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Fluorinated low molecular weight poly(phenylene oxide): Synthesis, characterization, and application in epoxy resin toward improved thermal and dielectric properties

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ABSTRACT

To explore the high performance epoxy resin with high thermal properties and low dielectric constant and loss for copper clad laminates (CCLs), poly(phenylene oxide) (PPO) with low molecular weight is usually used as a modifier. Toward this end, a fluorinated redistributed poly(phenylene oxide) (F-rPPO) with number-average molecular weight of 3.0 ~ 6.2 × 10^3 g/mol was synthesized via the redistribution reaction of commercial PPO with 4,4′-(hexafluoroisopropylidene) diphenol (BPAF) using benzoyl peroxide (BPO) as an initiator. The structure of F-rPPO was characterized by ^{1}H NMR, ^{19}F NMR and FT-IR, respectively. F-rPPO was employed in the modification of diglycidyl ether of bisphenol A (DGEBA)/methylhexahydrophthalic anhydride (MeHHPA) epoxy resin, and the effect of F-rPPO on the curing behaviors and resulting thermosets were investigated. The results showed that the cured EP/F-rPPO resins exhibited improved thermal and dielectric properties, as well as lower moisture absorption. At 40 phr F-rPPO (based on DGEBA), the cured EP/F-rPPO resin possessed a higher T_g of 146 °C and $T_{d5\%}$ of 363 °C than that of 129 °C and 321 °C for the pristine epoxy resin, respectively. Moreover, EP/F-rPPO exhibited a lower moisture absorption (0.33%), dielectric constant and loss (2.69 and 0.0132 at 12 GHz) compared to the pristine epoxy resin (0.48%, 2.93 and 0.0303 at 12 GHz, respectively). This work provides an easy and effective solution to fabricate the high performance epoxy resins modified by PPO to better meet the requirement of CCLs.

1. Introduction

Epoxy resins (EPs) are the most commonly used matrix polymers for copper clad laminates (CCLs) by virtue of the good processability, high adhesion, excellent chemical resistance and balanced mechanical properties, that is excellent quality and reasonable price [1–3]. With the rapid development of CCLs towards the enhanced circuit density, higher transportation speed and better reliability, it is necessary for matrix materials to possess the higher glass transition temperature (T_g), thermal stability, moisture resistance and lower dielectric constant and loss [4–6]. However, common epoxy resins are insufficient to satisfy these requirements, particularly in thermal and dielectric properties [7,8].

Poly(phenylene oxide) (PPO) is considered as a promising candidate to remedy these deficiencies of epoxy resins due to its exceptionally low dielectric constant (D_k) and dielectric loss factor (D_f), as well as outstanding mechanical properties, high thermal stability and low moisture uptake [9–11]. Many efforts have elucidated that PPO is a competitive modifier to improve the thermal and dielectric properties, and water resistance of polymers over cyanate resins [12,13], bismaleimide resins [14], and styrene-ethylene/butylene-styrene resins [15]. Nevertheless, the compatibility between commercial PPO (number-average molecular weight (M_n) > 2.0 × 10^4 g/mol usually) and epoxy resins is quite poor owing to the big difference in chemical structure. Besides, the high viscosity originated from high molecular weight PPO

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leads to difficult mixing with epoxy resins, to phase separation in EP/PPO and consequently to the deteriorated performance [16–18]. It is extremely imperative to improve the compatibility between commercial PPO and epoxy resins.

The usage of low molecular weight PPO is an effective way to enhance the processability and compatibility with epoxy resins. Su et al. [19] synthesized a series of epoxy-terminated poly(alkyl-phenylene oxide) (EPPO) with low M_n (2.3 ~ 2.6 × 10^3 g/mol) via oxidative polymerization. However, the EP/EPPO resin cured by dicyandiamide (DICY) exhibited high D_k of 5.78 and D_f of 0.03 at 5 MHz, probably due to the asymmetric molecular structure of PPO caused by alkyl. Furthermore, the copper amine catalyst commonly used in oxidative polymerization also raised the D_k if removed not completely. In contrast, the redistribution reaction of high molecular weight PPO with phenols in the presence of a radical initiator is a straightforward strategy to obtain low molecular weight PPO [20,21]. Weng et al. [22] synthesized BPA-redistributed PPO (A-rPPO) with low weight-average molecular weight (M_w) of 5.3 ~ 6.6 × 10^3 g/mol via the redistribution reaction of PPO with bisphenol A (BPA). The D_k of diglycidyl ether of bisphenol A (DGEBA)/A-rPPO resin (100:10 in weight, $M_w = 6.2 \times 10^3$ g/mol) cured by methyl nadic anhydride/methylhexahydrophthalic anhydride/pyridine was reduced to 3.79 from 4.40 at 10 MHz for the pristine epoxy resin, decreased by 13.9%. While indicating a decline in D_k, the D_k of 3.79 was still relatively high for advanced CCLs. Similarly, Hwang et al. [23] prepared A-rPPO to modify the epoxy resin of DGEBA/4,4′-diaminodiphenylmethane (DDM), in which A-rPPO possessed a lower M_w of 0.9 ~ 3.7 × 10^3 g/mol. At the weight ratio of 100 to 15 for DGEBA to A-rPPO, the cured resin exhibited a lower D_k of 3.23 and D_f of 0.0179 at 1 GHz, respectively, which revealed the significance of low molecular weight for the modifier.

It is proved that the redistribution reaction may endow PPO with low molecular weight to improve the epoxy resins. More intriguingly, the redistribution reaction may also endow PPO with multi-function groups in the molecular chains due to the varieties of phenolic compounds. Generally, the introduction of fluorinated substituents is beneficial for improving the dielectric properties and moisture resistance of materials due to their large molecular free volume, small dipole and low polarizability. For instance, Luo et al. [24] synthesized fluoro-terminated hyperbranched PPO (FHPPO) and prepared the DGEBA/FHPPO composites with low dielectric constant, dielectric loss and moisture absorption. In consideration of the simplicity and convenience of the redistribution reaction, it is more significant to lower the dielectric parameters of epoxy resins by introducing fluorinated redistributed PPO.

In this work, a novel fluorinated redistributed PPO (F-rPPO) was prepared by the redistribution reaction of PPO with 4,4′-(hexafluoroisopropylidene) diphenol (BPAF) using benzoyl peroxide (BPO) as a radical initiator. F-rPPO with lower M_n of 3.0 ~ 6.2 × 10^3 g/mol was introduced to modify the DGEBA/MeHHPA epoxy resin. The resulting epoxy resins of EP/F-rPPO are expected to show improved thermal properties, moisture resistance, and lower dielectric constant and loss, due to the presence of low polar F-rPPO and fluorinated groups with large free volume. The curing behavior of EP/F-rPPO was investigated in detail, and the properties of cured EP/F-rPPO resins, including T_g, thermal stability, moisture resistance and dielectric properties were further tested to investigate the modification effect of F-rPPO.

