

# Synthesis and properties of an epoxy resin containing trifluoromethyl side chains and its cross-linking networks with different curing agents

Zhongguo Liu, Gang Zhang, Zhuang Liu, Hongcheng Sun, Chengji Zhao, Shuang Wang, Guibin Li, Hui Na\*

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Qianjin Street 2699#, Changchun 130012, PR China

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## ABSTRACT

The epoxy resin with a trifluoromethyl side chain, (3-trifluoromethyl) phenylhydroquinone epoxy resin (3F-PQE), was synthesized via a three-step procedure. The chemical structures were confirmed by FT-IR,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and elemental analysis. A series of trifluoromethyl epoxy networks has been prepared with four curing agents: poly (propylene glycol) bis (2-aminopropyl) ether (D230), 2-methylimidazole (2MI), 4, 4'-methylene-dianiline (DDM) and phthalic acid anhydride (PA). All samples exhibited excellent thermal stabilities (the decomposition temperature of 5% weight loss ( $T_d$ )) ranged from 335 to 362 °C in  $\text{N}_2$  and 291–355 °C in air). The 3F-PQE-DDM sample showed the highest  $T_g$  of all the samples. Moisture absorption of 3F-PQE-DDM and 3F-PQE-PA at 80 °C for 24 h was no more than 1 wt %. The cured fluorinated epoxy resins exhibited that the contact angles were more than 90°, which is the hydrophobic properties.

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## 1. Introduction

Epoxy resins are widely used as matrices in advanced composites due to their intrinsic stiffness, chemical and heat resistance derived from a heavily cross-linked structure. In recent years, epoxy resins have been used in electrical insulation applications to withstand system voltage in support structures because of the ease in molding to any desired shape, low cost, light weight, and good electrical insulation properties of the cross-linked polymer matrix [1–4]. The rapid growth of applications has also prompted extensive research in the electric and electronic industries.

Incorporation of fluorine into the epoxy resins has been intensively explored because of the unique characteristics of fluorine substitution. Generally, fluorine incorporation can low the dielectric constant, low optical loss and moisture absorption, increase thermal stability, and also improve chemical stability [5–11]. Thus, fluorinated epoxy resins are considered to be one of the potential candidates for electronic packaging materials.

Many epoxy resins based on fluorine have been developed over past few decades. Tao et al. [12] reported that a novel fluorinated epoxy resin, containing  $\text{CF}_3$  groups, was successfully synthesized by a four-step procedure. The fluorinated epoxy resins exhibited a high glass-transition temperature, low dielectric constant and low water

absorption. Hsieh et al synthesized a novel UV-curable fluorinated epoxy acrylate with fluoroalkyl ( $\text{C}_5\text{F}_{11}$ ) units in the side chain [13]. The designed fluorinated epoxy acrylate exhibited a contact angle of about 151°, which is in the superhydrophobic range. In our previous work, a novel epoxy resin was prepared containing fluorine in the side chain, (3-Trifluoromethyl) phenylhydroquinone epoxy (3F-PQE), but we only confirmed the structure by FT-IR and  $^1\text{H}$  NMR [14]. The cured properties of epoxy have not been researched.

To obtain the materials with high performance applications, it is necessary to know and to understand the relationships between the structure of a material and its properties [15]. In this study, we focused on the relationship between structure and properties of the resins obtained by introducing a trifluoromethyl group into the epoxy backbone. We describe the synthesis and characterization of epoxy resins, 3F-PQE, cured with four different curing agents. The thermal stability, glass-transition temperature ( $T_g$ ) and moisture absorption, as well as contact angle were studied in detail. This study provides a way to obtain a better epoxy resin with suitable curing agents.

## 2. Experimental

### 2.1. Materials

Poly (propylene glycol) bis (2-aminopropyl) ether (D230) and epichlorohydrin (ECH) were purchased from Aladdin Reagent

\* Corresponding author. Fax: +86 431 85168870.

E-mail address: [huina@jlu.edu.cn](mailto:huina@jlu.edu.cn) (H. Na).

(Shanghai, China). (3-trifluoromethyl) aniline and 1,4-benzoquinone were purchased from Beijing Chemical Company (Beijing, China). 4,4'-methylene-dianiline (DDM), phthalic acid anhydride (PA) and 2-methylimidazole (2MI) were obtained from the China Medicine (Group) Shanghai Chemical Reagent Corp (Shanghai, China). All other chemicals mentioned in this paper are obtained from Beijing Chemical Company and used without further purification.

