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Estrogenic activity research of a novel fluorinated bisphenol and preparation of an epoxy resin as alternative to bisphenol A epoxy resin

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ABSTRACT

A low estrogenic activity bisphenol 3,5-bis(trifluoromethyl)phenylhydroquinone (BTFMHQ) and its corresponding epoxy resin (BTFMEP) were synthesized via a multi-step procedure including the Meerwein arylation reaction, and followed by nucleophilic reaction. The chemical structures of two monomers were confirmed by their ^{1}H NMR spectra. After curing, the properties of this fluorinated epoxy resin were measured and compared with the commercial epoxy resin diglycidyl ether of bisphenol A (DGEBA). As the result, BTFMEP exhibited good dimensional stability, excellent hydrophobic and low dielectric properties. Furthermore, BTFMEP showed a high glass transition temperature of 142 °C and a lower coefficient thermal expansion (CTE = 55.03 ppm/°C) than that of DGEBA (CTE = 60.71 ppm/°C). Moreover, BTFMEP exhibited the contact angle of 99.6°, which satisfied the standard of hydrophobic material. In addition, BTFMEP showed lower dielectric properties than DGEBA, because the introduction of side groups with high fluorine content into the material improved the electronegativity of epoxy material and reduced the polarizability of molecules efficiently. Herein, we believe the novel epoxy resin (BTFMEP) has a wide application prospect as the alternative to DGEBA.

1. Introduction

Epoxy resin, as one of the most important thermosetting materials, has been widely used in coating, adhesives, aerospace and electronics industry due to its outstanding adhesion, lower density, high strength, good durability, excellent chemical resistance [1–11]. As one of conventional epoxy resins, diglycidyl ether of bisphenol A (DGEBA) has been found in over 90% of thermosetting epoxy resins worldwide, in a market with a global production currently exceeding 2 million tons per year [12,13]. However, there are two main problems to restrict the application of DGEBA in human daily lives. The one problem is the properties of DGEBA could not satisfy the demand for advanced materials, such as good thermal stability, excellent hydrophobic, flame retardance and dielectric properties. The other one is bisphenol A (BPA) as the precursor of DGEBA possesses the similar structure to estrogens, which has been recognized as an endocrine disruptor. The estrogenic activity of BPA could increase the risk of reproductive disorder and cancer [14,15]. In addition, a small amount of BPA can still release from the epoxy resin with time due to its not completely stable chemical bonds. Therefore, the trace residual of BPA is usually detected in foods and liquids stored containers made from or lined with BPA-containing materials [16,17]. As the result, it is necessary to maintain a strict monitoring of the release of BPA from DGEBA, and the application of DGEBA has been restricted in many countries.

Over the past years, a lot of researchers have been focused on the preparation of novel epoxy resin to replace the DGEBA. As is well known, almost all of the epoxy resins are produced via the reaction of bisphenol monomer and epichlorohydrin. Thus, it is confirmed that the structure of bisphenol has a direct influence on the properties of epoxy resin. Numerous alternative BPA-free precursors have been reported and intended to promote the properties of epoxy resins and satisfied the demand of the advanced materials. For instance, Liu et al. [18] synthesized a novel bisphenol with –CF_3 side chains as the precursors of the fluorinate epoxy resin. The results showed the highest T_g of materials was 135 °C, 15 °C lower than DGEBA . Lin et al. [19] synthesized 2, 6-dimethyl phenol-dicyclopentadiene and aimed to obtain a low dielectric constant epoxy resin. The results exhibited that novel epoxy material possessed dielectric properties was 2.8 at 1 MHz, which was lower than DGEBA. Na et al. [20] synthesized a novel 2, 6-Naphthalenediol containing 4-fluorobenzoyl side chains and furtherly prepared its corresponding epoxy resin. The epoxy material showed a remarkably higher T_g = 170 °C than DGEBA. It also possessed a lower dielectric constant (2.97 at 1 MHz) than DGEBA .

There are many similar reports about designing the functional

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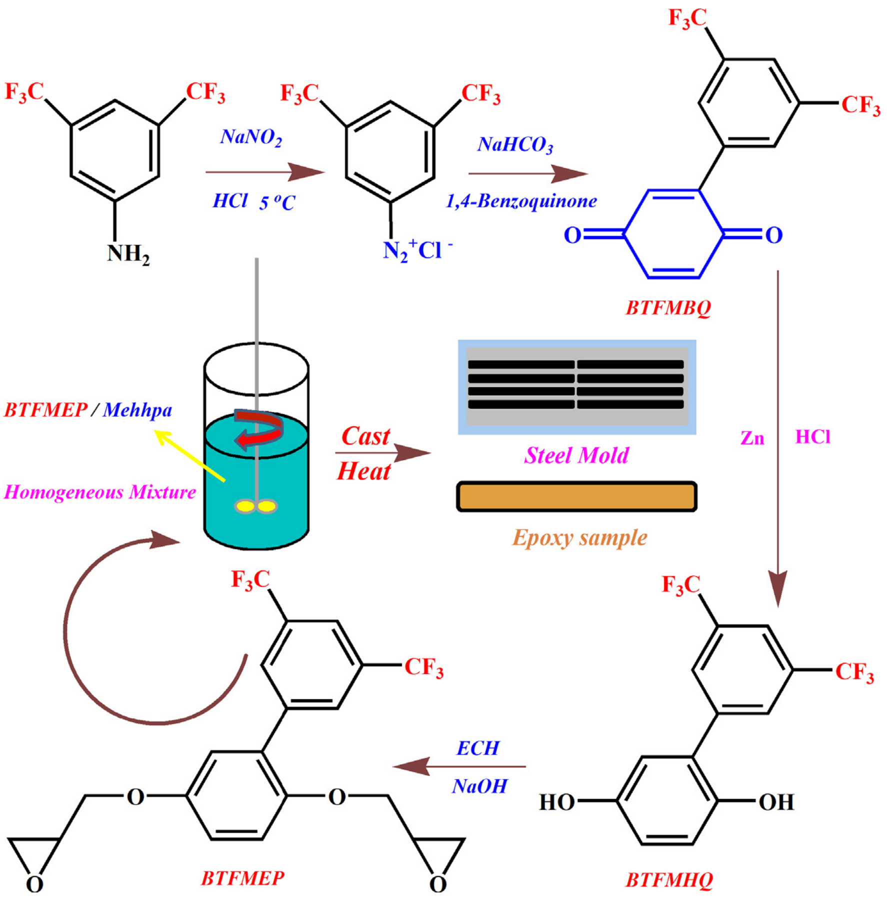

Scheme 1. The synthetic route of BTFMHQ and BTFMEP.

structure of bisphenol as the precursor and then obtaining the high performance epoxy resins as the alternative to DGEBA [16,21,22]. Unfortunately, few researchers estimated the estrogenic activity of the functional bisphenol or examined the degree of toxicity between the novel bisphenol and BPA. It is necessary to consider whether there is a real significance of alternating DGEBA only in performance but ignore the potential harm of human health.

