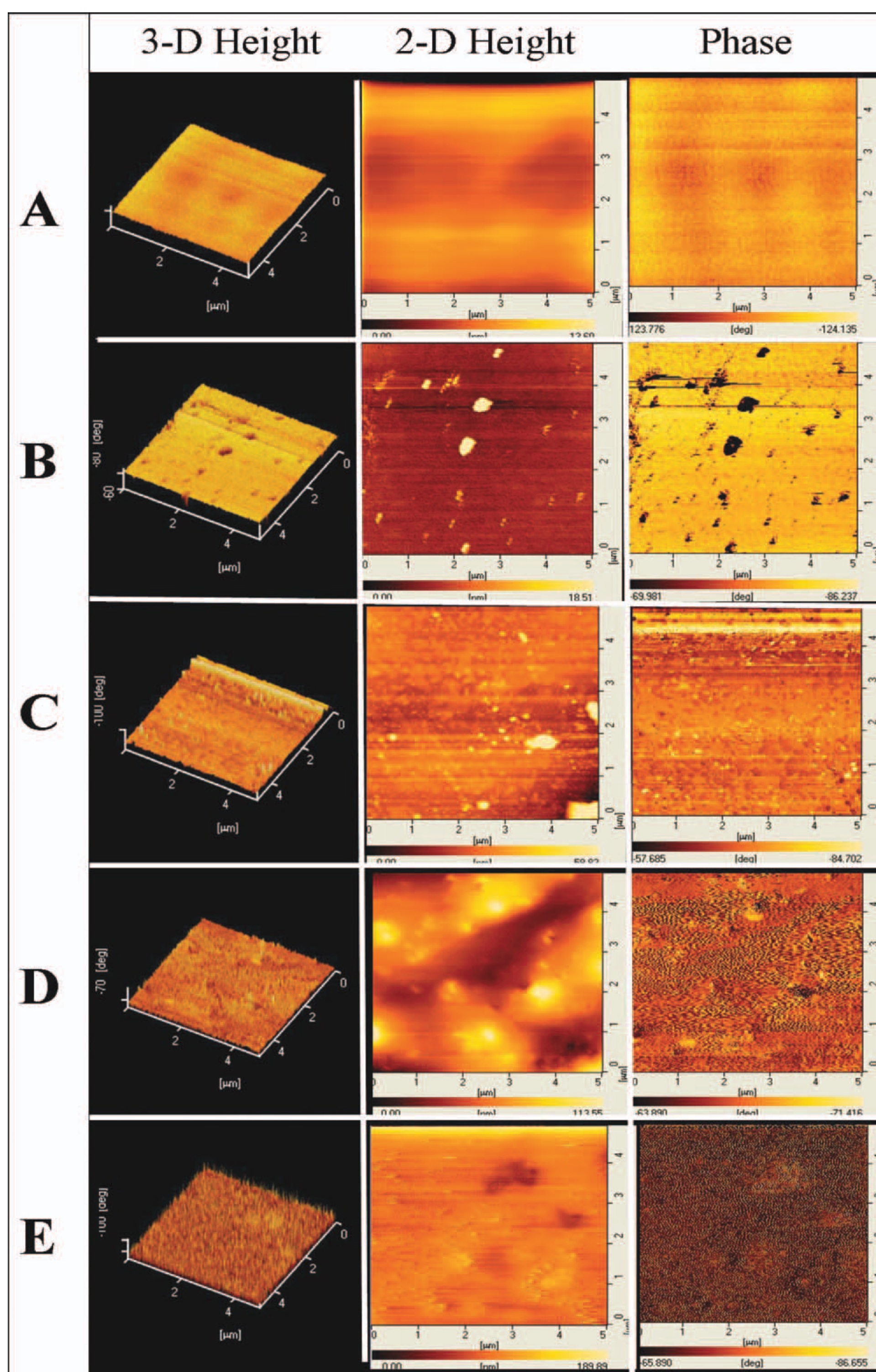


Figure 6 SPM images of A: 1F9D, B: 3F7D, C: 5F5D, D: 7F3D, E: 9F1D. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

epoxy resins had low water adsorption equivalent to that of the pure DGEBA epoxy resins. The fluorinated side chain (CF_3) was used to impart hydrophobicity to the surface of the gate dielectric and epoxy resins were employed to improve its wetting properties. The water adsorption values decreased by 1% and the contact angle increased by 10°compared to the pure DGEBA epoxy resins.[31]

Morphology of the cured epoxy resins

The wetting behavior of the cured epoxy resins can be explained in terms of morphology, observed by