## 2.2. Monomer synthesis

### 2.2.1. Synthesis of (3-trifluoromethyl)benzoquinone (3F-BQ) monomer

3-aminobenzotrifluoride (80.5 g, 0.5 mol) and 200 mL of deionized water were added into a 1000-mL breaker equipped with a mechanical stirrer, a dropping funnel, and a thermometer. Then, hydrochloric acid (168 mL, 11.8 M) was added dropwise into the solution. The solution was added from a dropping funnel to a well-stirred mixture of concentrated water solution (90 mL) of sodium nitrite (34.5 g, 0.5 mol) in the breaker. To keep the temperature below 5 °C, ice was added. The mixture was stirred at 0–5 °C for 1 h and a transparent solution was obtained. The resulting solution was filtered and added dropwise into a mixture of 1,4-benzoquinone (54 g, 0.5 mol), sodium bicarbonate (126 g, 1.5 mol) and deionized water (200 mL). The reaction mixture was stirred at 8–10 °C for 3 h, and then at room temperature for another 3 h. The resulting mixture was filtered and the precipitate was washed with deionized water five times. Then, the obtained yellow solid was dried at 50 °C in a vacuum oven for 24 h. Yield: 89%. Mp: 68 °C (DSC). *m/z*: 252.

### 2.2.2. Synthesis of (3-trifluoromethyl)phenylhydroquinone (3F-PQ) monomer

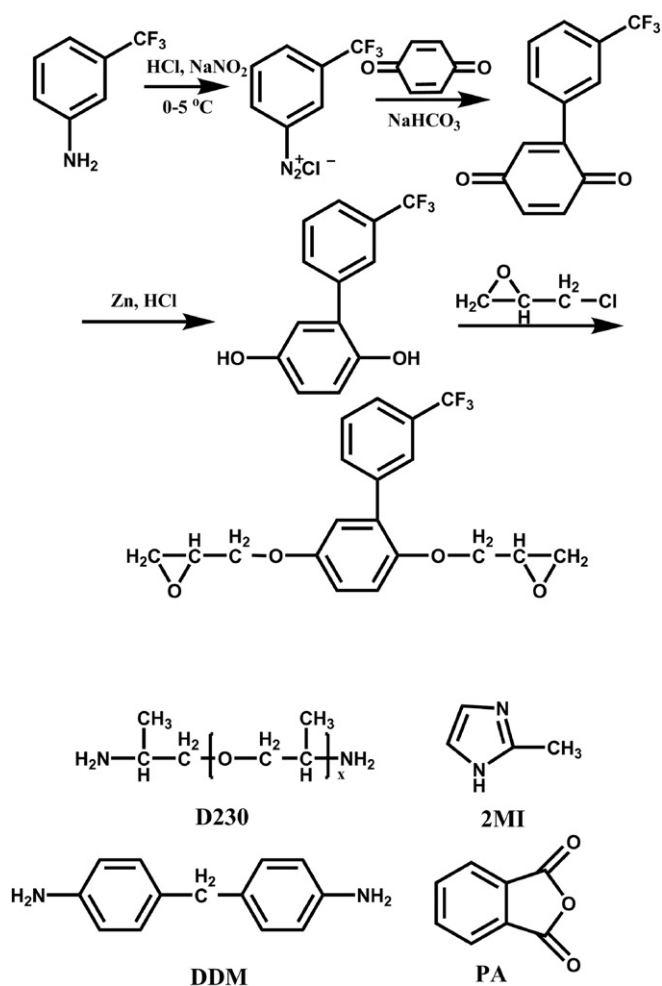
The yellow solid (3F-BQ), Zn powder (130 g, 2 mol), and 500 mL of deionized water were placed into a 3000-mL, three-necked flask equipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to 90 °C with stirring, followed by the addition of concentrated hydrochloric acid (126 mL) dropwise at a rate of 1 drop per second. After completing the addition, the reaction system was allowed to reflux for 2 h. Then, the hot mixture was filtered. After cooling the filtrate, the white precipitate was filtered, dried and recrystallized from toluene to give white needles. Yield: 78%. Mp: 88 °C (DSC). *m/z*: 254.

### 2.2.3. Synthesis of (3-trifluoromethyl)phenylhydroquinone epoxy (3F-PQE)

A mixture of 3F-PQ (32 g, 0.126 mol), epichlorohydrin (191.25 mL, 2.44 mol) and tetrabutylammonium bromide (4.25 g) was stirred in a three-neck flask at 90 °C for 10 h. After cooling to room temperature, the excess epichlorohydrin was removed at a reduced pressure. Subsequently, toluene (191.25 mL) and NaOH (18.25 g, 30 wt % solution) were added and kept at 90 °C for 3 h. Then, the mixture was washed by distilled water at room temperature until the water was neutral. The excess toluene and water were distilled under reduced pressure. The solid product was dried in a vacuum oven at room temperature for 12 h. The 3F-PQE was a brown, viscous liquid. Yield: 91%.

## 2.3. Preparation of the cured epoxy resins

The 3F-PQE was cured with D230, 2MI, DDM and PA, respectively. Scheme 2 shows the procedure for the preparation of epoxy networks with the curing agents. According to the Epoxide Equivalent Weight (EEW) values, the stoichiometric amounts of D230, DDM and PA were added into the epoxy mixtures with tetrahydrofuran as the solvent. The molar ratio of 3F-PQE and 2MI was 2:1.