According the research and our previous work [23–25], we find that the introduction of fluorine groups into epoxy monomer could promote the properties of the epoxy resin thoroughly. Therefore, we synthesized a novel fluorinated bisphenol monomer 3, 5-bis(trifluoromethyl)phenylhydroquinone (BTFMHQ) as the precursor of the epoxy resin with a rigid 3,5-bis(trifluoromethyl) biphenyl structure via Meerwein arylation reaction (Scheme 1). Meanwhile, we focused on the estrogenic activity of BTFMHQ and compared with estrogen and commercial bisphenol (bisphenol A and bisphenol F) by a methylthiazolyldiphenyltet-razolium bromide (MTT) assay using MCF-7 (human breast adenocarcinoma cell line) as an estrogen receptor . Furthermore, we researched the relationship between the structure and the properties of the novel 3, 5-bis(trifluoromethyl)phenylhydroquinone epoxy resin (BTFMEP) obtained by introducing both stiff and fluorinated groups into the backbone. For this purpose, the synthesis and characterization of BTFMHQ and BTFMEP were firstly described and the properties of the cured BTFMEP materials, including thermal stability, glass transition temperature (T_g), coefficient thermal expansion (CTE) and dielectric properties, as well as contact angle were studied in detail and compared with the commercial DGEBA epoxy resin. We believed that this research would provide a way to obtain a series of high performance epoxy resins for alternating DGEBA thoroughly.

2. Experimental

2.1. Materials

Benzimidazole, 1,4-benzoquinone and sodium bicarbonate were purchased from Beijing Chemical Company (Beijing, China). Epichlorohydrin (ECH) was obtained from TCI Shanghai Development Co., Ltd. DGEBA (KDS-8128) was purchased from Kukdo Chemical (Kunshan) Co., Ltd. Methylhexahydrophthalic anhydride (Mehhpa), 3,5-bis(trifluoromethyl)aniline, bisphenol A (BPA) and bisphenol F (BPF) were obtained from Energy Chemical. Co. Sodium hydroxide (NaOH), sodium nitrite ($NaNO_2$) and tetrabutylammonium bromide were purchased from Sinophram Chemical Reagent Co., Ltd. All other reagents and solvents were obtained commercially and used without further purification.

2.2. Synthesis of monomer 3,5-bis(trifluoromethyl) benzoquinone (BTFMBQ)

3,5-Bis(trifluoromethyl)aniline(114.56 g, 0.5 mol) and 200 mL of deionized water were added into a 1000 mL three-necked flask equipped with a mechanical stirrer, a dropping funnel, and a thermometer. The mixture was kept at the temperature below 5 °C with ice bath. Then, hydrochloric acid (168 mL, 11.8 M) was added into the solution dropwise. The sodium nitrite solution (124.5 g) with a concentration of 27.7% was added from a dropping funnel to a well stirred mixture into the flask. The mixture was stirred at 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 kept at room

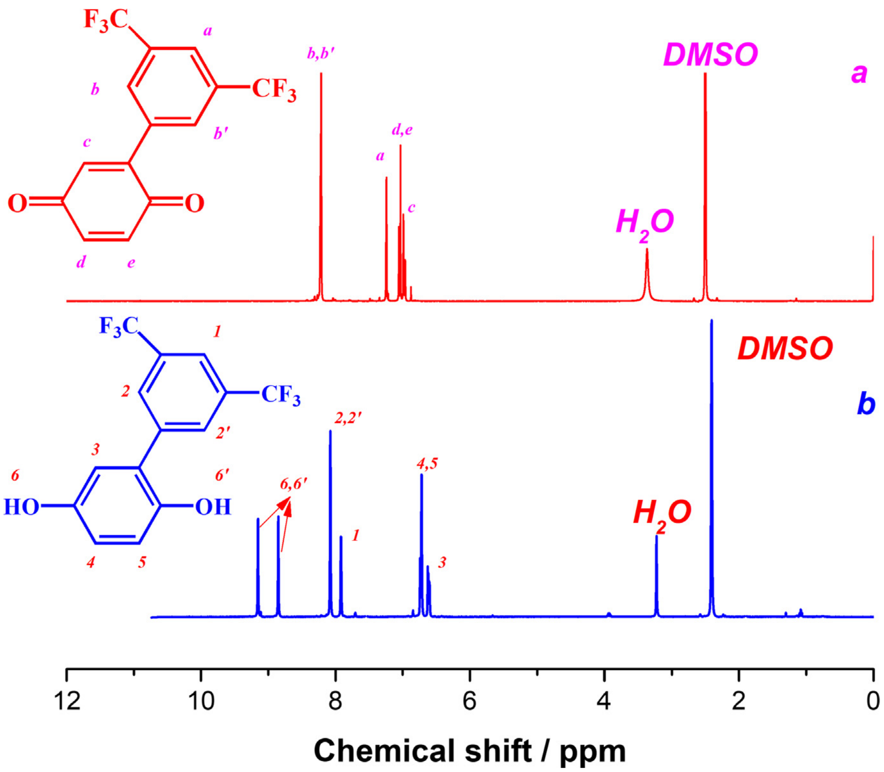

Fig. 1. ^1H NMR spectra of monomers BTFMBQ (a) and BTFMHQ (b).

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: 83.3%).

