



## Novel low phosphorus-content bismaleimide resin system with outstanding flame retardancy and low dielectric loss

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### ABSTRACT

A novel modified bismaleimide resin system (BDP) with significantly improved flame retardancy and decreased dielectric loss was successfully prepared by copolymerizing 4,4'-bismaleimidodiphenyl methane (BDM) with 2,2'-diallyl bisphenol A (DBA) and 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO). Compared with BDM/DBA resin, BDP resin has obviously different crosslinked structure, and thus simultaneously improved dielectric properties and flame retardancy. Most attractively, with a very low content of phosphorus element, the BDP resins show significantly improved flame retardancy. For example, when the content of phosphorus is as low as 0.5 wt%, the flame retardancy of BDP resin is evaluated to be UL94 V-0 level, while that of BD resin is classified as UL94 V-1 level; in addition, the total heat release (THR) of BDP resin reduces to about 61% of that of BD resin, and similar phenomenon is also observed on the weight ratio of CO/CO<sub>2</sub>. This outstanding flame retardancy of BDP resins is attributed to the attractive phosphorus-nitrogen synergistic effect. The main flame retardancy mechanism of BDP resins is evaluated to be condensed phase mechanisms. On the other hand, BDP resins exhibit improved dielectric properties; specifically, the dielectric constant and loss at 1 GHz of BDP resin with 19.7 wt% of phosphorus are 2.90 and 0.0058, only about 92% and 51% of that of neat BD resin, respectively. These interesting results demonstrate that the co-reaction of DOPO with BD resin is important, and the method proposed herein is a new approach to develop high performance resins with attractive flame retardancy and dielectric properties.

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### 1. Introduction

Developing high performance polymers with good flame retardancy is one hot subject of present polymer science and engineering because they are increasingly demanded by many cutting-edge fields including aerospace, micro-electrics, construction, textile, etc. [1–3], but unfortunately, almost all polymers don't have good flame retardancy.

Based on lots of previous investigations, by adding flame retardant to a polymer has been proved to be a common and effective method to endow polymers with good flame retardancy. Flame retardants include many sorts, among them phosphorus-containing flame retardant is regarded as the right alternative of halogen-free flame retardant owing to its high efficiency and low toxicity [4–7]. 9,10-Dihydro-9-oxa-10-phosphaphenanthrene-10-oxide (DOPO) is the representative phosphorus-containing flame

retardant, besides the merits of phosphorus-containing flame retardants, DOPO also has good thermal stability, therefore a lot of researches focused on preparing flame retardant polymers by utilizing DOPO and its derivatives [8–11], for example, DOPO based epoxides and curing agents were synthesized [12–18]. These researches obtained some interesting and positive results, however some important topics have not been studied. As we've known that excellent dielectric property (low dielectric constant and loss) is considered to be one key property of high performance resins for micro-electric field; unfortunately, the influence of flame retardant on dielectric properties of polymers is seldom studied. On the other hand, when DOPO and its derivatives were used to prepare flame retardant resins, the content of phosphorus generally should be larger than 2.5 wt% to get desirable flame retardancy (for example, UL94 V-0 level) [19], however, a larger content of phosphorus is not beneficial to maintain the thermal stability of the resin. Therefore, it is of great importance and interesting for studying these topics, this is also the target of our investigation described herein.

Bismaleimide/diallyl bisphenol A (BD), derived from the 2,2'-diallyl bisphenol A (DBA) modified bismaleimide resin (BDM), is

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claimed to possess outstanding integrated performance including outstanding thermal and moisture resistance, good processing characteristics, and high mechanical strength [20,21], so BD system has been employed to be high performance matrices for advanced composites, adhesives, and insulating coatings [22–25]. However, the flame retardancy of BD resin is not good, belonging to V-1 order according to UL94 tests. Therefore, BD resin is selected as the model for our investigation.

This paper gives the first presentation on preparing a novel flame retardancy resin system (BDP) based on BD resin and DOPO, and the discussion about the effect of the stoichiometry between BD and DOPO on the properties of BDP resins. This investigation is expected to propose a new approach to develop high performance flame retardant resins with simultaneously improved integrated performance, especially dielectric properties.

## 2. Experimental

### 2.1. Raw materials

4,4'-Bismaleimidodiphenol methane (BDM), was obtained from Institute of Northwestern Chemical Engineering (China). 2,2'-Diallyl bisphenol A (DBA) with a purification of 85% was purchased from Laiyu Chemical Factory in China. DOPO (the content of phosphorus atom is 14 wt%) was purchased from Eutec Chemical Co., Ltd (China).

### 2.2. Preparation of uncured samples for measurements

BDM and DBA was mixed with a molar ratio of 1:1, and then the mixture was put into a polyethylene (PE) bag, and ground into even mixture for differential scanning calorimeter (DSC) tests.

A mixture of BDM and DOPO (the molar ratio is 1:2), the mixture of DBA and DOPO (the molar ratio is 2:1), or the mixture of BDM, DBA and DOPO (the molar ratio is 3:1:2) was also prepared using above procedure for Differential Scanning Calorimeter (DSC) and thermogravimetric (TG) tests.

### 2.3. Preparation of BD and BDP prepolymers

According to Table 1, appropriate quantities of BDM and DBA were placed in a beaker with a mechanical stirrer and a thermometer. The mixture was heated to 125–135 °C and maintained within that temperature with stirring until a clear and brown liquid was obtained. The liquid was maintained at that temperature for additional 25 min to obtain a transparent liquid, which was BD prepolymer.

According to Table 1, appropriate quantities of DBA and DOPO were placed in a beaker with a mechanical stirrer and a thermometer. The mixture was heated to 125–135 °C and maintained within that temperature with stirring until a clear and yellow liquid was obtained (a tiny amount of which was used to record the FTIR spectrum). And then pre-weighted BDM was added into the beaker at 125–135 °C with stirring until a transparent liquid, and kept at

that temperature for 25 min to obtain a homogeneous liquid, which was coded as BDP prepolymer.

### 2.4. Preparation of cured BD and BDP resins

Each prepolymer was thoroughly degassed at 130 °C, and poured into a preheated (130 °C) metal mould, followed by curing per the curing procedure of 150 °C/2 h+180 °C/2 h+220 °C/3 h. After that the cured sample was demolded and postcured in an air oven at 230 °C for 4 h.

### 2.5. Measurements

DSC analyses were done using DSC 200 F3 (Netzsch, Germany) in the temperature range between 50 and 320 °C at a heating rate of 10 °C/min in a nitrogen atmosphere.

Fourier Transform Infrared (FTIR) spectra of each resin were recorded between 400 and 4000  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$  on a Nicolet 5700 infrared spectrometer (USA).