2. Experimental

2.1. Materials

PPO (Xyron® S201A) was supplied by Tokyo Asahi Kasei Chemical Co., Ltd. Diglycidyl ether of bisphenol A (DGEBA) with an epoxy equivalent of 196 g/mol and methylhexahydrophthalic anhydrid (MeHHPA) were purchased from Hunan Sinopec Baling Petrochemical Co., Ltd and Beijing Innochem Co., Ltd, respectively. Tris(dimethylaminomethyl) phenol (DMP-30), bisphenol A (BPA) and 4,4′-(hexafluoroisopropylidene) diphenol (BPAF) were obtained from Shanghai Aladdin Chemistry Co., Ltd. Benzoyl peroxide (BPO) was provided by Shanghai Alfa Aesar Chemistry Co., Ltd and was recrystallized before use. All other solvents were obtained from various commercial sources and used as received.

2.2. Redistribution reaction of PPO with BPAF

The redistribution reaction of PPO with BPAF was performed in the presence of BPO. The typical procedure was as follows. 50 g PPO was first dissolved in 200 mL toluene at 90 ℃ under nitrogen. Subsequently, 25 g BPAF (50 phr, based on the quality of PPO) was added and stirred to be well dissolved, and then, 50 mL solution of BPO in toluene (1 g/10 mL) was dropwise added within 1.5 h. The reaction was maintained at 90 ℃ for another 3 h. After cooling to the room temperature, the solution was added into excessive methanol to precipitate the product. The mixture was filtered and washed with saturated aqueous solution of $NaHCO_3$ to remove the residual BPO. An off-white product (F-rPPO) was finally obtained after drying in vacuum at 110 ℃ for 24 h.

2.3. Curing reaction of EP/F-rPPO

A formulated amount of F-rPPO was added to epoxy prepolymer DGEBA, and the mixture was stirred at 150 ℃ until well combined. Afterwards, the mixture was cooled to 80 ℃ and a stoichiometric amount of MeHHPA was added as a curing agent, followed by being stirred for 30 min to obtain a homogeneous solution. After the addition of accelerator DMP-30, the mixture was poured into the preheated molds and successively cured at 100 ℃ for 2 h, 140 ℃ for 2 h, 180 ℃ for 2 h and post-cured at 200 ℃ for 2 h.

2.4. Characterization

Gel permeation chromatography (GPC) was performed using a RI-201H differential refractive index detector (Shodex, Japan) with K-804L/K-G chromatographic column (Shodex, Japan) at the room temperature with chloroform as an eluent and polystyrene as standard. ^{1}H nuclear magnetic resonance (^{1}H NMR) and ^{19}F nuclear magnetic resonance (^{19}F NMR) spectra were obtained from an Avance III, 600 MHz NMR spectrometer (Brucker, Germany) with $CDCl_3$ as solvent. X-ray photoelectron spectroscopy (XPS) was carried out with an Escalab Xi + spectrometer (ThermoFisher, USA), which was equipped with the Al Ka excitation radiation (hν-1486.6 eV). Fourier transform infrared (FT-IR) spectra were recorded by a Vertex70 spectroscope (Bruker, Germany). The viscosity was measured by a DV3TLV viscometer (Brookfield, USA) with LV-4 spindle at 100 ℃ and 20 rpm. Dynamic mechanical analysis (DMA) was carried out with a Q800DE DMA instrument (TA, USA) under a three-point bending mode. Samples were tested from 30 ℃ to 225 ℃ at a heating rate of 3 ℃/min and a frequency of 10 Hz. Thermogravimetric analysis (TGA) was conducted with a STA449C analyzer (Netzsch, Germany) under nitrogen from 30 ℃ to 800 ℃ at a heating rate of 10 ℃/min. Dielectric properties of circular samples with diameter of 14 mm and thickness of around 1 mm were investigated on a 4294A dielectric analyzer (Agilent, USA) by using the standard capacitance method [25] at 10 ~ 100 MHz. Dielectric properties of samples with dimensions of 16 mm × 8 mm × 2 mm at high frequency (12 ~ 18 GHz) were measured by a E5071C vector network analyzer (Agilent, USA) via waveguide method [26]. All dielectric measurements were conducted at the room temperature. The moisture absorption of sample is calculated as the formula $(W - W_0)/W_0 \times 100\%$, where W_0 and W represent the weight of sample before and after being immersed in water at 25 ℃ for 24 h. All samples were pre-dried before test.

3. Results and discussion

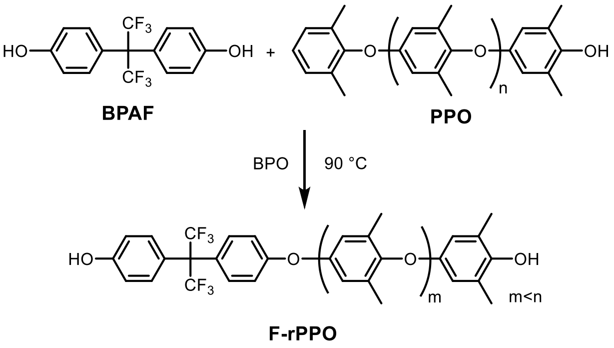
3.1. *Synthesis of low molecular weight F-rPPO (GPC)*

Low molecular weight PPO is readily obtained by the redistribution reaction of commercial PPO with bisphenols in the presence of initiators, which is highly designable due to the variety of bisphenols [21,27]. In order to introduce the fluorinated substituents with low polarizability and large free volume into the redistributed PPO, the fluorinated bisphenol, BPAF, is reacted with PPO to obtain fluorinated redistributed PPO (F-rPPO). As reported previously [20], BPO is considered as an effective initiator in the free-radical-initiated redistribution reaction and thus acted as an initiator in this reaction. The samples of F-rPPO from redistribution reaction using different amounts of BPO and BPAF are named as Fx-y, where x and y represent the amount of BPO and BPAF (phr, based on the quality of PPO), respectively. For brevity, Fx-y is simplified as Fx when y is equal to 50. The preparation route of F-rPPO is given in Scheme 1.

According to reports [9,13], the molecular weight of redistributed PPO is significantly associated with the amount of initiator and bisphenol compound utilized in redistribution reaction. In order to obtain F-rPPO with low molecular weight, first, the effect of BPAF amounts on the molecular weight of resulting F-rPPO is investigated. The decrease of F-rPPO molecular weight after redistribution is traced by GPC. As shown in Table 1, when a reasonable amount of BPO (10 phr) is employed, the M_n of F-rPPO is decreased from 1.9 × 10^4 g/mol for original PPO to the range of 3.0 ~ 6.6 × 10^3 g/mol, which shows a considerable decline. More specifically, the M_n of F-rPPO is reduced to a suitable range for epoxy processing (<4.0 × 10^3 g/mol) as the BPAF amount goes up to 20 phr, and reaches a minimum value of 3.0 × 10^3 g/mol at 50 phr BPAF. Moreover, no significant decline in molecular weight appears as the BPAF amount increases over 50 phr, indicating that the redistribution reaction seems to reach an equilibrium state ($M_n \approx 3.0 \times 10^3$ g/mol).