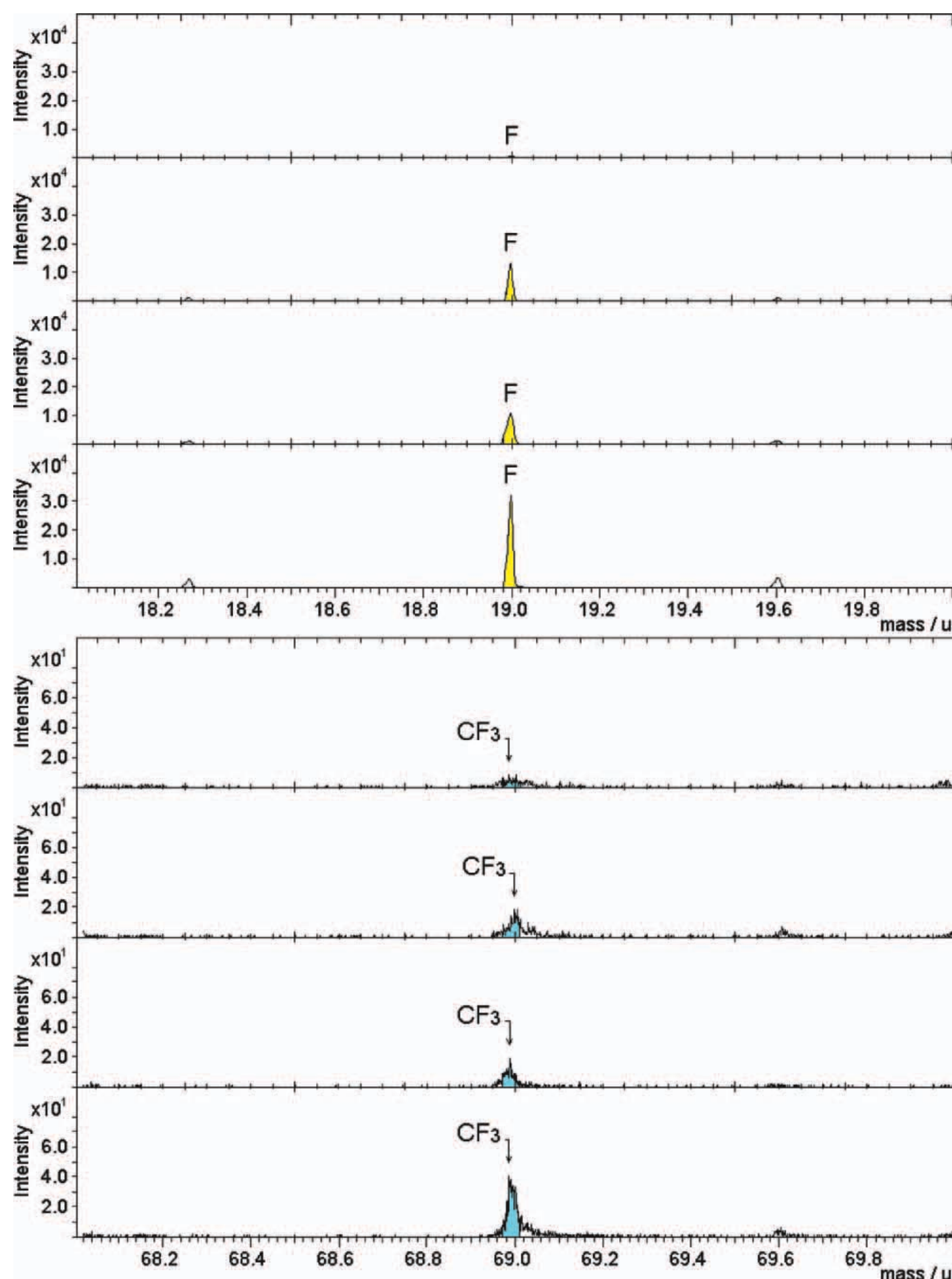


Figure 7 The TOF-SIMS spectrum of epoxy resins. (a) 0F10D; (b) 3F7D; (c) 7F3D; (d) 10F0D. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

SPM. Figure 6 shows the SPM micrograph of the epoxy resins. The surface roughness of epoxy resins significantly increased as the DGEBF content increased. Because hydrophobic properties are known to be enhanced by increase of surface roughness,[36] hydrophobic surfaces are commonly prepared through a combination of surface roughening and reduction of the surface energy.[37,38] Increased roughness implies increased hydrophobicity. The results of SPM accounted for greater free volume and low crosslinking density as CF_3 groups were incorporated into the linear structure of epoxy resins.

Surface components of ToF-SIMS

Time-of-fight secondary ion mass spectrometry (ToF-SIMS) was used to investigate surface components. ToF-SIMS takes advantage of the destructive nature of the ion probe. Atoms can be knocked free from the surface by the bombarding ions, and the ionized atoms are analyzed by conventional mass spectrometry. Because a large number of different types of ions can be emitted from the surface, ToF-SIMS provides more detailed information about surface chemistry. The water contact angle of cured epoxy resin surface increased due to incorporation of CF_3 groups