2.3. Synthesis of 3, 5-bis(trifluoromethyl)phenylhydroquinone (BTFMHQ)

The yellow solid BTFMBQ (213 g), Zn powder (130 g), and 500 mL of deionized water were placed into a 3000 mL, three-necked flask quipped with a mechanical stirrer, a condenser, and a dropping funnel. The mixture was heated to 90 °C with stirring, followed by the addition of hydrochloric acid (30 wt%, 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 red needle crystals. (Yield: 77.2%).

2.4. Synthesis of 3, 5-bis(trifluoromethyl)phenylhydroquinone epoxy resin (BTFMEP)

A mixture of 32.2 g (0.1 mol) 3,5-bis(trifluoromethyl)phenylhydroquinone, 160 mL ECH and 1.0 g tetrabutylammonium bromide were stirred in a three-neck flask at 90 °C for 6 h. After cooling to room temperature, the excess ECH was removed at a reduced pressure. Subsequently, 160 mL toluene and 28.8 g NaOH (50 wt% solution) were added and the mixture was kept at 90 °C for 3 h. Then the mixture was washed and distilled under reduced pressure. Finally, the white crystalline product was obtained by drying in a vacuum oven 12 h at 60 °C (Yield: 85.5%).

2.5. Preparation of cured epoxy samples.

Stoichiometric amount of Mehhpa (3.36 g) was added into BTFMEP (4.34 g). The mixture was stirred continuously for 1 h, and then benzimidazole (1 wt% of the mixture) was added into the mixture as the curing accelerator. After stirring for 30 min, the mixture was put into the vacuum oven in order to remove the entrapped air. Finally, the mixture was poured into a polish mould and cured at 120 °C for 2 h, 160 °C for 2 h and 200 °C for 2 h to obtain the cured epoxy materials. Similarly, we obtained the cured epoxy resin sample of DGEBA for comparison.

2.6. MTT assay

MCF-7 cells were maintained in RPMI 1640 supplemented with 10% (V/V) fetal bovine serum (FBS), 100U/mL penicillin and 100 μg/mL streptomycin. MCF-7 cells were seeded into 96-well plates (0.6×10^4 cells/well) for 6 h, and then incubated with 2 μM/L BTFMHQ / DMSO (Dimethyl sulfoxide), estrogen / DMSO, BPA / DMSO and BPF / DMSO at 37 °C in a 5% CO_2 humidified incubator for 24 h, respectively. DMSO without any bisphenols was used as the negative control, BTFMHQ, estrogen and commercial bisphenol (BPA and BPF) were used as positive controls. Cell proliferation was then measured by a MTT assay as previously described.

2.7. Characterization

^1H NMR spectrum was measured on a 500 MHz Bruker Avance510 spectrometer at 298 K with DMSO-d_6 and Chloroform-d as the solvent and tetramethylsilane as the standard. FT-IR spectra were obtained with a Nicolet Impact 410 Fourier transform spectrometer using KBr pellets.

Differential Scanning calorimeter (DSC) was performed on a DSC Q20 (TA Instruments, New Castle, DE, USA), in the temperature region of 10–200 °C at a heating rate of 10 °C min^{-1}. Thermal mechanical analysis (TMA) was carried out with a TMA Q 400 analyser (TA Instruments, New Castle, DE, USA) over a temperature range of 0–200 °C at a heating rate of 10 °C min^{-1}.

Thermogravimetric analysis (TGA) was conducted on a Pyris 1 TGA analyzer (Perkin-Elmer, USA). The samples were heated from 100 °C to

800 °C at a rate of 10 °C min^{-1} under nitrogen atmosphere. Before the heating scan, all the samples were pre-dried under N_2 at 100 °C for 10 min to remove the residual water and solvent.

Dielectric constants of the samples were measured with the help of Hewlett-Packard 4294A apparatus at room temperature and the test frequency was in the range of 1–10^6 Hz.

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.

3. Results and discussion

3.1. Characterization of monomers

Fig. 1 shows ^{1}H NMR spectra of monomers BTFMBQ and BTFMHQ, respectively. In their spectra, all the signals could be attributed to the expected protons on the monomers. According to Fig. 1 (a), the peaks at 8.23 ppm and 7.26 ppm were attributed to the protons on fluorinated aromatic rings of side chains, while the peaks in the range from 6.92 to 7.12 ppm were assigned to the protons on 1,4-benzoquinone. The result indicated that BTFMBQ was synthesized successfully via a Meerwein arylation reaction. Furthermore, we could clearly observe the new peaks that were attributed to the hydroxyl group in Fig. 1 (b). Meanwhile, other signals were assigned to the expected protons on the aromatic rings. Thus it indicated that the monomer of 3,5-bis(trifluoromethyl)phenylhydroquinone (BTFMHQ) was also prepared successfully.

Fig. 2 displays the ^{1}H NMR spectrum of the fluorinated epoxy monomer BTFMEP. In the spectrum, the signals of 2, 2′, 3, 4, 5 were attributed to the protons on the aromatic rings respectively. Especially, the proton peaks in the range from 2.5 to 3.0 ppm and from 3.8 to 4.4 ppm were assigned to the methylene ($-CH_2-$) groups of glycidol ether. Therefore, the results indicated that the fluorinated epoxy resin (BTFMEP) was synthesized successfully.

The FT-IR spectra of monomers BTFMBQ, BTFMHQ and BTFMEP are shown in Fig. 3 , respectively. In the curve of BTFMBQ, the absorption bands observed at 1675 cm^{-1} can be attributed to the skeleton vibration of carbonyl group (C=O). A sharp and strong characteristic band at 1270 cm^{-1} was found in Fig. 3, which was attributed to the $-CF_3$ absorption of the side group. In the curve of BTFMHQ, there was a new peak at 3300 cm^{-1} was attributed to the hydroxyl (–OH) group. Meanwhile, the peak of (C=O) at 1675 cm^{-1} disappeared. It was proved that the reduction reaction was carried out completely. Similarly, the peak of hydroxyl (–OH) could not been seen and the characteristic absorption peak of oxirane ring vibration appeared at 912 cm^{-1} in the curves of BTFMEP, which demonstrated that the epoxy group had been successfully introduced into the monomer.