Based on the above results, the effect of initiator BPO amount is further explored. As listed in Table 2, the M_n of F-rPPO is markedly decreased with increasing BPO amount from 2.5 to 10 phr. It is interestingly found that the redistribution reaction reaches an equilibrium state at the same condition (BPO of 10 phr and BPAF of 50 phr). Noteworthily, the excessive amount of BPO leads to a slightly increase in the molecular weight, which is probably explained by the fact that the fraction with lower molecular weight is washed off during precipitation due to its better solubility in methanol [28]. Given these results, F-rPPO with expected low molecular weight (3.0 ~ 6.6 × 10^3 g/mol) is successfully obtained via the redistribution reaction.

For comparison, the classical BPA-redistributed-PPO (A-rPPO) was also prepared under the appropriate condition. The GPC traces of original PPO, F-rPPO (F10) and A-rPPO (A10) are depicted in Fig. 1. It is obvious that a shoulder peak corresponding to the high molecular weight part of original PPO remains both in the traces of F-rPPO and A-rPPO, which was commonly observed in researches on redistribution [21,28,29]. Nevertheless, F-rPPO displays a notably lower proportion of high molecular weight part (10.1%) compared with A-rPPO (36.0%), indicating that the BPAF-redistribution reaction possesses a higher degree of redistribution than the classical BPA-redistribution reaction, which is further discussed together with the mechanism of redistribution.



Scheme 1. Preparation route of F-rPPO.

Table 1
GPC results of F-rPPO prepared with different amounts of BPAF.

Sample	BPO (phr)	BPAF (phr)	M_n[a] (×10^3 g/mol)	M_w/M_n	High M[b](%)
PPO	–	–	19	2.0	–
F10-10	10	10	6.6	2.7	12.5
F10-20	10	20	3.6	2.7	11.4
F10-30	10	30	3.4	2.6	10.5
F10-40	10	40	3.3	2.4	10.3
F10-50	10	50	3.0	2.5	10.1
F10-60	10	60	3.0	2.6	9.2

[a] Based on low molecular weight peak on bimodal curve.
[b] Peak area ratio of high molecular weight part.

Table 2
GPC results of F-rPPO prepared with different amounts of BPO.

Sample	BPO (phr)	BPAF (phr)	M_n[a](×10^3 g/mol)	M_w/M_n	High M[b](%)
PPO	–	–	19	2.0	–
F2.5–50 (F2.5)	2.5	50	6.2	2.7	31.8
F5-50 (F5)	5.0	50	4.7	2.7	21.5
F10-50 (F10)	10	50	3.0	2.5	10.1
F20-50 (F20)	20	50	3.1	2.8	12.6
A-rPPO (A10)	10	50[c]	2.0	1.4	36.0

[a] Based on low molecular weight peak on bimodal curve.
[b] Peak area ratio of high molecular weight part.
[c] BPA instead of BPAF.

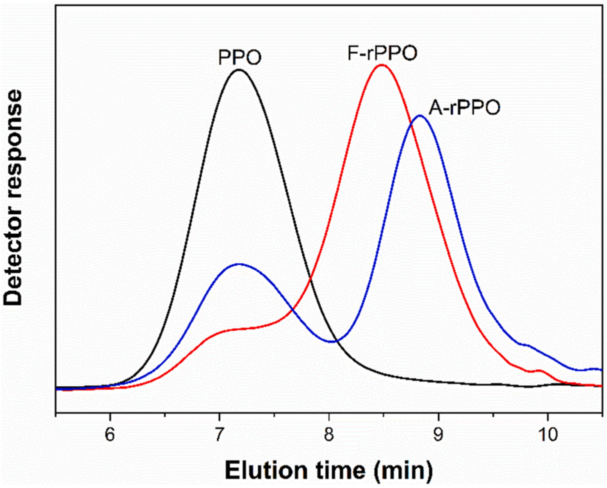


Fig. 1. GPC traces of original PPO, F-rPPO (F10) and A-rPPO (A10).

3.2. *Characterization of F-rPPO*

The structure of F-rPPO is characterized by ^{1}H NMR (Fig. 2), ^{19}F NMR (Fig. 3) and FT-IR spectra (Fig. 4). A typical ^{1}H NMR spectrum of F-rPPO (F10) is shown in Fig. 2. F-rPPO displays two characteristic signals at $\delta = 2.10$ for the methyl protons and $\delta = 6.47$ for the aromatic rings. Furthermore, peaks at $\delta = 6.82–6.97$ for the phenolic hydrogens and $\delta = 8.20$ for the terminal OH protons of F-rPPO chains are also observed. The results prove that F-rPPO with expected molecular structure was

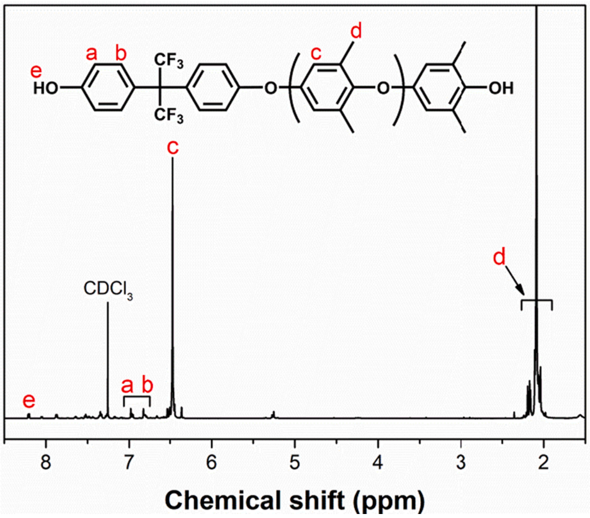


Fig. 2. ^{1}H NMR spectrum of F-rPPO (F10).

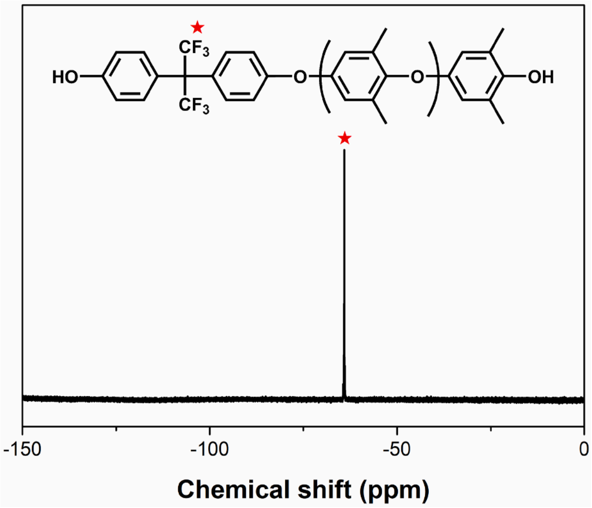


Fig. 3. ^{19}F NMR spectrum of F-rPPO (F10).