**Scheme 1.** Structures and schematic synthesis route for 3F-PQ, 3F-PQE, D230, 2MI, DDM and PA.

Then, the mixtures were stirred for about 20 min at 40 °C. Part of the solution was poured onto a glass slides and the other was poured into a highly polished mould. The glass slides and the mold were dried in a vacuum oven at 40 °C for 24 h to remove the solvent. The curing process of epoxy samples was performed at 140 °C for 2 h, 160 °C for 2 h, 190 °C for 2 h and 220 °C for 1 h. The samples on the glass slides were used to measure the contact angle.

## 2.4. Characterization

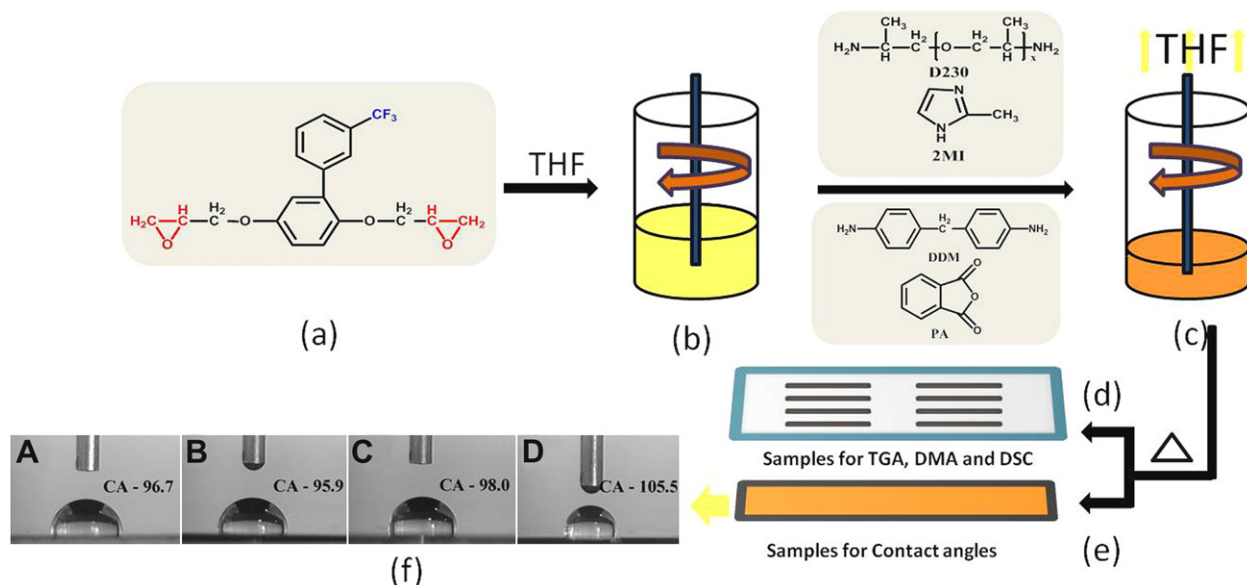
The <sup>1</sup>H and <sup>13</sup>C NMR spectrum were measured on a 500 MHz Bruker Avance 510 spectrometer using deuterated dimethyl sulphoxide (DMSO-d<sub>6</sub>) as the solvent with tetramethylsilane (TMS) as a reference.

Fourier-transform infrared (FT-IR) spectra were measured with a Nicolet Impact 410 Fourier-transform spectrometer with scanning from 400 to 4000 cm<sup>-1</sup> using KBr disks.

Differential scanning calorimetry (DSC) was performed using a Mettler Toledo DSC 821<sup>e</sup> instrument in the temperature range 35–250 °C at a heating rate of 10 °C/min under nitrogen.

Dynamic mechanical analysis (DMA) was performed using a DMA Q 800 analyzer using a three-point bending mode over a temperature range of 50–250 °C at the heating rate of 3 °C/min at a constant frequency of 1 Hz.

Thermogravimetric analysis (TGA) was conducted using a Perkin–Elmer TGA-2 thermogravimetric analyzer. The samples were



**Scheme 2.** Preparation of the cured epoxy resins and water contact angle test of the 3F-PQE samples (f): (A) D230; (B) 2MI; (C) DDM; (D) PA.

heated to 100 °C and kept at this temperature for 5 min to make sure that the residual water and solvent had been removed completely, and then heated from 100 to 700 °C at a rate of 10 °C/min under a nitrogen or air atmosphere.

Contact angle measurements were performed on a JC2000C2 contact angle goniometer (Shanghai Zhongchen Powereach Company, China) by the sessile-drop method with a micro syringe at room temperature. Static contact angles were obtained from water droplets on the surface of the cured epoxy samples. More than 8 contact angles were averaged to get a reliable result for each sample.

Elemental analysis was carried out with a flash EA 1112 analyzer.