3.2. Estrogenic activity (BTFMHQ, estrogen, BPA and BPF)

MTT assay as the common method to investigate estrogenic activity of bisphenols by viability of MCF-7 cells [26,27]. The in vitro cell proliferation of BTFMHQ was investigated with MCF-7 cells (Fig. 4). The cells were exposed to BTFMHQ at 2 μM for 24 h followed by cell proliferation evaluation by MTT assay. DMSO acted as negative control, while estrogen, BPA and BPF acted as positive control. Compared with negative control (DMSO), each positive control group presented the cell proliferation rate of 27% (Estrogen), 19.5% (BPA) and 11.6% (BPF), respectively. Meanwhile, BTFMHQ exhibited the lowest cell proliferation rate (3%) among the positive controls. The decrease of estrogenic activity could be explained by the significant difference in the molecular structure between BTFMHQ and other monomers (Estrogen, BPA and BPF) . Therefore, the result suggested that BTFMHQ can be considered as a genuinely safer alternative to BPA and BPF.

The estrogenic activity of different monomer was also investigated by fluorescence microscopy. MCF-7 cells treated with BTFMHQ (B), estrogen (C), BPA (D) and BPF (E) at 2 μM for 24 h was visualized by fluorescence microscopy (Fig. 5). Compared with DMSO (A) negative control group, estrogen and commercial bisphenol (BPA and BPF) induced a higher fluorescence intensity than DMSO group, demonstrating that the commercial bisphenol significantly improved the cellular proliferation. BTFMHQ hardly induced cell proliferation efficiency, indicating that the BTFMHQ monomer presented lower estrogenic activity than BPA and BPF.

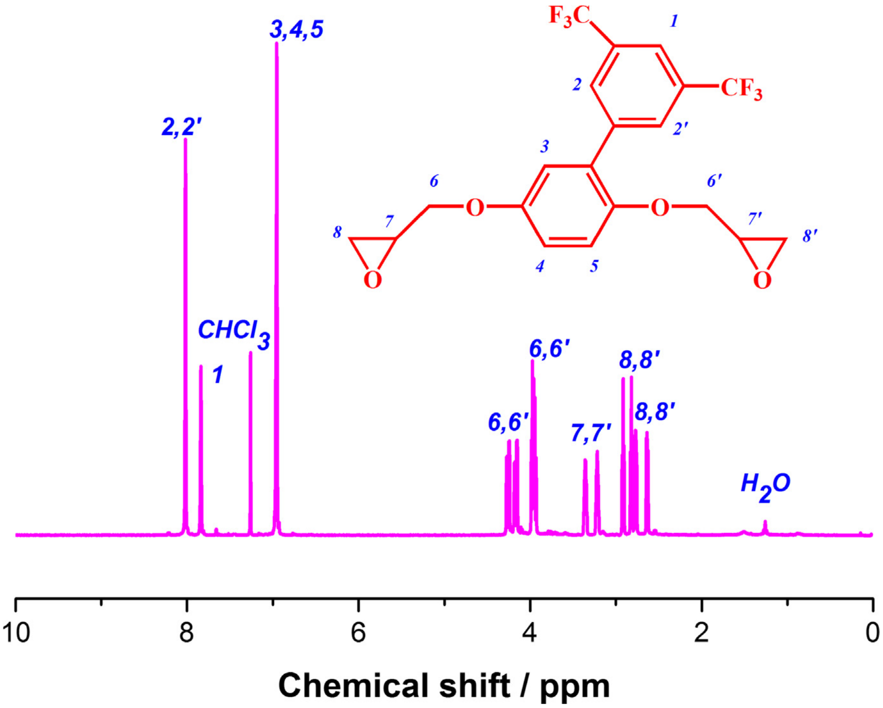

Fig. 2. ^{1}H NMR spectrum of fluorinated epoxy resin BTFMEP.

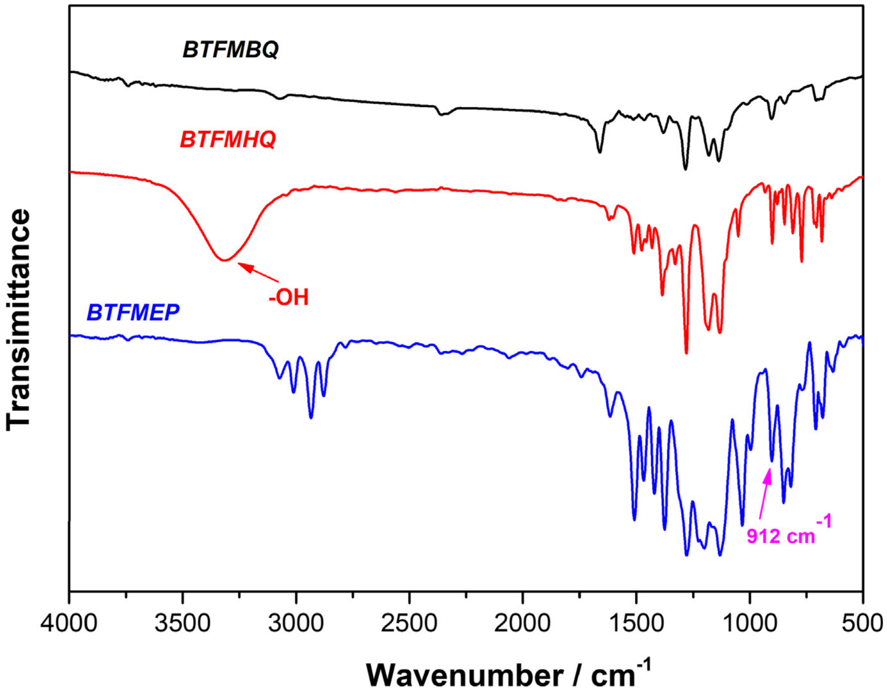

Fig. 3. FTIR spectra of BTFMBQ, BTFMHQ and BTFMEP.