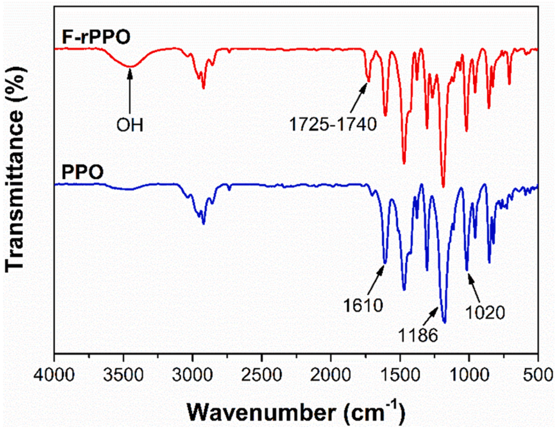


Fig. 4. FT-IR spectra of original PPO and F-rPPO (F10).

prepared successfully.

To reveal the relationship between the molecular weight and the fluorine content of F-rPPO, ^{19}F NMR and XPS analysis were carried out. As shown in Fig. 3, the representative ^{19}F NMR spectrum of F-rPPO (F10) exhibits a single peak at $\delta = -64.2$ belonging to the trifluoromethyl group, which indicates that the fluorinated groups were introduced into the F-rPPO via the redistribution reaction successfully. Furthermore, the fluorine content of F-rPPO with different molecular weight was measured by XPS, and the results are provided in Table 3. As expected, the fluorine content of F-rPPO is increased with the decrease in M_n because of the single terminal BPAF group at each F-rPPO molecular chain, which is favorable to the modification on epoxy resin for lower dielectric constant and water absorption.

FT-IR spectra of original PPO and F-rPPO (F10) are recorded in Fig. 4. Both PPO and F-rPPO exhibit the characteristic peaks at 1020 cm^{-1} and 1186 cm^{-1} corresponding to C-O stretching, as well as absorption at 1610 cm^{-1} for aromatic ring stretching. The significant differences between FT-IR spectra of PPO and F-rPPO are observed at 3450 cm^{-1} for OH groups, 1740 cm^{-1} and 1725 cm^{-1} for carbonyl groups existed in F-rPPO. The increased intensity of hydroxyl absorption at 3450 cm^{-1} is ascribed to the increase of terminal phenolic groups originated from BPAF, which corroborates the occurrence of redistribution reaction. The absorption around 1740 cm^{-1} and 1725 cm^{-1} is probably originated from the initiator BPO. During redistribution reaction, the benzoate ester derived from the initial reaction of BPO might be linked at the *ortho* methyl group of PPO phenolic end group **(BPO-I)** and at the *para* site of 2,6-dimethylphenol **(BPO-II)** [20], as described in Scheme 2.

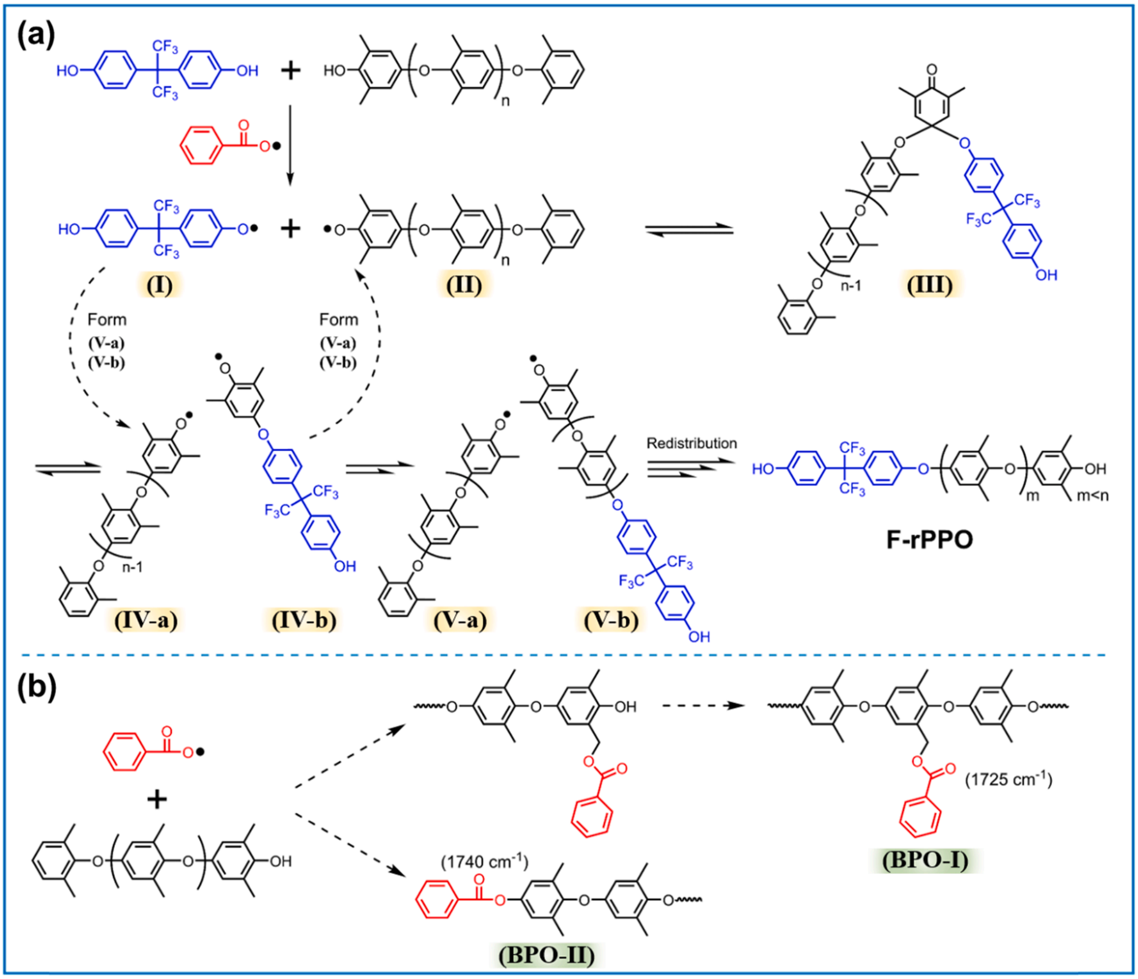
3.3. Mechanism of redistribution

On the basis of the radical mechanism widely accepted for redistribution reaction of PPO [30–32], a possible mechanism for BPAF-redistribution reaction is given in Scheme 2. In the presence of free radicals from initiator BPO, the phenolic hydroxyl groups of BPAF and PPO are first initiated to generate the monomeric phenoxy radicals **(I)** and polymeric phenoxy radicals **(II)**, respectively. Subsequently, the monomeric phenoxy radicals **(I)** attack the *para* position of the terminal group in polymeric phenoxy radicals **(II)** with n degree of polymerization to form the quinone ketal intermediate **(III)**. After the coupling of these radicals, the redistribution yields the dimer phenoxy radicals **(IV-b)** and polymeric phenoxy radicals **(IV-a)** with ($n - 1$) degree of polymerization. As a result, the degree of polymerization for F-rPPO is decreased to an equilibrium value of m ($m < n$) by repeating the process. Besides, partial benzoate ester groups from initiator BPO were incorporated into the structure of products to form **(BPO-I)** and **(BPO-II)**, which was confirmed by FT-IR.

