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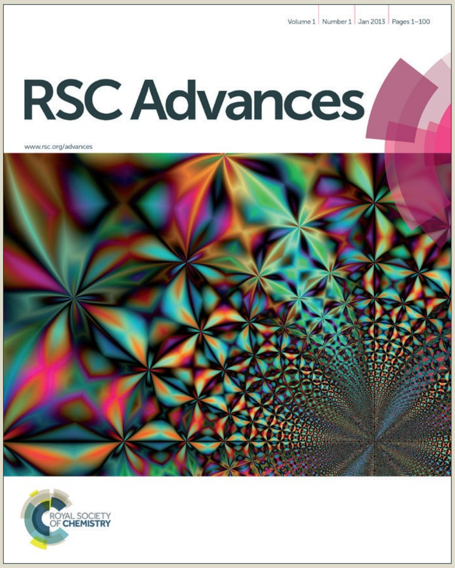

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Synthesis and Characterization of a Phosphorus-containing Flame Retardant with Double Bonds and its Application in Bismaleimide Resins

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Abstract: A novel phosphorus-containing flame retardant, bis (4-(allyloxy)phenyl) phenylphosphonate (APP), is synthesized. The structure of APP is systemically characterized by fourier transform infrared spectrometer (FTIR) and nuclear magnetic resonance spectrometer (^{1}H NMR, ^{13}C NMR and ^{31}P NMR). Subsequently, APP is added into bismaleimides (BMI) resin to prepare flame retardant materials, coded as P-DBMI resin. The effects of APP contents on mechanical properties of P-DBMI resins are studied. Besides, thermogravimetric kinetics, UL-94 tests, limited oxygen index (LOI), scanning electron microscope, residual analysis are investigated to reveal the thermal properties and flame retardancy of P-DBMI resin. The results indicate that P-DBMI resin with good mechanical properties, thermal stability and flame retardancy were obtained simultaneously.

Key Words: Phosphorus-containing, flame retardant, bismaleimide

1. Introduction

In recent years, developing novel high performance resins with more desirable properties has become the hottest subjects of polymer science. Bismaleimides, as representative of thermosetting resin, is widely used in fields of aerospace, aviation and electronics industries [1, 2]. But there are still some disadvantages, such as brittleness, high processing temperatures and flammability, which restrict its development [3, 4]. Hence, most of the research efforts on bismaleimides focused on improving the above-mentioned disadvantages. In our previous investigation, novel bismaleimide composites modified by aligned reduced graphene oxide sheets coated with Fe_3O_4 nanorods [5] and bismaleimide composites modified by hyperbranched polysilane grafted reduced graphene oxide [6] were prepared respectively, both of which exhibit excellent mechanical and tribological properties. Though many investigations about modification of bismaleimides have been reported, methods to enhance their flame retardancy were seldom reported previously. At present, adding flame retardants into polymer is an effective method for preparing flame retarding polymers [7]. So designing and synthesizing high-performance flame retardants for bismaleimides is of high significance in application.

For concerns of environment and human health, halogen-free flame retardants have received considerable attention in recent years, because halogen-containing flame retardants can produce poisonous and corrosive smoke and gases during combustion [8, 9]. Phosphorus-containing flame

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retardant is considered as a kind of promising halogen-free flame retardant due to its advantages of low smoke, low toxicity, low corrosion and good performance, which are very efficient in many polymers [7, 10]. When burning, these phosphorus-based flame retardants can form foamed char layers as protective barriers between flame and the underlying polymer, which results in combustion suppression [11]. However, there are still some drawbacks of phosphorus-containing flame retardants, such as poor matrix compatibility [12, 13]. Fortunately, developing novel reactive flame retardants that can participate the curing reaction of polymer matrix is an effective method to enhance compatibility of flame retardants with polymer matrix.

In this paper, a novel phosphorus-containing reactive flame retardant possessing active double bonds, bis(4-(allyloxy)phenyl)phenylphosphonate (APP), was firtly prepared and incorporated into bismaleimides resin. Because of existence of active double bonds, this novel flame retardant APP can participate in curing reaction of bismaleimide resin, so the compatibility was improved to some extent. While, the addition of phosphorus-based flame retardants into polymers generally cause decrease of mechanical properties of resin [14, 15]. So in this paper, except diallylbisphenol A (DBA)，bisphenol A bisallyl ether (BBE), acting as toughening agent and active diluent [16], were added into the above system to enhance mechanical properties and improve processability. Thereby, novel bismaleimide resin with good mechanical properties, thermal stability and flame retardancy were prepared successfully.