Moisture absorption of the samples was determined by measuring the change in weight between the dry and wet samples. The cured samples were dried at 80 °C until constant weight. After immersion in deionised water at 20 °C, 40 °C, 60 °C and 80 °C for 24 h each, the samples were taken out, wiped with tissue paper, and their weights were quickly measured. Moisture absorption of the samples was calculated:

$$\text{Moisture absorption} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{wet}}} \times 100\%$$

where  $W_{\text{dry}}$  and  $W_{\text{wet}}$  are the weights of the dry and the corresponding water-absorbed sample, respectively.

### 3. Discussion

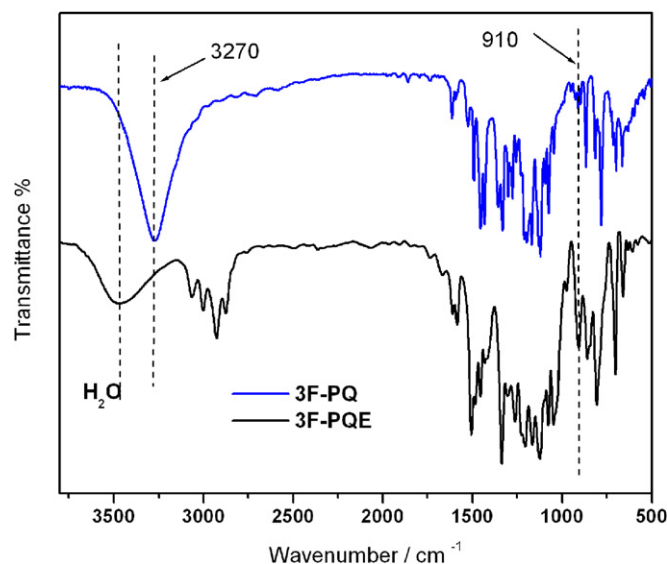
#### 3.1. Characterization of monomers

Fig. 1 shows the FT-IR spectra of 3F-PQ and 3F-PQE. Notably, the absorption peak of the hydroxyl group (-OH) of 3F-PQ around 3270  $\text{cm}^{-1}$  was sharpened but it disappeared in 3F-PQE (around 3400  $\text{cm}^{-1}$  was the absorption peak of water). From the spectrum of 3F-PQE, a characteristic absorption peak of the oxirane ring vibration ( $\Delta$ ) was observed at 911  $\text{cm}^{-1}$ , while no such peak was observed for 3F-PQ. Therefore the epoxy groups had been successfully introduced into 3F-PQE molecules.

For elemental analysis: Calculated for (C<sub>13</sub>H<sub>9</sub>O<sub>2</sub>F<sub>3</sub>): C, 61.42%; H, 3.54%. Found: C, 61.51%; H, 3.46%. Calculated for (C<sub>19</sub>H<sub>17</sub>O<sub>4</sub>F<sub>3</sub>): C, 62.30%; H, 4.64%. Found: C, 62.40%; H, 4.55%. Elemental analyses of the synthesized 3F-PQ and 3F-PQE are in good agreement with

calculated results. From the previous results it was determined that 3F-PQ gained two oxirane rings successfully.

Scheme 1 shows the synthetic route of 3F-PQ and 3F-PQE. According to a similar synthetic process previously reported by Liu et al. [16], the bisphenol monomer was prepared. The structure of the bisphenol monomer was identified by FT-IR, <sup>1</sup>H NMR, <sup>13</sup>C NMR and elemental analysis. As shown in Fig. 2, the proton peaks at 8.87 and 9.02 ppm were assigned to the proton of the hydroxyl group that could not be observed in the spectrum of the corresponding 3F-PQE. New peaks, 8, 8', 9, 9', 10 and 10', appeared in 3F-PQE. The peaks around 3.85 and 4.30 ppm were attributed to methylene (-CH<sub>2</sub>-, 8, 8'), while the peaks from 2.59 to 2.81 ppm were assigned to methylene (-CH<sub>2</sub>-, 10, 10'). The peaks at 3.19 and 3.30 ppm were attributed to methane (9, 9'). The other peaks were consistent with 3F-PQ. The <sup>13</sup>C NMR spectrum gave the following results (C<sub>13</sub>H<sub>9</sub>O<sub>2</sub>F<sub>3</sub>, 500 MHz, DMSO-d<sub>6</sub>, ppm): 117.13, 117.92, 123.93, 126.22, 127.13, 129.70, 129.95, 133.72, 140.53, 147.61, 151.15. The <sup>13</sup>C NMR spectrum gave the following results (C<sub>19</sub>H<sub>17</sub>O<sub>4</sub>F<sub>3</sub>,