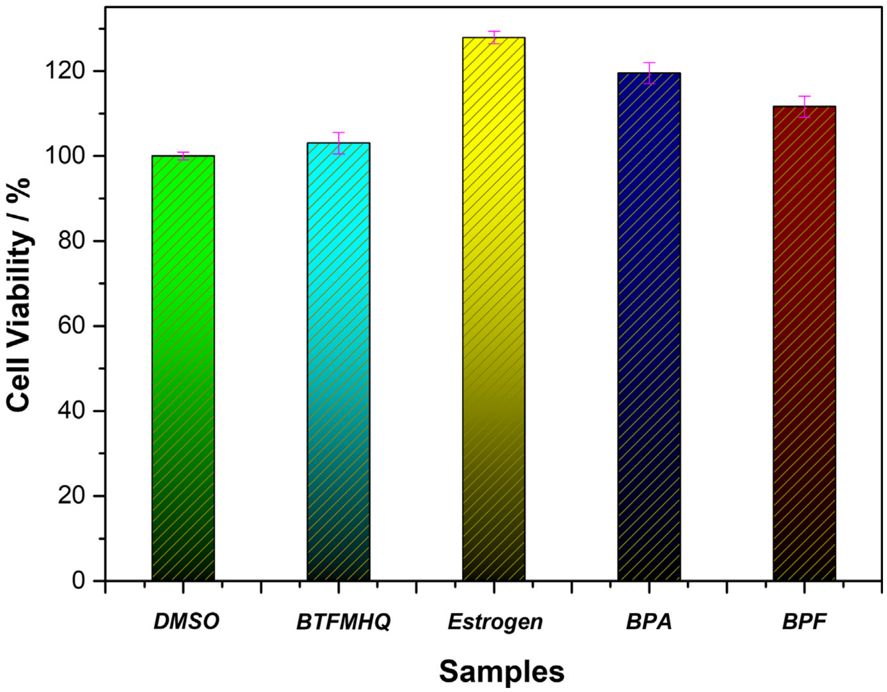

Fig. 4. Cell viability of MCF-7 exposed to different bisphenols and estrogen in 24 h.

3.3. Thermal properties of cured epoxy resin (DSC, TGA and TMA)

Research on the mechanism of T_g variation and the prediction of T_g change are critical for engineering design and application of epoxy resins [28,29]. Fig. 6 shows the DSC curves of cured epoxy resins in order to make a comparison of T_g between BTFMEP and the commercial epoxy DGEBA. As the result, it was observed obviously that all the epoxy resins possessed high T_g values. It was because that every anhydride group could react with epoxy group to form ester in the curing process and thus improving the crosslinking density of the materials. Furthermore, the novel fluorinated epoxy BTFMEP shows a T_g of 142 °C, 8 °C lower than that of DGEBA (150 °C). It may be explained that 3,5-bis(trifluoromethyl)phenyl as the side group occurred molecule movement easier than DGEBA as the temperature increased . In addition, the large 3,5-bis(trifluoromethyl)phenyl side group could produce the steric hindrance between the epoxy monomers, thus reducing the crosslinking density of the material. Hence, the fluorinated epoxy of BTFMEP showed a slightly lower T_g than the conventional epoxy resin.

Figs. 7 and 8 show the TGA curves and differential thermogravimetric (DTG) curves of the epoxy resin samples measured under N_2 atmospheres, respectively. The relevant thermal decomposition data, including the decomposition temperature of 5% and 10% weight loss

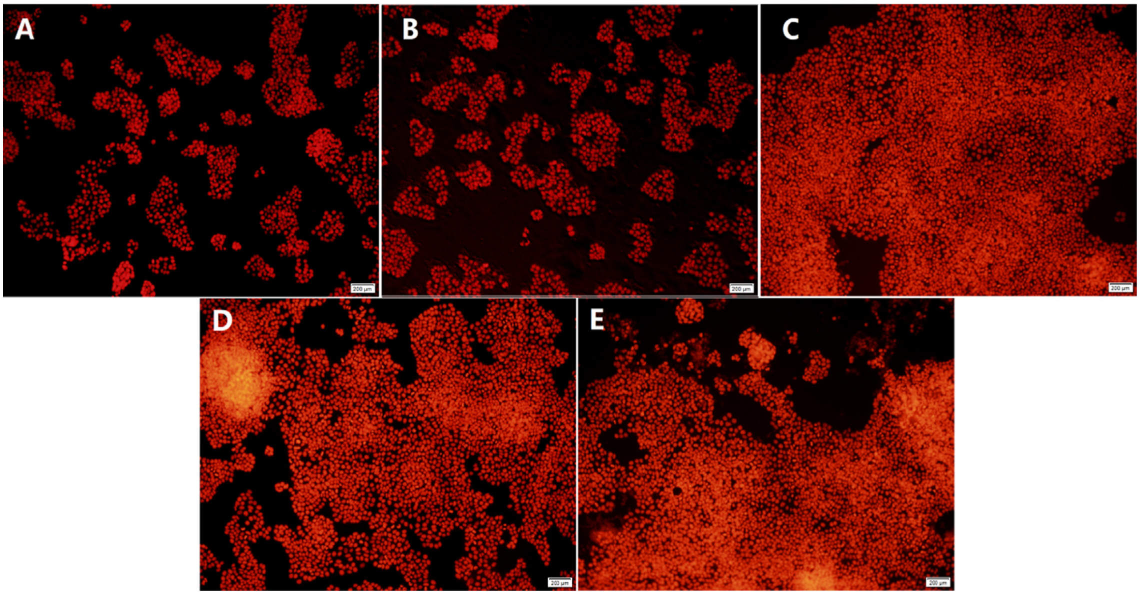

Fig. 5. Fluorescence microscopy of MCF-7 proliferates after exposing to different bisphenols, (A–E) represents monomers of DMSO, BTFMHQ, Estrogen, BPA and BPF respectively.