$^{31}\text{P}$  NMR spectra were performed on a Bruker Avance 400 Spectrometer (Germany) at 400 MHz using  $\text{DMSO-d}_6$  as the solvent.

Dynamic Mechanical Analysis (DMA) scans were performed using TA DMA Q800 apparatus from TA Instruments (USA). Single cantilever clamp geometry was used. DMA tests were carried out from room temperature to 325 °C with a heating rate of 3 °C/min at 1 Hz. The dimensions of each sample were  $(35 \pm 0.02) \times (13 \pm 0.02) \times (1.0 \pm 0.02) \text{ mm}^3$ .

A Scanning Electron Microscope (Hitachi S-4700, Japan) coupled with energy disperse X-ray spectrometer (EDS) was employed to observe the morphologies of the fractured surfaces of the charred layers samples. The resolution of the secondary electron image is 1.5 nm under 15 kV. All samples should be dried at 105 °C for 6 h before tests.

Dielectric constant and loss were performed with an Agilent E4991A measurement system (USA) at 30 °C by a two-parallel-plate mode over a wide frequency from 1 MHz to 1 GHz. The dimensions of each sample were  $(50 \pm 0.02) \times (50 \pm 0.02) \times (1.0 \pm 0.02) \text{ mm}^3$ , and all samples were dried under vacuum at 105 °C for 1 h before tests.

TG analyses were performed using PerkinElmer TGA-7 (USA) at a heating rate of 10 °C/min with a flow rate of 100 mL/min in a nitrogen atmosphere from 50 to 800 °C. The initial decompose temperature ( $T_{di}$ ) was defined as the point of intersection at which the tangent of onset temperature and the tangent of the maximum degradation rate temperature ( $T_{max}$ ).

UL94 tests were performed according to ASTM (D63-77). The dimensions of each sample were  $(125 \pm 0.02) \times (13 \pm 0.02) \times (1.6 \pm 0.02) \text{ mm}^3$ .

Limited Oxygen Index (LOI) values were measured on a Stanton Redcraft Flame Meter (UK) according to ASTM D2863/77. The dimensions of each sample were  $(100 \pm 0.02) \times (6.5 \pm 0.02) \times (3 \pm 0.02) \text{ mm}^3$ .

Flammability of resins was characterized using a cone calorimeter performed in an FTT device (UK) according to ISO 5660 with an incident flux of 35  $\text{kW/m}^2$ . The dimensions of each sample were  $(100 \pm 0.02) \times (100 \pm 0.02) \times (3 \pm 0.02) \text{ mm}^3$ .

## 3. Results and discussion

### 3.1. Curing behavior and mechanism of BD and BDP prepolymers

It is known that the curing behavior of a thermosetting resin determines its crosslinking network, and thereby the properties of the cured resin, so the curing behavior is the first issue needing to be investigated on developing any new thermosetting resins and related materials.

**Table 1**  
Formulations of BD and BDP resins.

Resin	Weight ratio		
	BDM	DBA	DOPO
BD	140	70	0
BDP1	140	70	8.1
BDP2	140	70	13.0
BDP3	140	70	16.2
BDP4	140	70	19.7

Fig. 1 shows the DSC curves of BD and BDP prepolymers. It can be seen that BD prepolymer shows an exothermic peak; while with the addition of DOPO to BD prepolymer, besides the main exothermic peak at the similar temperature range, an additional shoulder peak appears in the side of low temperature, indicating that a new reaction occurs in the BDP system. In other words, BD and BDP resins have different curing mechanisms.

In order to find the reason behind the different curing mechanisms, the reactions among BDM, DBA and DOPO were evaluated using DSC analyses, and corresponding curves are shown in Fig. 2. It can be observed that DOPO can not homo-polymerize over the whole temperature range tested; while the base line of DBA goes upwards when the temperature is higher than 180 °C, this is attributed to the occurrence of the rearrangement of diallyl bisphenol ether. Because the purity of DBA is about 85%, and there are some amounts of diallyl bisphenol ether which will be rearranged to DBA at high temperature, the rearrangement is an exothermic reaction. The mixture of DBA/DOPO shows a similar curve as DBA, indicating that there is no co-reaction between DOPO and DBA. In addition, DOPO will be dissolved in DBA at room temperature, so the melting point of DOPO can not be observed in the DSC curve of DBA/DOPO. However, interestingly, the mixture has an exothermic peak appearing at 130–190 °C, suggesting the existence of the co-reaction between BDM and DOPO, which is significantly lower than the reaction between BDM and DBA. Therefore in the case of BDM/DBA/DOPO system, BDM prefers to cure with DOPO rather than with DBA, meaning that the full amount of DOPO will co-react with BDM.

It has been accepted that the curing mechanism of BD resin contains multiple reactions [26,27], including “Ene addition” and “Diels–Alder” reactions between maleimide group of BDM and allyl group of DBA, and the self-polymerization of BDM via double bonds of maleimide groups (Scheme 1(1)). While in the case of BDP system, besides above reactions in BD system, there is a reaction between double bonds of maleimide rings in BDM and P–H groups in DOPO (Scheme 1(2)), hence an additional shoulder peak appears in the side of low temperature (Fig. 1). This will be confirmed by following FTIR and NMR analyses.

Fig. 3 shows FTIR spectra of DOPO, BD, DBA/DOPO and BDP prepolymers. The FTIR spectrum of DBA/DOPO prepolymers has the P–H absorption at 2386  $\text{cm}^{-1}$ , further proving that DOPO can not react with DBA. The spectra of BDP prepolymers seem to be the combination of those of DOPO and BD prepolymers, however the

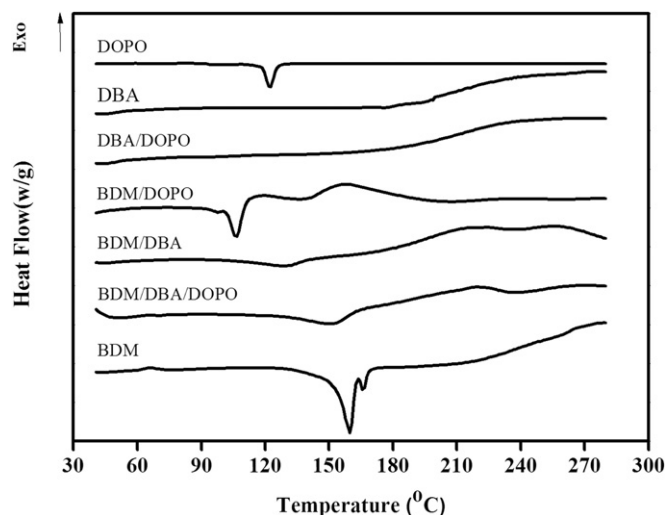


Fig. 2. DSC traces of monomers and mixtures.

strong P–H absorption at 2386  $\text{cm}^{-1}$  can not be found in the spectra of BDP prepolymers, suggesting that there is a reaction between P–H in DOPO and double bond of BDM (Scheme 1 (2)), this will be further confirmed by  $^{31}\text{P}$  NMR spectra.