**Fig. 1.** FT-IR spectra of 3F-PQ and 3F-PQE.

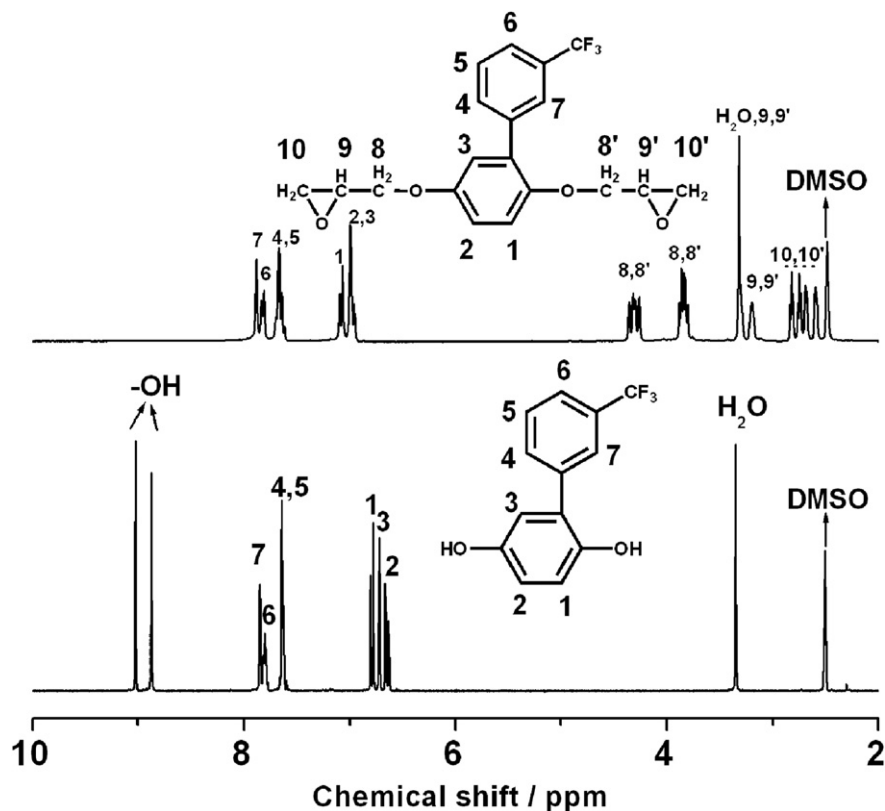


Fig. 2.  $^1\text{H}$  NMR spectra of 3F-PQ and 3F-PQE.

500 MHz,  $\text{DMSO-d}_6$ , ppm): 44.36, 50.52, 70.40, 115.55, 116.17, 117.50, 124.55, 126.72, 129.85, 130.01, 134.09, 139.47, 150.21, 153.35. Both  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra indicated that the 3F-PQE was synthesized successfully.

### 3.2. Thermal behavior of cured epoxy resins

TGA traces of the cured epoxy samples provide their thermal stability and thermal degradation behavior [17]. Fig. 3(a, b) shows the TGA curves of epoxy thermosets with different curing agents under an  $\text{N}_2$  (a) or air atmosphere (b). Table 2 gives the relevant thermal decomposition data, including the decomposition temperature of 5% weight loss ( $T_d$ ), the temperature of maximum weight loss rate ( $T_{\text{max}}$ ), the char residues at 700 °C and Integral procedural decomposition temperature (IPDT) [20].  $T_d$  for epoxy thermosets ranged from 335 to 362 °C (in  $\text{N}_2$ ) and 291–355 °C (in air). All of the four networks can satisfy thermal stability requirement (>200 °C) for an electric packing material.

As shown in Table 2, the  $T_d$  of 3F-PQE-D230 was lower than the others under either nitrogen or air. Because introducing an aliphatic chain of D230 into 3F-PQE network reduced the thermal stability of the epoxy polymers; while the epoxy polymer networks of DDM, PA and 2MI contain a large number of aromatic nucleus, imidazole rings and carbonyl groups, separately, which results in more stable networks than those for 3F-PQE-D230.

The thermogravimetric analysis (DTG), presented in Fig. 3(c, d), shows the main rapid peak of the epoxy-system degradation. The main peak is near 368–427 °C (in  $\text{N}_2$ ) and near 356–436 °C (in air). As shown in Fig. 3d, the first significant mass loss regions was from 317 to 460 °C, due to oxidation of some fragments and due to release of small-molecule degradation products [18,19]. But there was a small mass loss in the 3F-PQE-D230 system before the first peak, perhaps due to decomposition from free-radical chain scission and

D230 [18]. The second degradation stage follows from oxidation of the remaining carbonaceous char. However, as shown in Fig. 3(c, d), the first stage of mass loss in air was the same as the rapid mass loss in  $\text{N}_2$  that showed only one mass loss stage. No more than 1 wt % char remained after 650 °C in air condition. Compared to the results in  $\text{N}_2$ , a little more char can remain at 700 °C.