As mentioned above, when the redistribution reaction goes on, the molecular chains of original PPO shorten whereas the molecular chains of F-rPPO grow longer. In other words, a higher molecular weight of the resulting redistributed PPO is indicative of a lower molecular weight of the remained PPO. It can be known from Table 2 that the molecular weight of F-rPPO is slightly higher than that of A-rPPO under the same preparation conditions, which indicates that more PPO molecules participate in the BPAF-redistribution reaction. The result is also in accordance with the fact that lower proportion of high molecular weight PPO remained in F-rPPO (10.1%) than in A-rPPO (36.0%). These results suggest that the BPAF-redistribution reaction possesses a much higher degree of reaction compared to the classical BPA-redistribution reaction, which provides a more promising redistributed PPO for further modification.

Table 3
Fluorine content of F-rPPO with different molecular weight.

F-rPPO	M_n ($\times 10^3$ g/mol)	F content/wt%
F2.5	6.2	1.28
F5	4.7	2.04
F10	3.0	3.15



Scheme 2. (a) Rtion mechanism of PPO with BPAF and (b) possible chemical structures of by-product containing a benzoate ester group.

3.4. *Curing kinetics of EP/F-rPPO*

To better study the effect of F-rPPO on the curing behaviors of EP/F-rPPO systems, three kinds of F-rPPO with different M_n (3.0 × 10^3, 4.7 × 10^3 and 6.2 × 10^3 g/mol for F10, F5 and F2.5, respectively) were mixed with epoxy prepolymer DGEBA, then cured by MeHHPA. The cured EP/F-rPPO resins are named as EPz-Fx, in which z represents the addition amount of F-rPPO (phr, based on the quality of DGEBA, z = 20, 30 or 40) and Fx represents different F-rPPO (F10, F5 or F2.5). As a control, 20 phr of A-rPPO (A10, M_n = 2.0 × 10^3 g/mol) was also mixed with DGEBA and cured by MeHHPA to be named as EP20-A, and the cured DGEBA/MeHHPA resin without modifier is named as EP-0.

The nonisothermal curing kinetics of EP/F-rPPO curing systems is investigated through DSC [33]. Fig. 5 exhibits the DSC curves obtained at different heating rates of 5, 10, 15, and 20 °C/min, for the epoxy system before and after modification by F-rPPO (20 phr of F10). Both

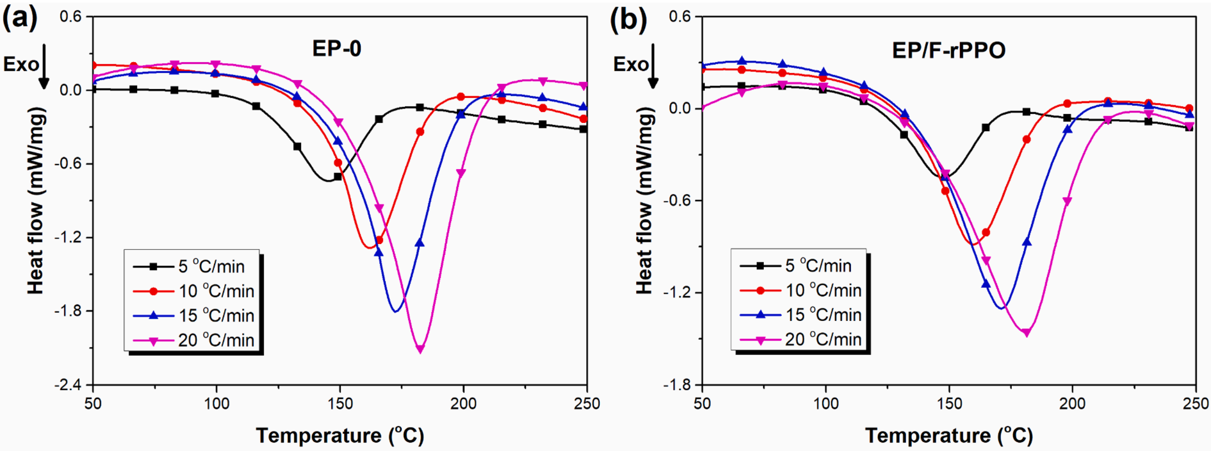


Fig. 5. Exothermic curves from DSC of (a) EP-0 and (b) EP/F-rPPO (EP20-F10).

EP-0 and EP20-F10 curing systems show one curing stage with an exothermic peak. The curing behavior of EP/F-rPPO can be evaluated by calculating the apparent activation energy (E_a) according to Kissinger's method [34], as shown in equation (1).

$$ln(\beta/T_p^2) = ln(AR/E_a) - E_a/RT_p \tag{1}$$

where β, T_p, A and R stand for the heating rate, peak exothermic temperature, pre-exponential factor and the ideal gas constant, respectively.

The calculated values of E_a for EP/F-rPPO and control EP/A-rPPO as well as EP-0 curing systems are listed in Table 4. Evidently, the E_a of EP/F-rPPO curing systems is affected simultaneously by the loading and the molecular weight of F-rPPO. The E_a of EP/F-rPPO shows an upward trend with the increase of F-rPPO loading for the same F-rPPO. As we know, the system viscosity significantly affects the reactivity during the curing process. Compared to DGEBA, F-rPPO has a higher molecular weight and the corresponding solution viscosity. Hence, as the loading of F-rPPO increases, the viscosity and E_a of the EP/F-rPPO curing system go up. Furthermore, it is easy to be understood that the same loading of higher molecular weight F-rPPO leads to the higher E_a and lower reactivity of the curing system owing to higher system viscosity brought by high molecular weight chains. The viscosity effect was further proved by comparing the viscosity of different EP/F-rPPO mixtures (Fig. S1), which fitted well with the E_a results. Noteworthily, the E_a of EP20-F10 (61.83 kJ/mol) is higher than that of EP-0 (52.68 kJ/mol), but is lower than that of EP20-A (63.14 kJ/mol). This suggests that the EP/F-rPPO curing system has a lower viscosity compared to EP/A-rPPO curing system, that is the lower viscosity of F-rPPO than that of A-rPPO at the same loading. It is in line with the GPC results that F-rPPO possesses less proportion of high molecular weight chains compared to A-rPPO, and thus exhibits a lower viscosity and higher reactivity to the curing system.