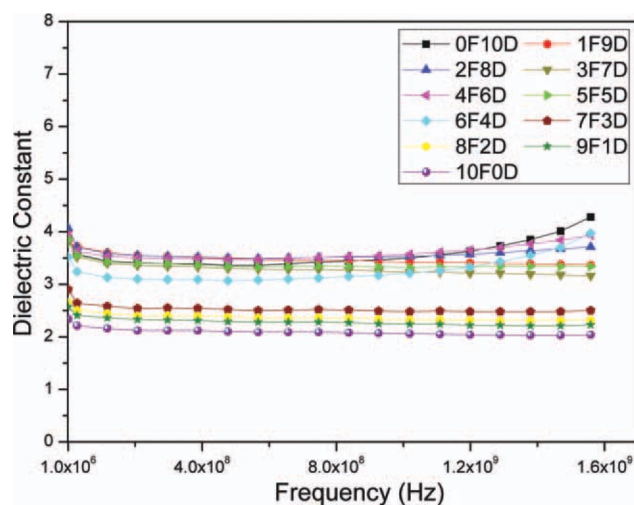


Figure 8 Dielectric constants of the epoxy resins as a function of frequency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

into epoxy resin structure. The 10F0D sample exhibited the largest contact angle because the CF_3 groups had low polarizability and high electronegativity.[12] Figure 7 shows that amount of water-repellent F atoms on the surface of the cured epoxy resin samples was increased due to the increase in DGEBF values.

Dielectric properties

The electrical properties of the cured epoxy resins were studied by measuring the dielectric constant (D_k). The D_k for the cured epoxy resins were measured by a dielectric spectrometer at different frequencies (1 MHz to 1.6 GHz) and ambient temperature. Figure 8 shows the variation of the real part of the permittivity of the specimens as a function of frequency. The D_k of the epoxy resins decreased steadily as DGEBF increased. The decreased dielectric constants of the fluorinated epoxy resins can be explained by the low polarizability of the C—F bond and the large free volume of CF_3 groups.[39,40] These results suggested that the CF_3 groups in the network structure of epoxy resins played an important role in electrical and dielectric performances. And, microphase separation of thermodynamically immiscible process decreased the crosslinking density of the polymer network structure and enhanced the free volume in specimens. The looser structure, which was likely the introduction of air-filled pores into the polymer structure, caused a dramatic reduction in the dielectric properties. The dielectric constant decreased to 2.0 lower than the value 2.77 of epoxy resins containing the perfluorobutenyloxy group.[16]

On the other hand, the dielectric loss of the epoxy resins referred to the imaginary part of a relative permittivity, as in the following equation:

$$\varepsilon r = \varepsilon r'(\omega) + i\varepsilon r'' \quad (\omega)$$

The dielectric loss was due to the inability of the polarizable units in the epoxy resin chains to align in phase with the increasing electric field frequency. Physically, the dielectric loss was related to the form of dissipative heat energy. In Figure 9, it showed decrease in dielectric loss with increasing DGEBF content. These results were discussed in terms of an overall enhancement small-scale molecular mobility by incorporation of CF_3 groups in epoxy resins, arising from loosened molecular packing of polymer chains, as compared to the pure DGEBA system. However, the value obtained in the range 9.8×10^{-3}–4.4×10^{-2}, were reasonably low compared to some of the other organic polymers and inorganic materials.

CONCLUSIONS

In this study, a novel fluorinated epoxy compound DGEBF was successfully synthesized and then thermally cured with aromatic diamine DDM. The glass transition temperature of epoxy resins with various degrees of DGEBF content was lower than that of pure DBEBA epoxy resins. Decomposition temperature at 5 and 10 wt % of weight loss ($T_{d5\%}$, $T_{d10\%}$) exhibited equivalent tendencies. The thermal stability of epoxy resins was investigated using the Horowitz–Metzger equation. The temperature of maximum ($T_{\max}$) weight loss rate and activation energy (E_a) decreased as DGEBF content in the epoxy resins increased. The surface energy, water absorption and

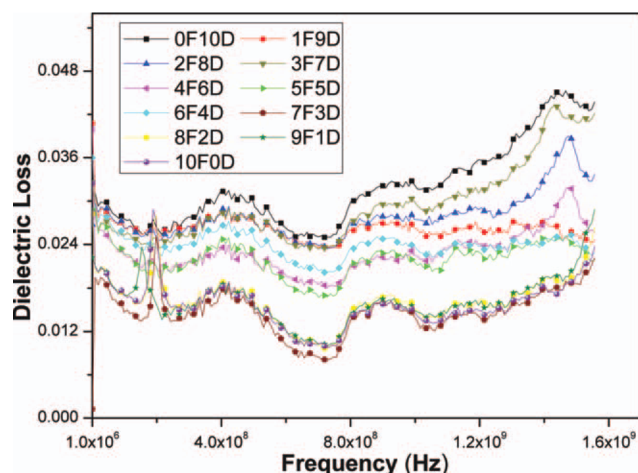


Figure 9 Dielectric losses of the epoxy resins as a function of frequency. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

dielectric constant of epoxy resins with different ratios of DGEBF were lower than those of pure DGEBA epoxy resins. These results were attributed to the incorporation of CF_3 groups into the network structure of epoxy resins.

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