Fig. 4 shows the  $^{31}\text{P}$  NMR spectra of DOPO and BDP2 prepolymer. Each of them has a strong peak, but which appears at different chemical shift because of the different environment of phosphorus atom induced by the reaction between DOPO and BDM. Similar results can be found in the corresponding spectra of other BDP prepolymers. Therefore, it is believed that DOPO has been successfully grafted on BDM.

On the other hand, Fig. 1 shows that with the addition of DOPO to BD prepolymer, the curing heats ( $\Delta H$ ) of BDP prepolymers are about 73.9–94.5% of that BD prepolymer, suggesting that the whole curing reaction of BDP system is a moderate one compared with that of BD. In other words, the curing reaction of BDP system avoids heat accumulation and thermal explosion, and thus becoming controllable, obviously it is a very attractive feature for fabricating thick materials.

Besides the chemical structure, the crosslinking density ( $X_{density}$ ) is another important parameter reflecting the structure of a cured thermosetting resin. The  $X_{density}$  value can be calculated by a semi empirical equation (Eq. (1)) based on DMA analyses [28].

$$\log_{10} G' = 7 + 293X_{density} \quad (1)$$

where  $G'$  is the storage modulus (Fig. 5) of the cured sample in the rubbery plateau region above the glass transition temperature ( $T_g$ ). Herein,  $G'$  is chosen as the modulus at that temperature which is 40 °C higher than  $T_g$ , and the corresponding  $X_{density}$  values of cured BD and BDP resins are summarized in Table 2. The  $X_{density}$  value of each BDP resin is slightly lower than that of BD resin, and the former decreases as the content of DOPO increases. As described above, a co-reaction between DOPO and BDM takes place at lower temperature compared with the homopolymerization of BDM, and the co-reaction between BDM and DBA, meaning that the amount of BDM homopolymer and that of the BDM/DBA copolymer will reduce, and thus leading to the decreased  $X_{density}$  values. The result gives further evidence of the curing behavior and mechanism as stated above.

### 3.2. Thermal resistance

For a thermosetting resin, its  $T_g$  is an important property because it is the maximum application temperature of the resin.

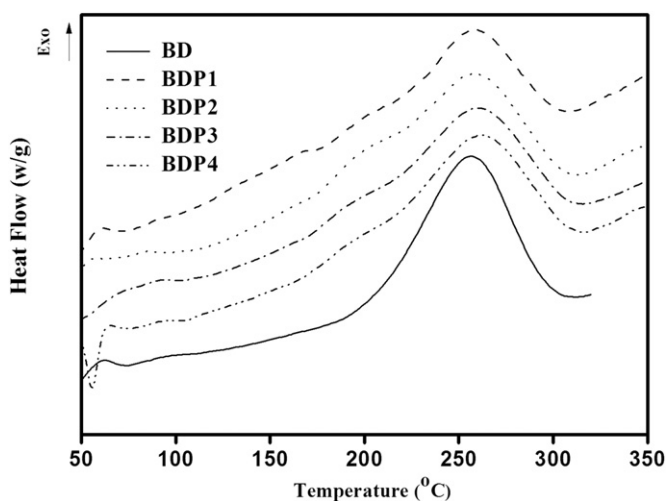
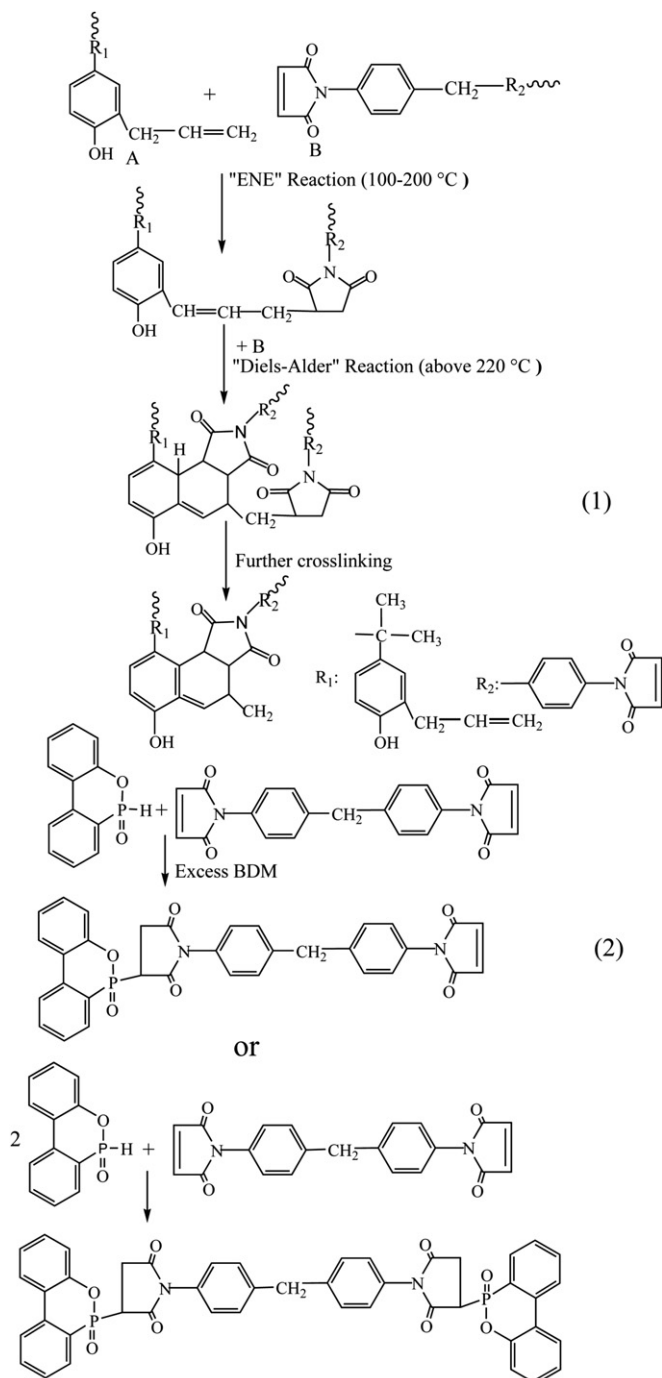
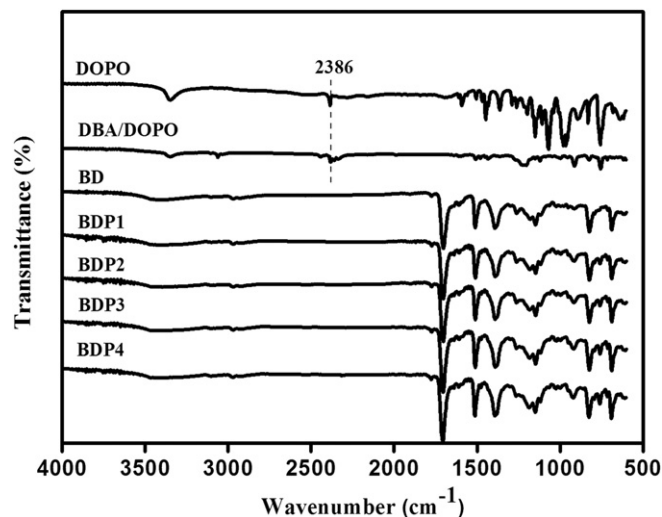