IPDT, proposed by Doyle [20], has been used to evaluate the distinct thermal stability of polymer composites. IPDT was calculated as follows:

$$\text{IPDT}(\text{°C}) = A \times K \times (T_f - T_i) + T_i$$

$$A = \frac{S_1 + S_2}{S_1 + S_2 + S_3}$$

$$K = \frac{S_1 + S_2}{S_1}$$

where  $T_i$  is the initial experimental temperature (100 °C in this paper) and  $T_f$  is the final experimental temperature (700 °C in this paper). The values of  $S_1$ ,  $S_2$  and  $S_3$  are the separate areas of the three regions in a TGA plot [21–23].

From Table 1, 3F-epoxy-D230 exhibited the lowest IPDT, 411.6 °C in  $\text{N}_2$  and 454.4 °C in air, attributed to the aliphatic chain curing agent. 3F-PQE-DDM and 3F-PQE-2MI showed IPDT higher than the others, because the aromatic nucleus and imidazole ring enhanced the inherent thermal stability of the polymer network. The high IPDT implies the epoxy resins' potential application for high thermal-insulating materials.

### 3.3. DMA and DSC

Studies on the mechanism of  $T_g$  variation and the prediction of  $T_g$  change are critical for engineering design and application of epoxy



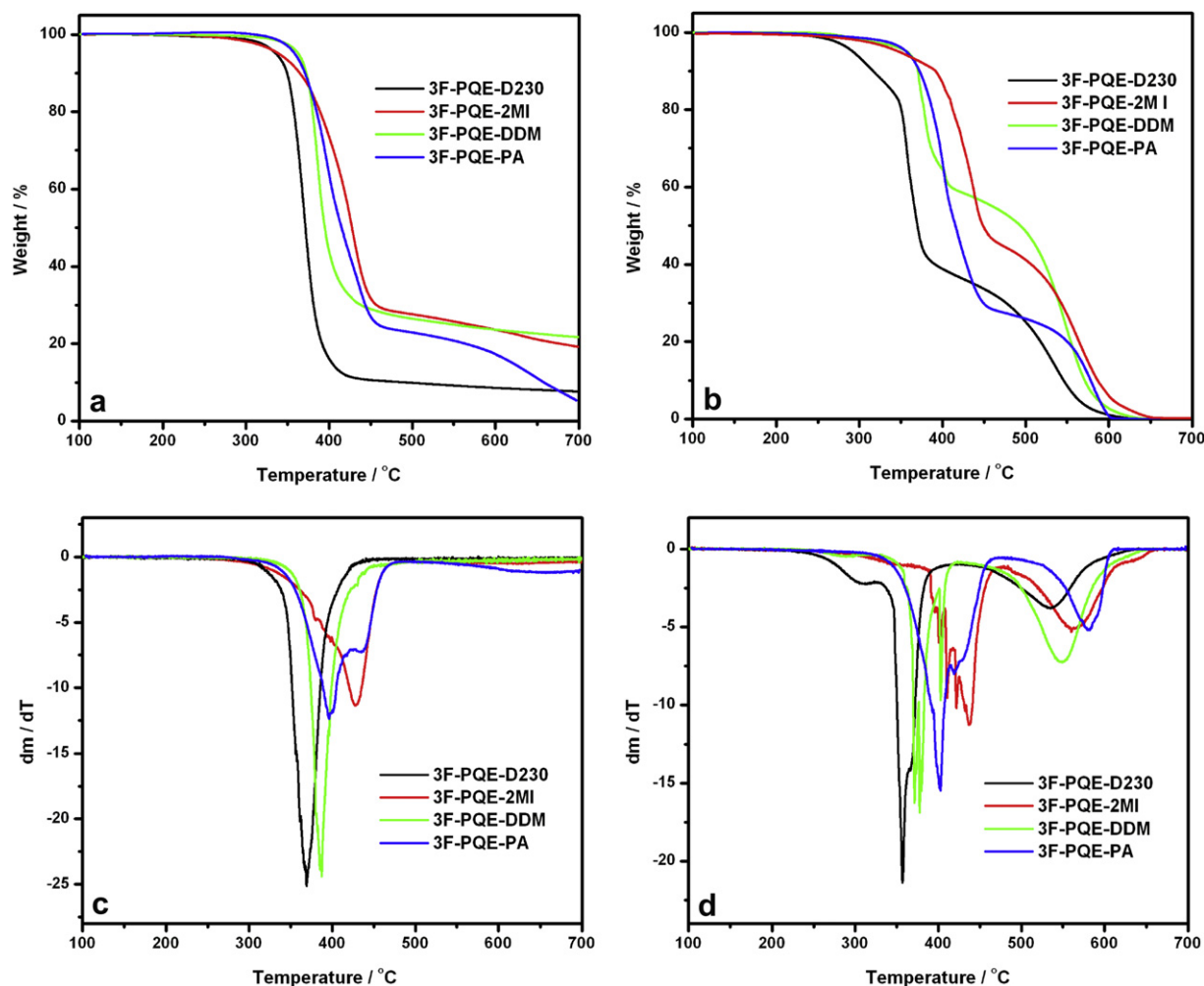


Fig. 3. TGA (a, b) and DTG (c, d) curves of 3F-PQE with four different curing agents (a, c at nitrogen atmosphere and b, d at air atmosphere).