($T_{d5\%}$and $T_{d10\%}$), the decomposition temperature for the maximum rate of weight loss (T_{dmax}) and the char residues at 800 °C are listed in Table 1. It was apparently observed that two kinds of epoxy resins both possessed high initial thermal decomposition temperature. The entire $T_{d5\%}$ exceeded 300 °C, which was attributed to the high crosslinking density of the complete curing reaction. Compared with DGEBA, BTFMEP showed two thermal decomposition steps. Meanwhile, all the thermal decomposition temperatures were slight lower than DGEBA. For instance, $T_{d5\%}$ (326 °C) of BTFMEP was 22 °C lower than DGEBA. Similarly, BTFMEP possessed a lower $T_{d10\%}$ (366 °C) than DGEBA. The result could be explained that the initial thermal decomposition of BTFMEP was earlier than DGEBA due to the large 3,5-bis(trifluoromethyl) phenyl side group degradation. In addition, the lower crosslinking density of BTFMEP than DGEBA could influence the thermal stability of the material we have mentioned before. As the temperature further increased, all of these side groups of 3,5-bis(trifluoromethyl) phenyl degraded completely. Then, BTFMEP decomposed as the same as the tendency of DGEBA, and showed another step of degradation at about 420 °C. Moreover, we could find the analogous phenomenon from the data of T_{dmax} and char residues. The T_{dmax} of BTFMEP was 432 °C, which was lower than T_{dmax} (438 °C) of DGEBA. Additionally, the char residue of BTFMEP was 5.38%, which was slightly lower than that of DGEBA (5.48%). Therefore, it could be concluded that BTFMEP possessed the lower thermal stability, which was caused by the decomposition of the 3,5-bis(trifluoromethyl) phenyl side groups basically.

As one of the most important properties of the advanced material, dimensional stability is an essential consideration of epoxy resins used

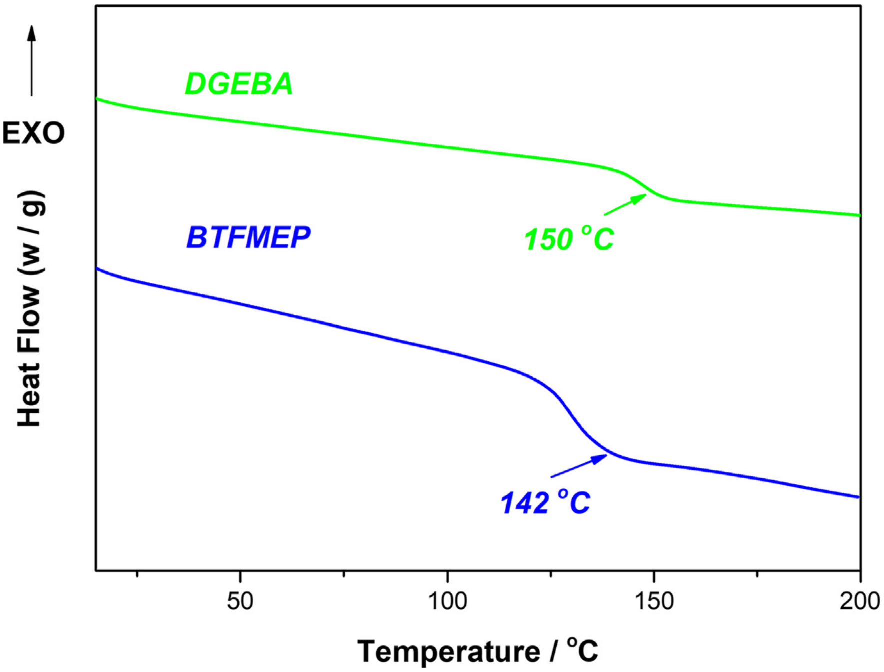

Fig. 6. DSC curves of BTFMEP and DGEBA epoxy samples.

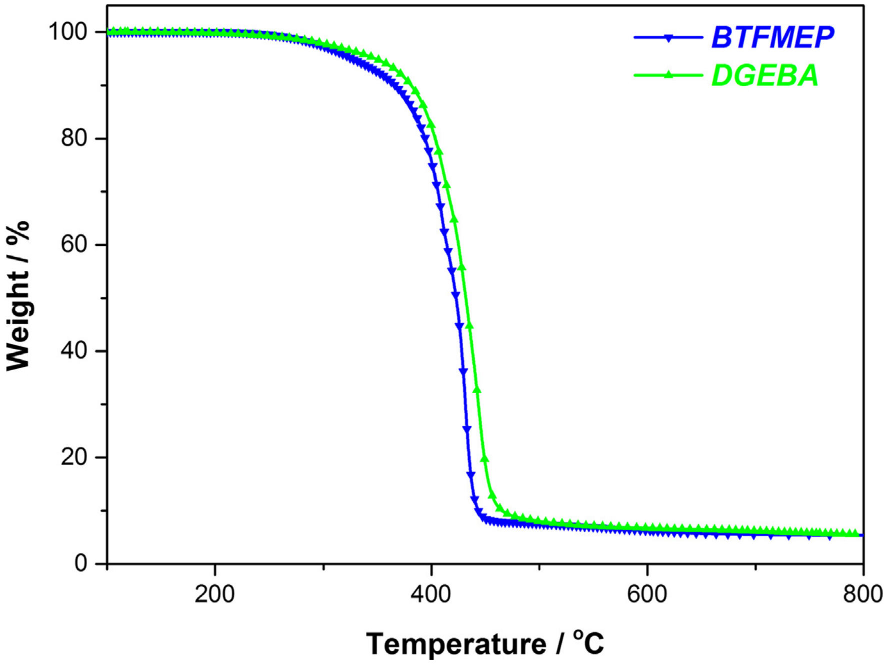

Fig. 7. TGA curves of cured epoxy resin samples.

in many demanding area. Dimensional change of DGEBA and BTFMEP from 0 °C to 200 °C (above the soften temperature) was evaluated by TMA. As shown in Fig. 9, the dimensional change of two epoxy materials increased almost linearly with the temperature increasing. Obviously, BTFMEP exhibited a smaller accumulated dimensional change than DGEBA. Furthermore, we compared CTE of BTFMEP (at glassy state) with DGEBA. The CTE of BTFMEP was 55.03 ppm/°C, nearly 5.7 ppm/°C lower than DGEBA. It was attributed to the stiff biphenyl structure of BTFMEP, which produced the steric hindrance and then restricted the thermal movement of molecular chain efficiently. Therefore, it could be concluded that the novel fluorinated epoxy BTFMEP exhibited better dimensional stability than DGEBA.