3.5. *Thermal properties of cured EP/F-rPPO resins*

DMA is carried out to investigate the thermomechanical properties of cured EP/F-rPPO resins, in which the peak of loss tangent (tan δ) is commonly used to determine T_g and to investigate the phase state of the cured resins. The tan δ and storage modulus (E') versus temperature are depicted in Fig. 6, and T_g values and E' (at 130 ℃) of all samples are listed in Table 5. As shown in Fig. 6a, the EP-F10 exhibits only one peak of tan δ, which evidences that the epoxy resin still remains a state of homogeneous phase after modification by F-rPPO. Besides, the T_g for all cured EP/F-rPPO resins is enhanced until a maximum value of 146 ℃ compared to 129 ℃ for EP-0, which is mainly originated from the movement restriction of molecular chains by rigid F-rPPO in the crosslinking networks [35], leading to the increased storage modulus of cured EP/F-rPPO resins.

Moreover, EP-F10 and EP-F5 possess higher T_g in comparison to EP-F2.5. This is primarily owing to the lower viscosity originated from lower molecular weight chains for F10 and F5, which contributes to form the well-combined crosslinking networks and improve the T_g. The T_g of EP-F2.5 decreases with increasing F-rPPO loading, which trend was also observed in literatures [9,23]. This suggests that the molecular weight of F2.5 (6.2×10^3 g/mol) is still relatively high that enlarges the hindrance on epoxy curing, especially at high addition. More spacing between the crosslinking networks resulted from incomplete curing lead to the lower T_g.

The thermal performance of EP/F-rPPO thermosets was evaluated by TGA under nitrogen atmosphere, and the TGA curves of EP-F10 are depicted in Fig. 7. The thermal stability is characterized by 5% weight loss temperature ($T_{d5\%}$) and the char residue at 800 ℃ as listed in Table 5. The $T_{d5\%}$ of EP20-F10, EP20-F5 and EP20-F2.5 are respectively 365 ℃, 367 ℃ and 361 ℃, which are all significantly higher than 321 ℃ for EP-0. Thanks to the high heat resistance of F-rPPO, better thermal stability of cured epoxy resin is realized after modification by F-rPPO, especially by F10 and F5 with lower M_n, which endow the epoxy resins with more complete curing reaction. It should be noted that the $T_{d5\%}$ of EP-F2.5 decreases rapidly with increasing F2.5 loading. It is probably originated from the increased viscosity by F2.5, resulting in the insufficient curing reaction and incomplete crosslinked epoxy structure. Additionally, the char residue of cured EP/F-rPPO resins is enhanced to a maximum of 11.7% from 5.2% for EP-0, suggesting potential flame-retardant properties of EP/F-rPPO thermosets.

Table 4
The apparent activation energy of different EP/F-rPPO curing systems.

Curing system	E_a (kJ/mol)	Curing system	E_a (kJ/mol)
EP-0	52.68	**EP20-F10**	61.83
EP20-A	63.14	**EP30-F10**	65.06
		EP40-F10	66.46
EP20-F5	65.15	**EP20-F2.5**	77.55
EP30-F5	66.90	**EP30-F2.5**	80.80
EP40-F5	74.37	**EP40-F2.5**	91.94

3.6. *Moisture resistance of cured EP/F-rPPO resins*

For CCLs and their derived electronic applications, the water, absorbed both on the surface and inside CCLs, has an undoubtedly detrimental effect on their thermal, mechanical and dielectric properties. In particular, the dielectric properties of resins are more sensitive to water due to its dielectric constant as high as 78 at 25 ℃. Furthermore, water also ionizes the ionic impurities, and accelerates the corrosion of CCLs. Therefore, the low moisture absorption is a vital characteristic for the advanced electronic materials. It can be seen from Table 6 that all cured EP/F-rPPO resins exhibit lower moisture absorption compared with EP-0. F-rPPO possesses low polarity, low surface energy and symmetrical structure [36], that is the intrinsic moisture resistance. The introduction of F-rPPO endows the cured EP/F-rPPO resins with the improved hydrophobicity and moisture resistance [37,38]. Consequently, the moisture absorption of the cured EP/F-rPPO resins is reduced with the increase of F-rPPO loading, which is conductive to maintain the low dielectric constant for modified resins.

3.7. *Dielectric properties of cured EP/F-rPPO resins*

The signal propagation speed in CCLs is inversely proportional to the dielectric constant (D_k), whereas the signal propagation loss is proportional to the dielectric loss factor (D_f). Therefore, materials with lower dielectric constant and loss are of great benefit for improving the signal propagation speed meanwhile minimizing the loss in electronic applications. The frequency dependence of dielectric properties for EP-F10, EP-F5 and EP-F2.5 is presented in Fig. 8(a, b), Fig. S2, Fig. S3, respectively. The detailed related data of cured EP/F-rPPO resins are collected in Table 6. The D_k and D_f of all cured EP/F-rPPO resins are significantly lower than those of EP-0 ($D_k = 3.43$, $D_f = 0.0219$ at 100 MHz). Moreover, the lower dielectric constant and loss are realized with increasing the loading of F-rPPO. The D_k for EP20-F10, EP30-F10 and EP40-F10 is decreased from 3.43 for EP-0 to 2.98, 2.94 and 2.88 at 100 MHz, respectively, which is attributed to the low polarizability of poly(phenylene oxide) structure and C-F bond, and the large free volume of -CF$_3$ groups. The contribution of fluorine is verified by comparing the D_k of EP20-F10 and EP20-A. When redistributed PPOs with similar molecular weight (F10 and A10) are independently used at the same loading, EP20-F10 shows a lower D_k than that of EP20-A, which proves a sharper D_k drop due to the existence of fluorinated group. And along with it, the decreased density of cured EP/F-rPPO resins also implies the increased free volume resulted from -CF$_3$ groups.

In addition to the loading, the molecular weight of F-rPPO has a significant effect on the dielectric properties of the thermosets as well. For epoxy resins modified by 40 phr F-rPPO, the D_k values follow the order: EP-F10 < EP-F5 < EP-F2.5. On the one hand, the incorporation of

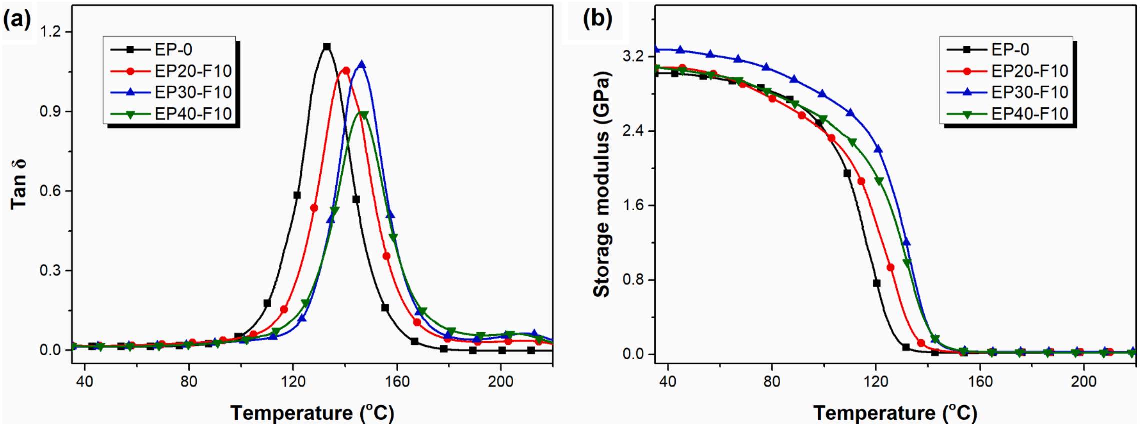


Fig. 6. (a) Tan δ and (b) storage modulus (*E*') curves of EP-0 and EP-F10.