Fig. 1. DSC traces of BD and DOPO/BD prepolymers.



**Scheme 1.** The reaction mechanisms in BD and BDP systems.

Generally, DMA is an effective method for measuring the  $T_g$  value of a thermosetting network. In this paper,  $T_g$  is defined as the peak (maximum) temperature in the  $\tan\delta$ -temperature plot from DMA tests as shown in Fig. 6. It can be observed that the  $T_g$  value slightly shifts toward a lower temperature with increasing the content of phosphorus. This phenomenon may be attributed to the different curing mechanism and thus slightly reduced  $X_{density}$  as discussed above. However, interestingly, when the content of phosphorus exceeds 0.5 wt%, the  $T_g$  value almost does not change. For example, the  $T_g$  value of BDP4 and BDP1 is 260 °C and 271 °C, about 93% and 95% of that of original BD resin, respectively. Note that they are higher than the  $T_g$  value (243 °C) of the phosphorus-containing

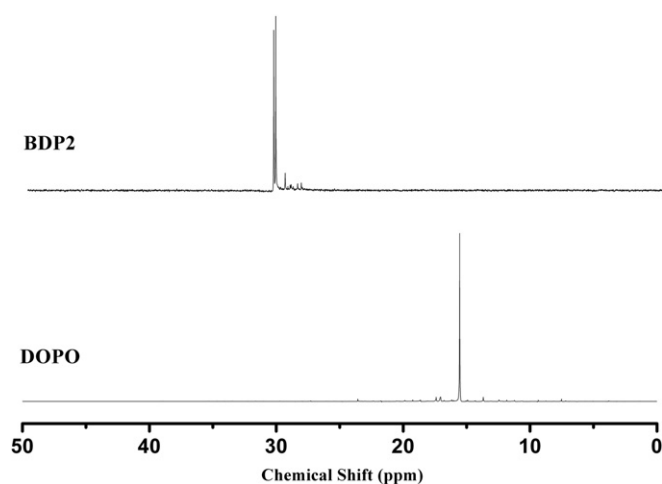


**Fig. 3.** FTIR spectra of DOPO, DBA/DOPO, BD and BDP prepolymers.

bismaleimide (bis-(3-maleimidophenyl) phenylphosphine, BMIP) homopolymer [29]. In other words, the thermal resistance of BDP systems is high enough for cutting-edge applications.

From the view of molecular structure, the intensity of the damping peak reflects the rigidity of materials, and the shape of  $\tan\delta$  peak may be used as a convenient indicator of the morphological state of the material [30]. It can be seen from Fig. 6 that all cured BDP resins have remarkably bigger intensities of  $\tan\delta$  peaks than cured BD resin, implying that the former has decreased rigidity compared with the latter. This result is reasonable because above discussion on the curing behavior and crosslinked structure proves that BDP resins have decreased amount of rigid BDM homopolymer and decreased  $X_{density}$ . According to above reasons, it is expected that the intensity of  $\tan\delta$  peak for BDP system increases with the increase of the content of phosphorus, however BDP4 does not follow this expectation, suggesting that there is another reason which is responsible for this result.

Interestingly, compared with other BDP resins, BDP4 also has obviously different shape of  $\tan\delta$  peak, which consists of a sharp peak and a shoulder in the direction of higher temperature, indicating that BDP4 has obvious multi-phase structure. This phenomenon can be mainly interpreted by the fact that the addition of DOPO to BD resin changes the curing mechanism and further the structure



**Fig. 4.**  $^{31}\text{P}$  NMR spectra of DOPO and BDP2.



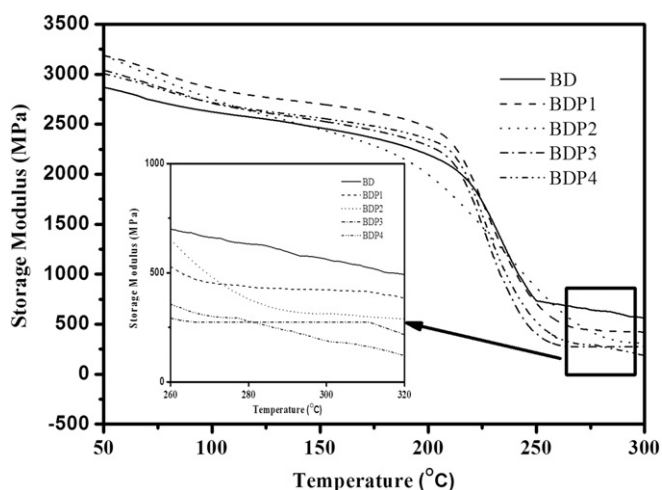


Fig. 5. Dependence of storage modulus on temperature of cured BD and BDP resins.

of cured networks; moreover, this variety is closely related with the content of DOPO. Specifically, when the content of DOPO is small, or the molar ratio of BDM and DOPO is greatly bigger than 1 (for example BDP1, BDP2, and BDP3), the main product of the crosslinked structure results from the “Ene addition” and “Diels–Alder” reactions between BDM and DBA, and thus the phosphorus-containing product is very small. With the increase of the content of DOPO, the molar ratio of BDM and DOPO decreases (for example, BDP4), because the reaction between BDM and DOPO has a priority to occur over that between BDM and DBA, so the amount of phosphorus-containing product increases, and thus the whole crosslinked structure exhibits a multi-phase structure. Therefore, it can be stated that the addition of DOPO to BD resin significantly changes the chemical structure of the resultant network.