3.4. Contact angle and dielectric properties

Wettability, as one of the important property of materials, not only greatly impairs the mechanical and thermal properties of epoxy resins, but also widely limits the usage of epoxy resins as electronic materials and coating. Therefore, the contact angles of all epoxy resin samples were measured to determine the relative wettability of the surface. As shown in Fig. 10, the contact angle of BTFMEP (B) was 99.6°, 26° higher than DGEBA. This result was attributed to the existence of high fluorine content groups in the structure, thus decreasing the surface wettability of the material.

To the best of our knowledge, epoxy resin has a wide application in

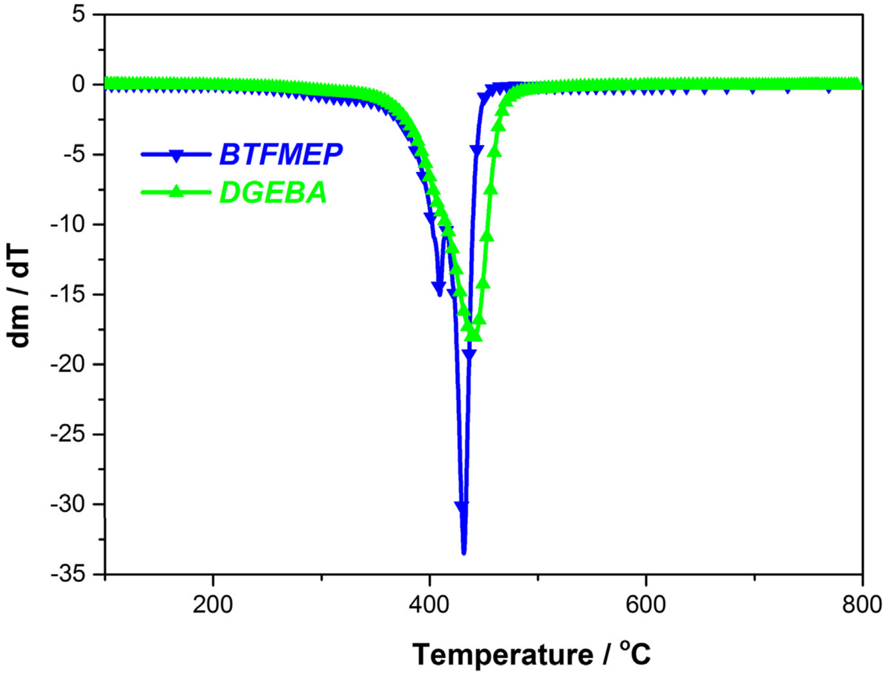

Fig. 8. DTG curves of cured epoxy samples.

Table 1
Thermal, gel fraction and dielectric properties of cured epoxy resins.

Samples	TGA [°C]			Char Yield [%]	DSC	Gel fraction[a]	TMA	Dielectric properties at 1 M [Hz]	
	$Td_{5\%}$	$Td_{10\%}$	Td_{max}	At 800 [°C]	T_g [°C]	%	CTE [ppm /°C]	D_k	D_f
DGEBA	348	381	438	5.38	150	97.8	60.71	3.01	0.0139
BTFMEP	326	366	432	5.48	142	91.2	55.03	2.59	0.0114

[a] Gel fraction (%) = $W_2/W_1 \times 100$. W_1: the initial weight of cured epoxy resin W_2: the weight of cured epoxy resin after marinating in DMSO for 24 h at 80 °C, then washed with deionized water for several times and dried at 100 °C at 24 h.

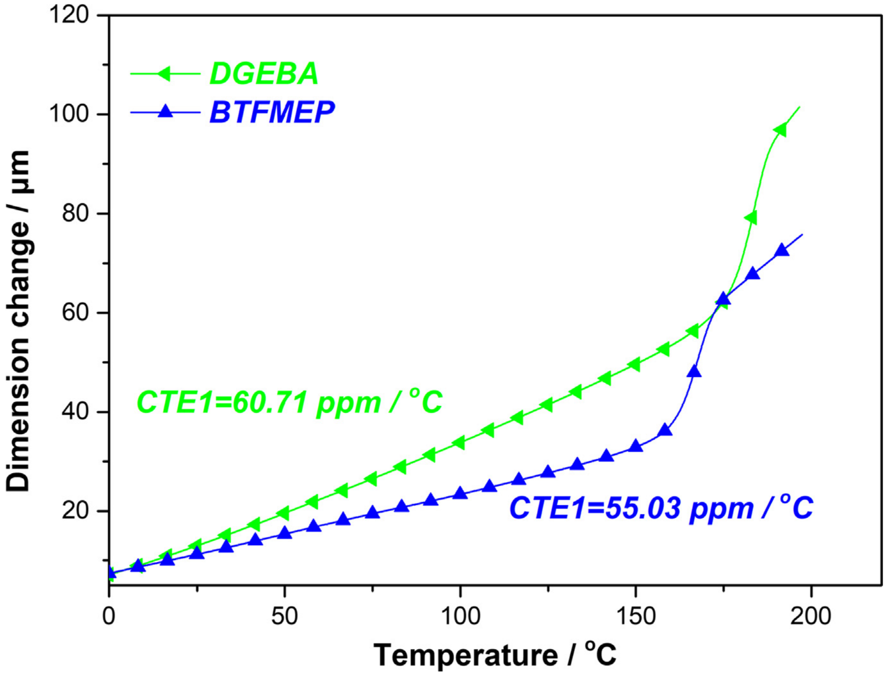

Fig. 9. TMA curves of cured epoxy samples.

electronic industry. Thus, BTFMEP as an alternative should possess the better dielectric properties than DGEBA. Dielectric constant D_k and the dielectric loss factor D_f, which are two important parameters for epoxy resins used for the electronic materials. Therefore, the preparation of epoxy resins with lower D_k and D_f is beneficial for improving propagating speed and reducing the propagation loss. Figs. 11 and 12 show the dielectric constant and dielectric loss of two epoxy samples, respectively. It could be obviously observed that BTFMEP showed lower dielectric constant (2.59 at 1 MHz) than DGEBA. The result can be explained by the introduction of high fluorine content side groups, which provided the small dipole of C—F bonds, thus making the molecule difficult to be polarized. Similarly, it could be obviously observed that all of the epoxy materials showed lower dielectric loss, although it exhibited an increasing tendency as the frequency increasing. As listed in Table 1, the D_f of BTFMEP was 0.0114 at 1 MHz, which was a bit lower than DGEBA (0.0139 at 1 MHz). This indicated that the introduction of high fluorine content group into the structure could decrease the dielectric properties obviously. Therefore, we believe that the novel fluorinated epoxy resin (BTFMEP) could replace DGEBA as the advanced electronic materials.