resins [18,24,25]. Thermal properties of the four final materials were compared and analyzed. Fig. 4 shows the storage energy and  $\tan \delta$  for 3F-PQE-DDM. The  $T_g$  of DMA was obtained by the maximum peak value of  $\tan \delta$ . Table 2 shows the ultimate  $T_g$  from measurements of DMA and DSC.  $T_g$  depends on the diverse cross-linking network with different cure agents. 3F-PQE-DDM network had the best cross-linking density. The bulky rigid aromatic group contributed to high  $T_g$ . Consequently, the flexible aliphatic chain of 3F-PQE-D230 resulted in the lowest cross-linking network compared to those with an aromatic rigid ring or imidazole ring. Table 2 shows that the  $T_g$ s of 3F-PQE-2MI and 3F-PQE-PA are almost the same.

DSC provides a general method to obtain the  $T_g$  of the samples, but it is less sensitive than DMA [26]. Fig. 5 shows the DSC curves of

the cured epoxy network. And the results of  $T_g$ s are also shown in Table 2. For all the curves, there were no exothermic peaks, indicating that the networks were cured completely. The sequence of the  $T_g$ s was: 3F-PQE-DDM > 3F-PQE-PA  $\approx$  3F-PQE-2MI > 3F-PQE-D230. These results follow from the incorporation of an aromatic rigid ring into the cross-linked network that increased the motion barrier of the 3F-PQE molecule. Furthermore,  $T_g$  of 3F-PQE-D230 was the lowest, due to the flexible aliphatic chain. This claim made it easier for the cross-linked network to move when the temperature rises.

### 3.4. Moisture absorption

Moisture absorption can plasticize the resin, causing a decrease in  $T_g$  as well as in mechanical properties [27]. Low moisture absorption is an important factor for advanced microelectronic packaging materials because the absorbed  $H_2O$  influence electrical-

**Table 1**  
Decomposition temperatures, residual chars and IPDT for 3F-PQE with D230, 2MI, DDM and PA.

	Nitrogen atmosphere				Air atmosphere			
	$T_{5\%}$ (°C)	$T_{max}$ (°C)	IPDT (°C)	Char (700 °C, wt %)	$T_{5\%}$ (°C)	$T_{max}$ (°C) <sup>a</sup>	IPDT (°C)	Char (700 °C, wt %)
3F-epoxy-D230	335.4	369.0	454.4	7.7	291.4	356.7	411.6	0.1
3F-epoxy-2MI	337.5	427.6	637.6	19.2	347.6	436.7	470.7	0.2
3F-epoxy-DDM	362.3	386.0	670.9	21.8	355.6	377.0	469.3	0.0
3F-epoxy-PA	358.7	396.1	485.7	5.3	355.2	401.7	437.0	0.0

<sup>a</sup> The second step under the air atmospheres.

**Table 2**  
 $T_g$ s and storage modulus for 3F-PQE with D230, 2MI, DDM and PA.

	Storage modulus (MPa)	$T_{g(DMA)}$ (°C)	$T_{g(DSC)}$ (°C)
3F-PQE-D230	2230	81	75
3F-PQE-2MI	1522	109	95
3F-PQE-DDM	1283	145	135
3F-PQE-PA	2563	114	92

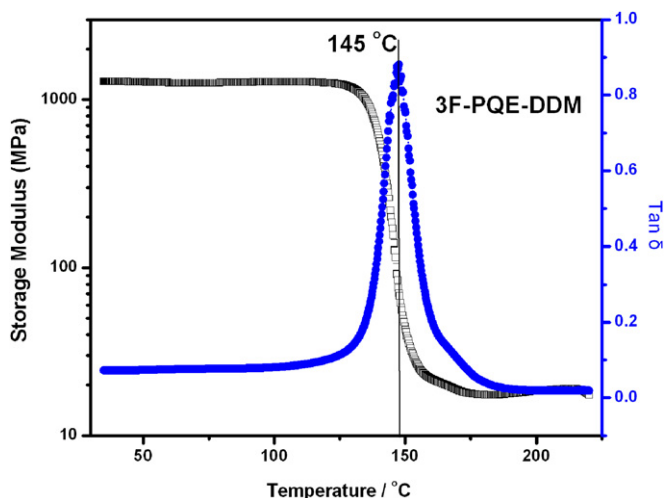


Fig. 4. DMA curves for 3F-PQE-DDM.

insulating and dielectric performance [28]. All samples were immersed in deionized water at a specified temperature for 24 h, was long enough for equilibrium sorption. As shown in Fig. 6, the weight of the samples increased with the increasing temperature. Due to the strong hydrophobic fluorine atom, the results clearly indicate that 3F-PQE-DDM and 3F-PQE-PA exhibited low water absorption, no more than 1 wt %. But in the networks of 3F-PQE-D230 and 3F-PQE-2MI, the aliphatic chain and imidazole group were the major factors of the moisture absorptions. Thus, the moisture absorptions of 3F-PQE-D230 and 3F-PQE-2MI were a little higher than the others, about 1.5 fold and 2.5 fold at 80 °C.