### 3.3. Dielectric properties of cured BD and BDP resins

To date, excellent dielectric property (especially low dielectric loss) becomes the first important property of the resins for micro-electric applications, so it is necessary to evaluate the dielectric properties when a new resin is developed for high performance electric materials.

Fig. 7 shows the dielectric constant and loss as a function of frequency for cured BD and BDP resins. All BDP resins exhibit very

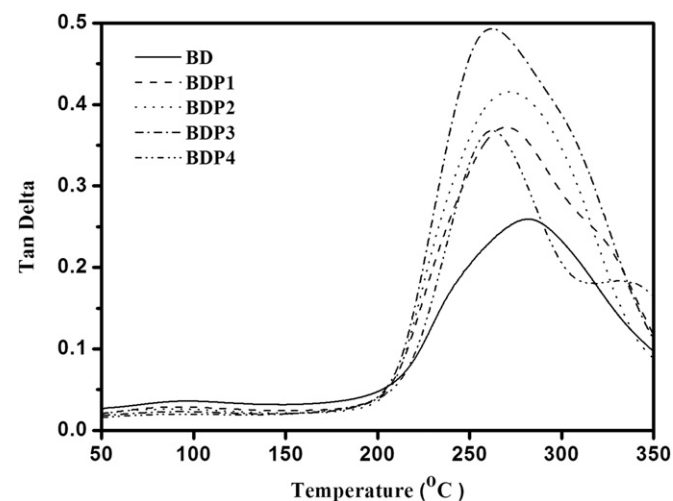


Fig. 6. Overlay curves of  $\tan\delta$  vs. temperature of cured BD and BDP resins.

Table 2

Typical data of  $\tan\delta$  peaks of cured BD and BDP resins.

Resin	$T_g$ (°C)	Intensity	Crosslinking density (mol/cm <sup>3</sup> )
BD	282	0.2593	9160
BDP1	271	0.3769	8920
BDP2	268	0.4170	8469
BDP3	261	0.4986	8319
BDP4	260	0.3763	7753

good stability of dielectric properties over a wide frequency range from  $10^7$  to  $10^9$  Hz as BD resin does. In addition, the former also has significantly lower dielectric constant and loss than the latter. On the other hand, the dielectric properties are greatly dependent on the content of DOPO, which initially increases as the content of DOPO increases, and then almost levels off when the content of DOPO is about 1.0 wt%. For example, the dielectric constant and loss at 1 GHz of BDP4 resin are 2.90 and 0.0058, only about 92% and 51% of that of BD resin, respectively.

According to Clasius–Mosotti equation as shown in Eq. (2) [31], the incorporation of a unit with low molar polarity and big molar volume to a molecule is beneficial to reduce the dielectric constant of the molecule. Interestingly, DOPO has a bulky pendant moiety and non-coplanar structure [32], hence the incorporation of DOPO to BD resin will decrease the dielectric constant. Similar results have been reported by other researchers [33]. On the other hand, in the case of the same chemical structure of a thermosetting resin, the dielectric properties of the resin are also dependent on the crosslinking density because dielectric properties of polymers generally depend on the orientation and relaxation of dipoles, meaning that which is accompanied with the movement of polymer chain segments [34], and thus the crosslinking density. As discussed above, compared with BD resin, BDP resins have decreased crosslinking densities, tending to provide a small restricting influence on the orientation and relaxation of dipoles in the applied electric field, and thus resulting in enlarged dielectric constant and loss. The data shown in Fig. 7 suggest that the effect from the chemical structure of DOPO on the dielectric properties is bigger than that from the reduced crosslinking density.

$$K = \frac{1 + 2(P_m/V_m)}{1 - (P_m/V_m)} \quad (2)$$

where  $P_m$  and  $V_m$  is the molar polarity and molar volume of an atom, respectively.

### 3.4. Flame retardancy and mechanism

The flame retardancy of cured BD and BDP resins is evaluated by UL94 vertical testing, LOI and Cone calorimeter. Table 3 shows the data of UL94 vertical tests. Compared with cured BD resin, all cured BDP resins have significantly decreased burning time, in addition, a much less amount of fume is produced and no dripping appears during the burning of cured BDP resins. Based on UL94 tests, the flame retarding level of cured BD resins is V-1 level; however, when the content of phosphorus increases to only 0.5 wt% (for example BDP1), the flame retardancy of the resultant BDP resin is classified as UL94 V-0. Note that this result is very attractive because generally the content of phosphorus should be larger than 2.5 wt%, the flame retardancy of DOPO-modified epoxies can reach V-0 order [19], indicating that the desirable flame retarding efficiency of cured BDP resins may be attributed to the phosphorus–nitrogen synergistic effect.

The LOI values of cured BD and BDP resins also confirm above statement (Fig. 8). Briefly, all cured BDP resins which have both P and N elements have significantly higher LOI values than cured BD

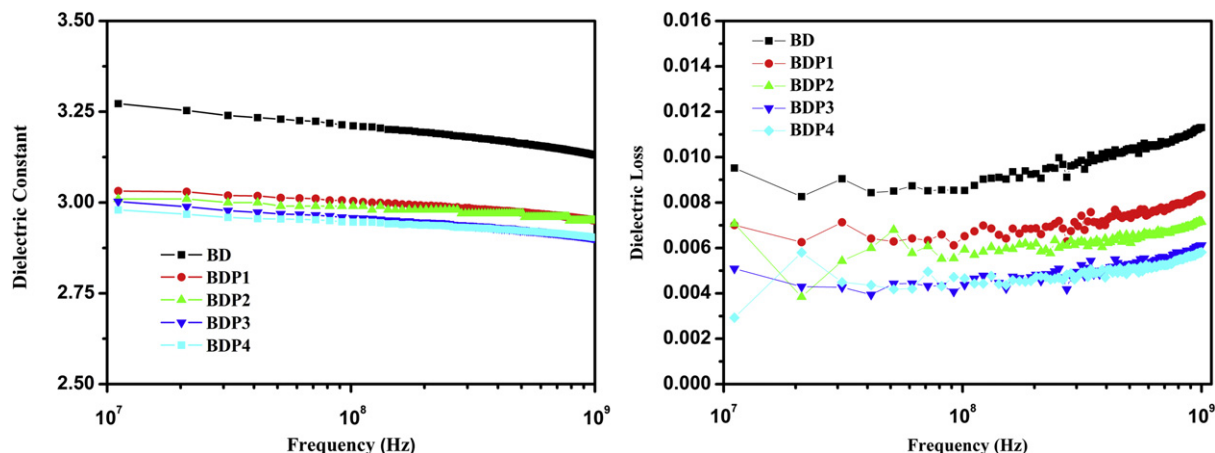


Fig. 7. Dependence of dielectric constant and loss of cured BD and BDP resins over a frequency range of  $10^7$ – $10^9$  Hz.

resin which only has N element, and the larger is the content of DOPO for BDP resins, the bigger is the LOI value. This is further suggested that there is the phosphorus-nitrogen synergistic effect in cured BDP resin.