4. Conclusions

We prepared a novel fluorinated bisphenol 3, 5-bis(trifluoromethyl) phenylhydroquinone (BTFMHQ) and epoxy resin (BTFMEP) via Meerwein arylation reaction, and followed by nucleophilic reaction.

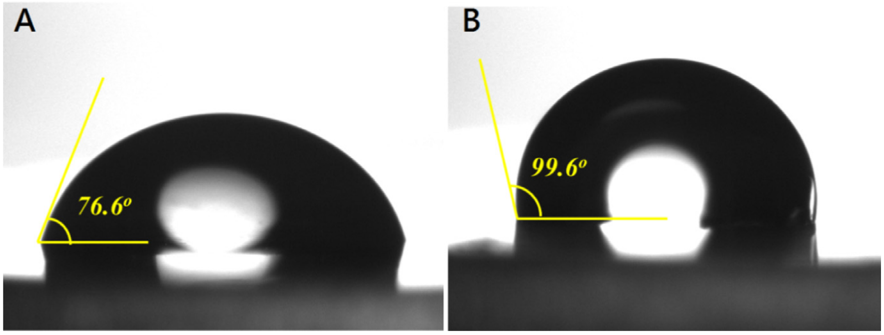

Fig. 10. Contact angles of cured epoxy resin DGEBA (A) and BTFMEP (B).

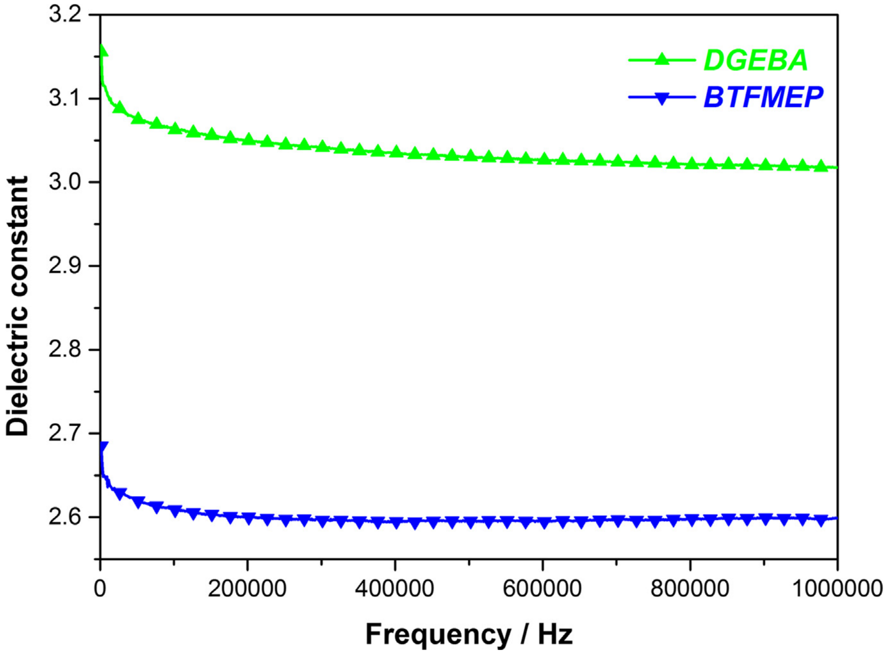

Fig. 11. Dielectric constants of cured epoxy resin samples.

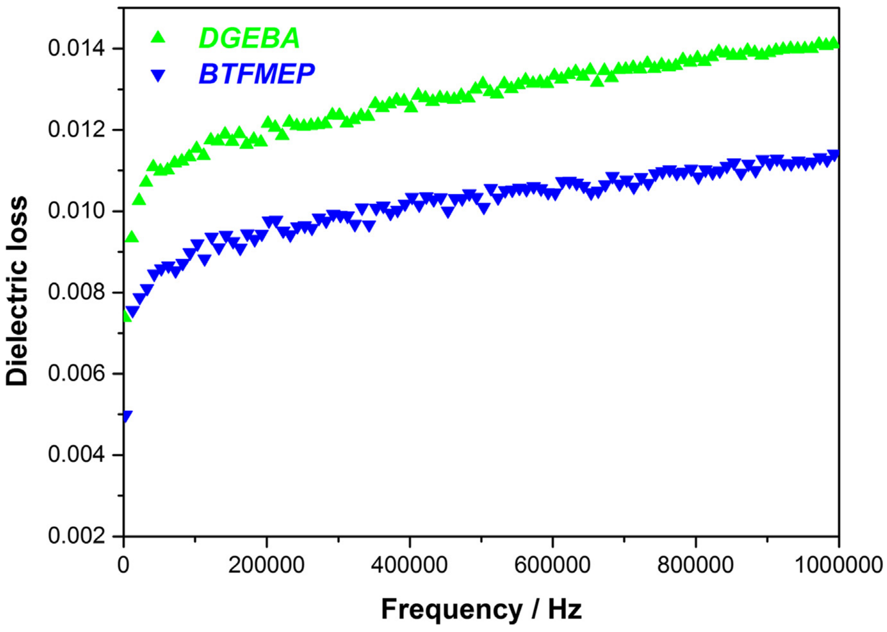

Fig. 12. Dielectric loss of cured epoxy resin samples.

Then we cured the novel epoxy with Mehhpa and measured the properties of the final cured system. By comparing the estrogenic activity between BTFMHQ and other commercial bisphenols (BPA and BPF), we found that BTFMHQ exhibited lower estrogenic activity than BPA and BPF. Meanwhile, BTFMEP showed better dimensional stability, hydrophobic and dielectric properties than DGEBA. Therefore, we believe that BTFMEP is a promising candidate to replace DGEBA as the advanced epoxy material for electronic and food packaging applications. These results could motivate the research on the design of novel epoxy resin as the safe and high performance alternative to DGEBA.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.eurpolymj.2018.09.020.

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