Table 5
DMA and TGA results of cured EP/F-rPPO resins.

M_n of F-rPPO ($\times 10^3$ g/mol)	Sample	F-rPPO addition (phr of DGEBA)	T_g (°C)	*E*' at 130 °C (GPa)	$T_{d5\%}$ (°C)	Residue at 800 °C (wt %)
	EP-0	–	129	0.11	321	5.2
2.0	EP20-A	20	136	0.36	284	3.0
	EP20-F10	20	140	0.52	365	7.6
3.0	EP30-F10	30	145	1.40	371	8.5
	EP40-F10	40	146	1.19	363	11.7
	EP20-F5	20	141	0.78	367	8.5
4.7	EP30-F5	30	142	0.86	363	8.7
	EP40-F5	40	146	1.28	366	8.3
	EP20-F2.5	20	141	0.92	361	6.5
6.2	EP30-F2.5	30	140	0.64	306	7.7
	EP40-F2.5	40	135	0.28	252	8.6

Table 6
Dielectric properties, moisture absorption and density of cured EP/F-rPPO resins.

M_n of F-rPPO ($\times 10^3$ g/mol)	Sample	F-rPPO addition (phr of DGEBA)	Moisture absorption (%)	Density (g/cm^3)	D_k at 100 MHz	D_f at 100 MHz
	EP-0	–	0.48	1.194	3.43	0.0219
2.0	EP20-A	20	0.54	1.187	3.15	0.0198
	EP20-F10	20	0.39	1.184	3.05	0.0198
3.0	EP30-F10	30	0.38	1.179	2.98	0.0188
	EP40-F10	40	0.33	1.177	2.88	0.0175
	EP20-F5	20	0.36	1.187	3.04	0.0197
4.7	EP30-F5	30	0.33	1.183	2.97	0.0187
	EP40-F5	40	0.29	1.177	2.94	0.0181
	EP20-F2.5	20	0.38	1.185	3.12	0.0205
6.2	EP30-F2.5	30	0.29	1.184	3.04	0.0191
	EP40-F2.5	40	0.18	1.183	2.98	0.0180

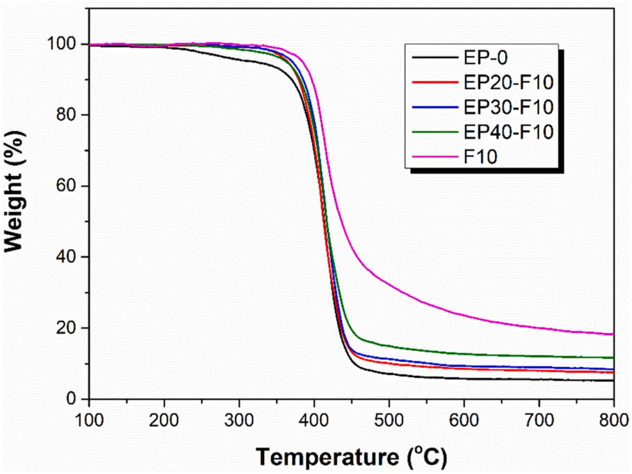


Fig. 7. TGA curves of EP-0 and EP-F10.

F-rPPO with higher molecular weight may lead to more spacing between the crosslinking networks and to the increased free volume, which reduces the D_k and D_f of cured epoxy resins [24]. On the other hand, the high molecular weight F-rPPO may also lead to more incomplete curing reaction of epoxy resin due to the high viscosity, in which the more residual polar groups raise the D_k and D_f. It can be concluded from the results that the effect of the viscosity increase by F-rPPO with higher molecular weight exceeds that of the free volume enlargement. Consequently, the D_k and D_f of cured EP/F-rPPO resins go up with the increase of F-rPPO molecular weight. Herein, EP40-F10 modified by F10 with lower molecular weight possesses the lower dielectric parameters (D_k = 2.88, D_f = 0.0175 at 100 MHz).

The development of high-speed and high-frequency CCLs has highlighted the significance of epoxy resin with low dielectric constant and loss at high frequency (over 5 GHz). Base on this, the D_k and D_f of EP-F10 at high frequency (12 ~ 18 GHz) were measured by waveguide method and the results are displayed in Fig. 8(c, d). At 12 GHz or more, the orientation polarization is unable to keep up with the change of electric field [39], leading to the decreased polarization intensity. As a result, the D_k of EP40-F10 is further reduced from 2.88 at 100 MHz to 2.69 at 12 GHz. It is noteworthy that EP30-F10 and EP40-F10 show a slightly increased D_f than EP20-F10 at 16–18 GHz, which may be derived from