In order to get more fire characteristic parameters, Cone calorimeter tests were conducted [35]. Fig. 9 shows the overlay curves of the heat release rate (HRR) as a function of time for cured BD and BDP resins, each cured resin shows one peak, but each cured BDP resin has a much narrower and smaller peak of HRR than cured BD resin. Specifically, the total heat release (THR) in Table 3 for BDP1, BDP2, BDP3 or BDP4 is only about 61%, 50%, 54%, or 55% of that of BD resin, respectively, indicating that BDP resins burn very slowly after ignition than BD resin, leading to improved flame retardancy. This statement is also confirmed by the decreased effective heat of combustion (EHC) shown in Table 3, and the mass loss rate (MLR) discussed below.

On the other hand, it can be seen from Fig. 9 that the curves of cured BDP2 and BDP3 resins slightly shift toward left, indicating that cured BDP2 and BDP3 resins are easier to be ignited than cured BDP4 and BD resins, the time to ignition (TTI) shown in Table 3 gives the detail data. However, interestingly, the time of flameout (TOF) values in Table 3 of BDP2, BDP3 and BDP4 resins are obviously lower than that of BD resin, indicating that the modified resins have self-extinguishing feature, which is also attributed to the flame retarding mechanism of BDP system. Specifically, when the material is heated to a temperature, phosphorus segments will decompose and liberate gas; this not only absorbs the heat, but also dilutes combustible gas, and hence endows the modified resins with low HRR and self-extinguishing feature. In other words, these data also indicate that gas-phase flame retarding plays a role in the improved flame retardancy of BDP resins.

**Table 3**  
Typical data of cured BD and BDP resins from cone calorimeter tests.

Resin	BD	BDP1	BDP2	BDP3	BDP4
P content (wt%)	0	0.50	0.80	1.0	1.2
N content (wt%)	5.2	5.0	4.9	4.8	4.7
UL94 Level	V-1	V-0	V-0	V-0	V-0
PHRR ( $\text{kW}/\text{m}^2$ )	452	214	205	191	257
THR ( $\text{MJ}/\text{m}^2$ )	74	45	38	41	42
TTI (s)	193	159	160	158	184
TOF (s)	590	575	510	525	525
SEA ( $\text{m}^2/\text{kg}$ )	859	670	565	490	480
TSR ( $\text{m}^2/\text{m}^2$ )	2743	1050	977	943	935
EHC ( $\text{MJ}/\text{kg}$ )	23.31	22.47	21.69	21.47	19.62
CO/CO <sub>2</sub> (w:w)	0.0307	0.0190	0.0170	0.0148	0.0137

Fig. 10 presents the curves of the mass loss rate (MLR) versus time for cured BD and BDP resins. The maximum peak (PMLR) of BDP resins is significantly lower than that of cured BD resin. For example, the PMLR value of BDP1, BDP2, BDP3 or BDP4 is only about 53%, 51%, 45%, or 73% of that of BD resin, respectively, indicating that the flame retarding mechanism of BDP resins is mainly condensed phase, which will be further discussed in detail later.

However, with careful comparison, the maximum peaks of the HRR and MLR for cured BDP4 resin are slightly higher than those of BDP1, BDP2 and BDP3, this phenomenon *seems* to be unexpected because BDP4 has a larger content of phosphorus element, so which is “expected” to have better flame retardancy (lower peaks of the HRR and MLR). According to the experimental data, some other factors are believed to play the domain role. As discussed above that the crosslinked structure of BDP4 shows multi-phase and lower  $X_{density}$  compared with those of other resins, hence the MLR and HRR values of BDP4 are higher than those of BDP1, BDP2 or BDP3.

It is generally accepted that the smoke and the toxicity released result in more deaths than the fire itself in real fire hazards [36,37]. The specific extinction area (SEA) represents the smoke released, and the weight ratio of CO/CO<sub>2</sub> evaluates the extent of combustion completeness and thus is commonly used to characterize the toxicity of gaseous product of heat decomposition and combustion.

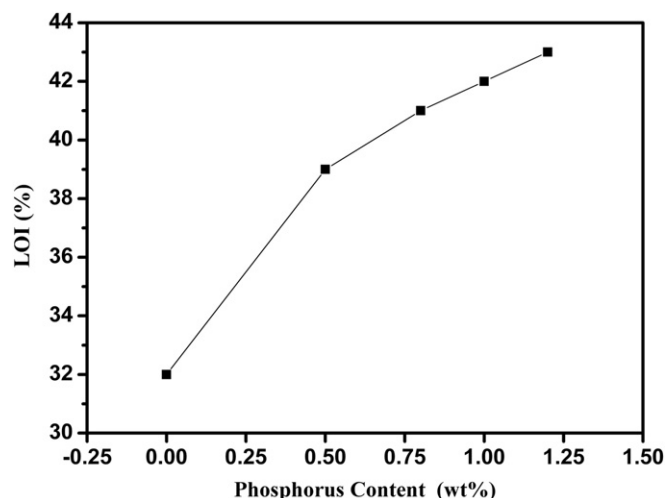


Fig. 8. LOI values of cured resins.

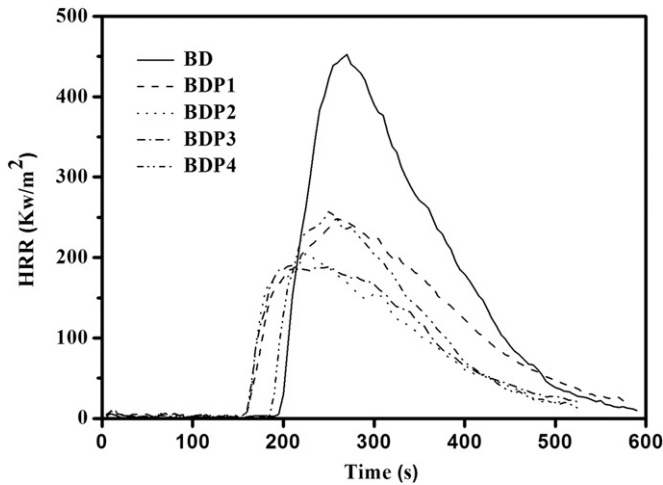


Fig. 9. Overlay curves of heat release rate as a function of time for cured BD and BDP resins.