### 3.5. Contact-angle studies

We measured the contact angles of water to determine the relative wettability of the cured fluorine-epoxy surfaces. Scheme 2(f) shows photographs of water drops on the samples and Table 3 summarizes the results. All the contact angles of the samples were more than 90°, indicating that the cured fluorinated

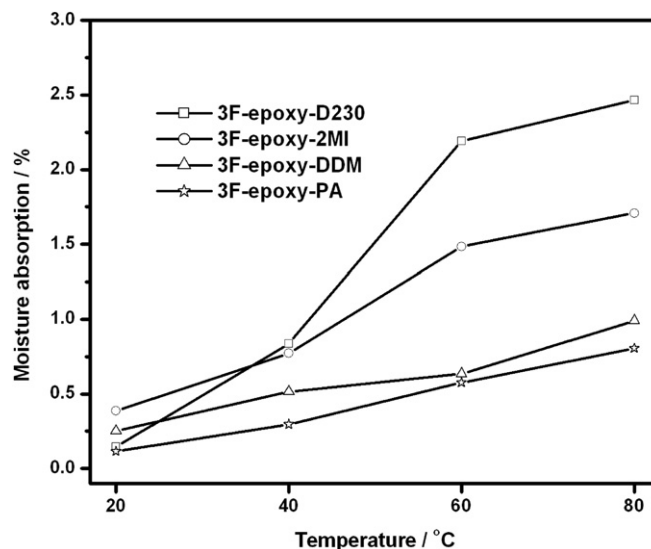


Fig. 6. Moisture absorption of 3F-PQE cured by D230, 2MI, DDM and PA.

Table 3

Water contact angles of 3F-PQE network and the fluorine content.

	F-content (wt %)	Contact angle of water (°)
3F-PQE-D230	11.60	96.73
3F-PQE-2MI	14.04	95.88
3F-PQE-DDM	12.03	98.08
3F-PQE-PA	11.11	105.50

epoxy resins exhibit a hydrophobic effect. Normally, the contact angles increase with rising fluorine content. However, although the fluorine content of 3F-PQE-PA was the lowest, the contact angle was 105.5°, the highest of the four samples. We infer that these results might follow from the emergence of hydrogen bonding between PA and epoxy causing the CF<sub>3</sub> groups organized on the surface [29].

## 4. Conclusions

We have prepared an epoxy resin containing CF<sub>3</sub> via three processes. Structures were characterized in detail. Cured systems were obtained by introducing four different curing agents (D230, 2MI, DDM and PA). All the cured resins showed high thermal stability, excellent low moisture absorption and some hydrophobic effect. Especially, 3F-PQE-DDM exhibited a high *T<sub>g</sub>* (145 °C by DMA). Additionally, 3F-PQE-PA with the lowest content of fluorine showed the highest contact angle (105.5°). And 3F-PQE-DDM showed contact angle of 98°. Meanwhile, the moisture absorption of 3F-PQE-DDM and 3F-PQE-PA were no more than 1 wt %, respectively. All the results indicated that 3F-PQE-DDM might be promising candidates in potential application materials.

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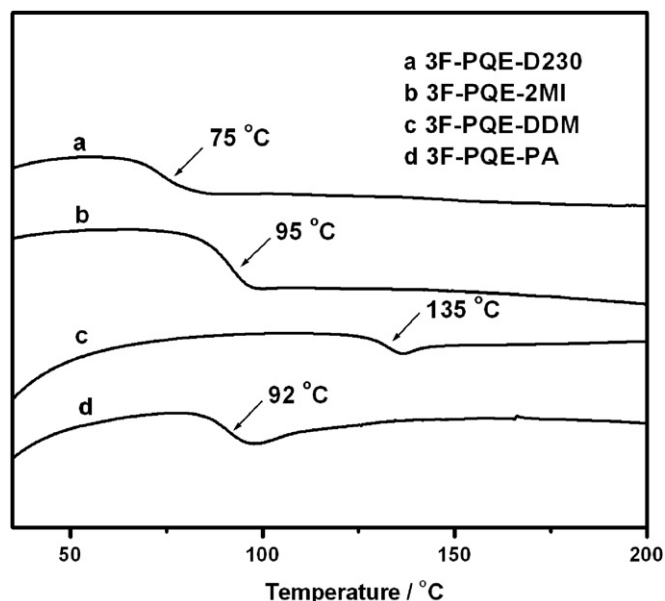


Fig. 5. *T<sub>g</sub>*S for 3F-PQE with four different curing agents by DSC.

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