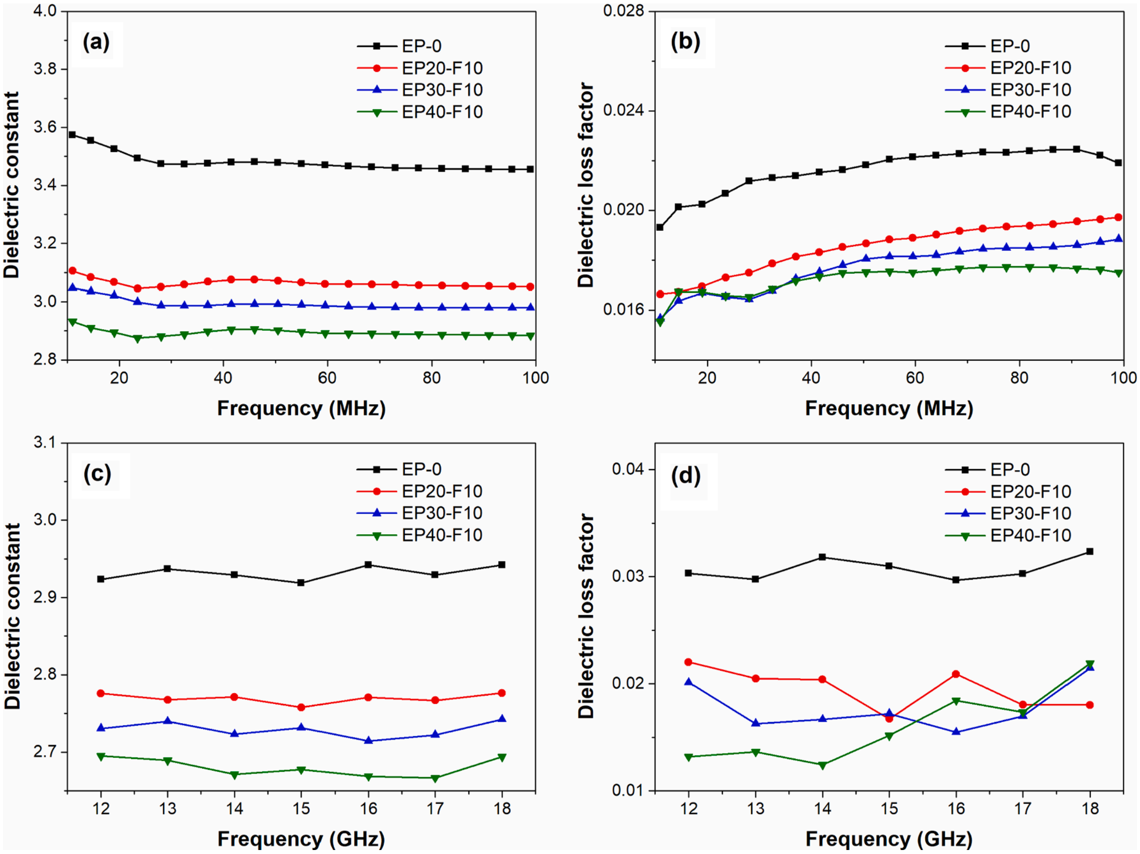


Fig. 8. Frequency dependence of dielectric properties for EP-0 and EP-F10: (a) dielectric constant and (b) dielectric loss factor at 10 ~ 100 MHz; (c) dielectric constant and (d) dielectric loss factor at 12 ~ 18 GHz.

Table 7
Comparison of this work with other PPO-modified epoxy resins reported in the literatures.

PPO[a]	Molecular weight ($\times 10^3$ g/mol) and addition[b] of PPO	Thermal properties[c]	Moisture absorption (%)	D_k	D_f	Ref.
F-rPPO	M_n: 3.0 40 phr	$T_g = 146$ ℃ (↑ 17℃) $T_{d5\%} = 363$ ℃ (↑ 42℃)	0.33	2.69 (12 GHz)	0.0132 (12 GHz)	This work
A-rPPO	M_n: 2.7 10 phr	$T_g = 133$ ℃ (↑ 7℃) $T_{d5\%} = 184$ ℃ (↓ 114℃)	-[d]	4.21 (10 MHz)	0.0150 (10 MHz)	[22]
A-rPPO	M_n: 0.6 40 phr	$T_g = 158$ ℃ (↓ 18℃) $T_{d5\%} = 392$ ℃ (↑ 5℃)	1.70	2.73 (1 GHz)	0.0115 (1 GHz)	[23]
A-rPPO-polysiloxane	M_n: 3.5 40 phr	$T_g = 177$ ℃ (↑ 26℃) $T_{d50\%} = 460$ ℃ (↑ 27℃)	-[d]	-[d]	-[d]	[29]
DCPD-rPPO	M_w: 3.7 40 phr	$T_g = 159$ ℃ (↓ 17℃) $T_{d5\%} = 407$ ℃ (↑ 20℃)	1.63	2.71 (1 GHz)	0.0140 (1 GHz)	[9]
MA-rPPO	M_n: 4.9 25 phr	$T_g = 140$ ℃	-[d]	2.82 (1 MHz)	0.0078 (1 MHz)	[35]
FHPPO	M_n: 2.5 40 phr	$T_g = 165$ ℃ (↓ 2℃) $T_{d5\%} = 304$ ℃ (↑ 10℃)	0.40	2.77 (1 MHz)	0.0142 (1 MHz)	[40]
EHPPO	M_n: 1.6 20 phr	$T_g = 134$ ℃ (↑ 35℃) $T_{d5\%} = 343$ ℃ (↑ 49℃)	-[d]	-[d]	-[d]	[41]
EPPO	M_n: 2.6 100 phr	$T_g = 155$ ℃ (↑ 37℃) $T_{d5\%} = 330$ ℃ (↑ 29℃)	-[d]	3.81 (1 MHz)	0.0234 (1 MHz)	[19]
EPPO	M_n: 3.0 100 phr	$T_{d5\%} = 397$ ℃ (↑ 5℃)	1.09	3.98 (1 MHz)	0.0410 (1 MHz)	[10]
PPOE	M_n: 3.2 100 phr	$T_{d5\%} = 409$ ℃ (↑ 17℃)	1.03	3.91 (1 MHz)	0.0387 (1 MHz)	[42]

[a] The structures of PPO are shown in Table S1.
[b] Based on the quality of epoxy prepolymer.
[c] The sorts of epoxy resins and curing agents are listed in Table S1.
[d] Not reported.

more space for polarized molecules to move when more F-rPPO employed. Table 7 summarizes previously reported comprehensive performance for epoxy resins modified by PPO. As shown in Table 7, the PPO-modified epoxy resins with low D_k (near 2.70), improved thermal properties and moisture resistance simultaneously are very rare. The F-rPPO reported in this study, is therefore a promising modifier to endow epoxy resins with low dielectric constant and loss, which meanwhile improves their thermal properties and moisture resistance.

4. Conclusions

In this paper, a novel fluorinated redistributed poly(phenylene oxide) (F-rPPO) with M_n of 3.0–6.2 × 10^3 g/mol was synthesized by the redistribution reaction of high molecular weight PPO and BPAF initiated by BPO, which possessed a higher degree of redistribution than the classical BPA-redistribution reaction. Next, the F-rPPO was used as a modifier for DGEBA/MeHHPA epoxy resin. Because of the rigid structure of F-rPPO, the cured EP/F-rPPO resins exhibited improved thermal stability and T_g compared to the pristine epoxy resin. Meanwhile, better moisture resistance of cured EP/F-rPPO resins was realized owing to the intrinsic moisture resistance of F-rPPO and low surface energy endowed by fluorine. Moreover, attributed to the low polarizability of F-rPPO and large free volume introduced by -CF_3 groups, the cured EP/F-rPPO resins possessed lower dielectric constant and loss compared to the pristine epoxy resin. Therefore, F-rPPO is believed to be a promising modifier for simultaneously enhancing the thermal and dielectric properties of epoxy resins to meet the high demand of advanced electronic applications.

CRediT authorship contribution statement

Yubin Zhou: Conceptualization, Writing – original draft. **Zhongquan Peng:** Resources, Funding acquisition. **Jingqi Ji:** Investigation, Formal analysis. **Yancheng Wu:** Investigation, Methodology. **Zhigeng Chen:** Investigation, Data curation. **Haohao Huang:** Validation. **Shumei Liu:** Writing - review & editing. **Jianqing Zhao:** Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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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.2021.110674.

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