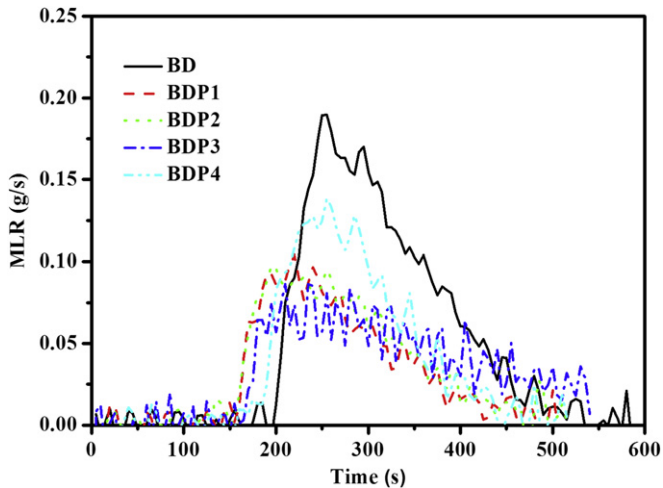


Fig. 10. Overlay curves of mass loss rate as a function of time for cured BD and BDP resins.

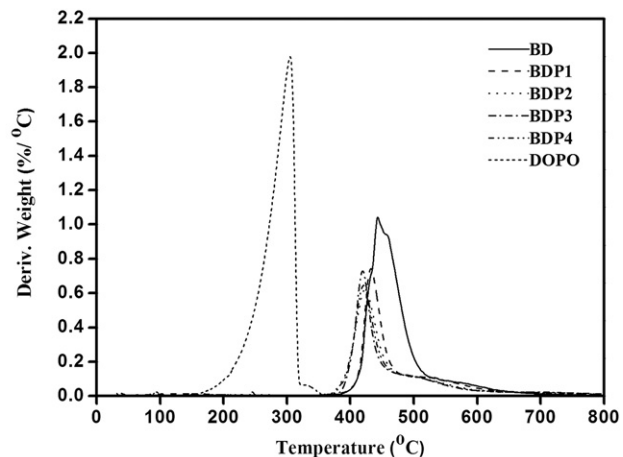
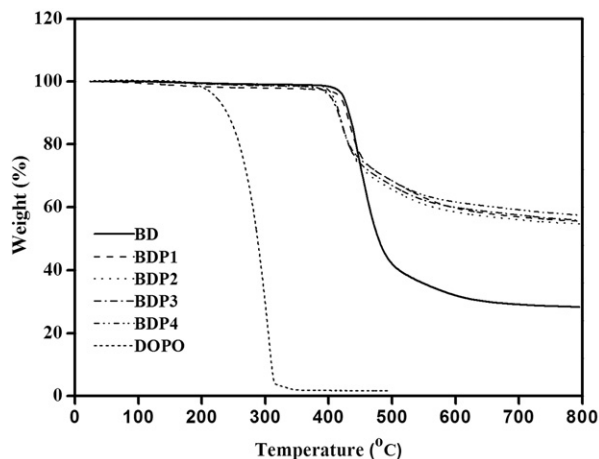


Fig. 11. TG and DTG curves of cured BD and BDP resins.

Table 3 shows that the content of DOPO has a significant effect on the SEA value and the weight ratio of CO/CO<sub>2</sub> for cured BDP resins. In detail, with the addition of DOPO to BD resin, SEA obviously decreases, and reaches the minimum value when the content of DOPO in cured BDP resin is 19.7 wt%, the minimum value of SEA is only about 34% of that for BD resin. On the other hand, the weight ratios of CO/CO<sub>2</sub> for BDP resins are significantly lower than that of cured BD resin, and the weight ratio of CO/CO<sub>2</sub> for BDP1, BDP2, BDP3 or BDP4 resins is only about 61.9%, 55.4%, 48.2%, or 44.6% of that of BD resin, respectively, indicating that BDP resins are much safer materials.

According to UL94, LOI tests and cone calorimeter results, it can be stated that the flame retardancy of BDP resins is significantly improved compared with BD resin.

In order to evaluate the flame retarding mechanism of the BDP system, TG analyses were carried out, and corresponding curves are shown in Fig. 11. The typical data, such as the initial decompose temperature ( $T_{di}$ ), the temperature with the maximum degradation rate ( $T_{max}$ ), and the char yield ( $Y_c$ ) at 800 °C, obtained from these curves are summarized in Table 4. It is interesting to observe that BDP resins have slightly lower  $T_{di}$  and  $T_{max}$  values than BD resin, this is expected from the changed chemical structure and decreased  $X_{density}$  induced by the presence of DOPO as described above; in fact, this is also ascribed to the breaking down of P–C bond [38]. Note that, with the small addition of DOPO to BD resin, the  $Y_c$  dramatically increases from 28.3% to 57.4%, indicating that there is a synergistic effect resulting from the phosphorus-nitrogen effect, which has been reported in many literature [39,40]. The significantly improved  $Y_c$  is very attractive for improving the flame retardancy. It is also in good agreements with the MLR as discussed above. The increased char at high temperature suggests that a condensed phase mechanism is the flame retarding mechanism for BDP system, which will be further confirmed by the morphologies and chemistry of the char.

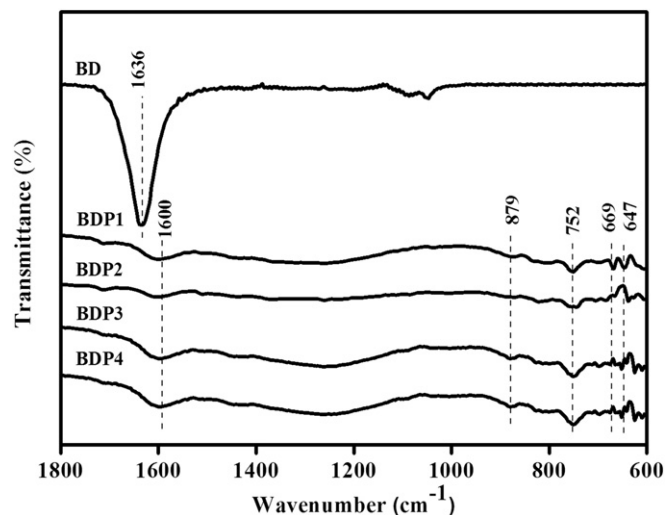
Fig. 12 shows the photographs of the chars collected after the cone calorimeter tests. It can be observed that the char of BD resin is loose and consists of fragile charred layers; however those of BDP resins are compact and hard charred layers. In addition, the chars of original and modified BD resins have different compositions reflected by the FTIR spectra (Fig. 13) and EDS data (Table 5) of these chars. In detail, with regard to the char of BD resin, its FTIR spectrum has a large and strong phenyl absorption peak (1636 cm<sup>-1</sup>), suggesting that the char of BD resin has a considerable amount of phenol groups; while for the char of BDP resin, we can observe the absorption peaks at 1600, 879, 752, 664 and 647 cm<sup>-1</sup>, assigning to

**Table 4**  
Characteristic data from TG analyses of cured BD and BDP resins.

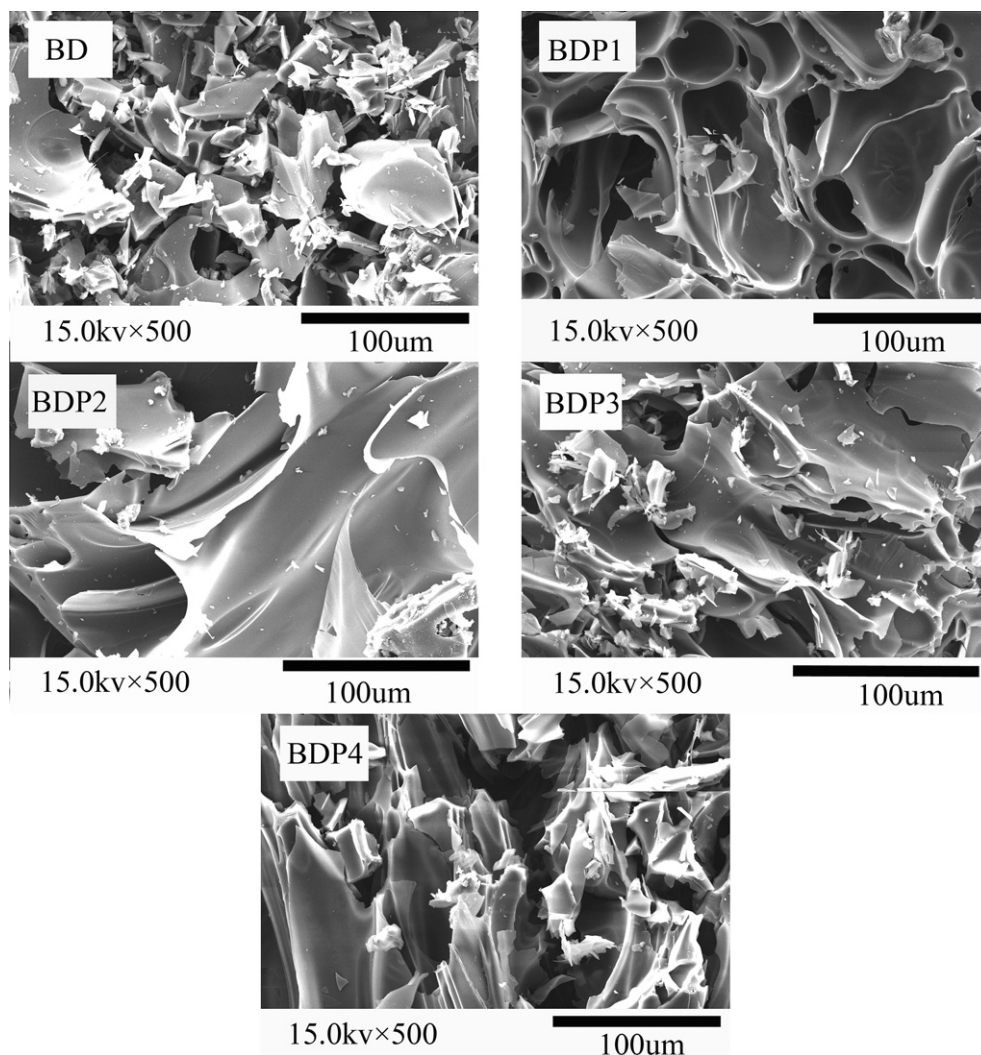
Resin	$T_{di}$ (°C)	$T_{max}$ (°C)	$Y_c$ at 800 °C (wt%)
BD	425	442	28.3
BDP1	418	432	55.6
BDP2	402	423	54.7
BDP3	403	422	55.9
BDP4	404	420	57.4
DOPO	263	305	–

the phenyl, P–O–P, P–O–C, P–N and PO<sub>3</sub> complex structures, respectively. On the other hand, EDS data show that the majority of the content of phosphorus and nitrogen atoms is still retained in the char of each BDP resin, while no nitrogen atom was detected in the char of BD resin, further confirming the existence of the phosphorus-nitrogen synergistic effect, which is the main reason why BDP resin with a very small content of phosphorus can have so outstanding flame retardancy.

From above discussion, it concludes that the flame retardancy mechanism of BDP resins contains both gas phase and condensed phase mechanisms, while the latter plays the main role.



**Fig. 13.** FTIR spectra of chars after cone calorimeter tests for BD and BDP resins.



**Fig. 12.** SEM micrographs of the chars of cured BD and BDP resins.



**Table 5**  
Element compositions of the residual chars for cured BD and BDP resins.

Char		Element composition (wt.%)			
		C	O	P	N
BD	Exterior	90.1	9.9	0	–
	Interior	94.2	5.8	0	–
BDP1	Exterior	87.5	9.0	0.5	3.0
	Interior	91.7	4.0	0.3	4.7
BDP2	Exterior	88.6	8.0	0.6	2.8
	Interior	90.1	5.0	0.5	4.4
BDP3	Exterior	86.4	10.0	0.8	2.8
	Interior	91.2	5.0	0.5	4.3
BDP4	Exterior	90.0	8.4	1.6	2.5
	Interior	90.9	3.4	1.6	4.1

#### 4. Conclusions

A novel low phosphorus-content bismaleimide resin with outstanding flame retardancy and low dielectric loss is developed by the copolymerization of BDM, DBA and DOPO. There is a co-reaction between BDM and DOPO, and the co-reaction has a priority to take place at obviously lower temperature over that between BDM and DBA. The chemical bonding of DOPO in the crosslinked structure endows the resin with obvious phosphorus-nitrogen synergistic effect on the flame retardancy. The main flame retardancy mechanism of BDP resins is evaluated to be condensed phase mechanism. On the other hand, BDP resins exhibit lower dielectric constant and loss than BD resin resulting from the different crosslinked structure induced by the incorporation DOPO to BD resin. This investigation demonstrates that the method proposed herein is a new approach to develop high performance resins with attractive flame retardancy and dielectric properties.

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