2. Experiments

2.1 Materials

Anhydrous magnesium sulfate, aluminium trichloride and N, N-dimethylaniline were purchased from Tianjin Fuchen Chemical Reagents Factory, China. Phenylphosphonic dichloride was purchased from Jiuding chemical (Shanghai) Technology Co. Ltd., China. 4-methoxyphenol and allyl chloride were purchased Aladdin Reagents (Shanghai) Co. Ltd., China. Sodium carbonate, hydrochloric acid and pyridine were purchased from Tianjin Fuyu Fine Chemistry Co. Ltd., China. 4, 4’-bismaleimidophenylmethane (BDM) was purchased from Hubei Fengguang Chemical Factory, Chian. Diallyl bisphenol A (DBA) was purchased from Laizhou Hualu accumulator Co. Ltd., China. Bisphenol A bisallyl ether (BBE) was purchased from Tianjin Jinbei Fine Chemistry Co. Ltd., China. Other reagents were commercial products of analytical grade and were used without further treatment.

2.2 Synthesis of Bis(4-methoxyphenyl)phenylphosphonate (MPP)

Phenylphosphonic dichloride (4.97 g, 2.5×10^{-2} mol), 4-methoxyphenol (7.67 g, 6.2×10^{-2} mol) and 50 ml dichloromethane were blended in a 250 ml three-necked flask equipped with a mechanical stirrer and a reflux condenser. After phenylphosphonic dichloride and 4-methoxyphenol were completely dissolved, 8.5 ml pyridine was added dropwise to the system for approximately 15 min. The system was allowed to further react at 25 ^{o}C for 14 h. The pH value of the resulting solution was adjusted to

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8-10 using solution of sodium carbonate. And the mixture was stirred for an additional 1h at ambient temperature. The solution of raw products was obtained after collecting organic phase via separating funnel. Next, the solvent was removed by rotary evaporator under reduced pressure. In virtue of recrystallization, pure MPP as white crystalline solid was obtained eventually.

FTIR (KBr, cm^{-1}): 1300 and 1260 (P=O), 1190 and 935 (P-O-C), 1035 (C-O-C). ^1H NMR (400 MHz, $CDCl_3$, ppm): 3.75 (s, 6H, $-O-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): 55.6 (s, 2C, $-O-CH_3$)

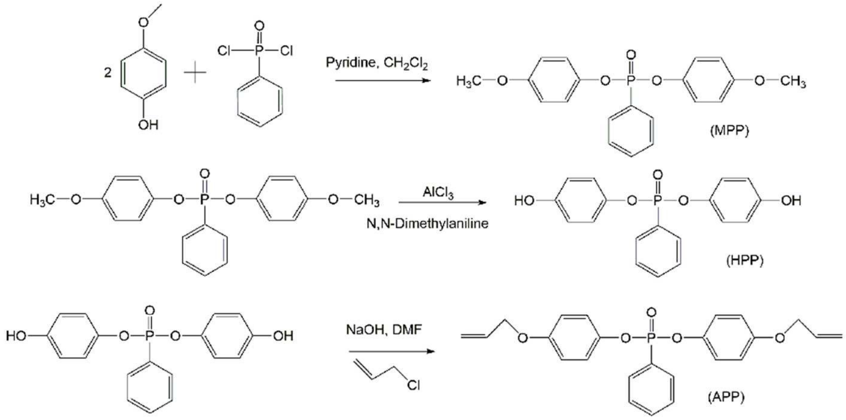
2.3 Synthesis of Bis(4-hydroxyphenyl)phenylphosphonate (HPP)

The above synthesized MPP (3.39 g, 9.2×10^{-3} mol) and 50 ml dry methylbenzene were charged into a 250ml three-necked flask equipped with a mechanical stirrer and a reflux condenser. After MPP was completely dissolved, $AlCl_3$ (6.86 g, 5.1×10^{-2} mol) was added into the above system. Then N, N-dimethylaniline (4.88 ml, 3.8×10^{-2} mol) was added dropwise to the system with the solution boiling. After 6 h further reaction, liquid was removed and the solid adhering to surface of three-neck flask was reserved. Then hydrochloric acid solution was charged into the three-neck flask. After cooling, the mixture was extracted with ethyl acetate and the organic phase was dried with sodium sulphate. At last, the solvent was removed by rotary evaporator under reduced pressure. Pure HPP, light brown crystalline solid, would be obtained by recrystallization operation.

FTIR (KBr, cm^{-1}): 3330 (-OH). ^1H NMR (400 MHz, DMSO-d_6, ppm): 9.42 (s, 2H, -OH).

2.4 Synthesis of Bis(4-(allyloxy)phenyl)phenylphosphonate (APP)

The above synthesized HPP (0.2 g, 5.85×10^{-4} mol) was dissolved into N, N-dimethylformamide with stirring in a 250 ml three-necked flask. After APP dissolved completely, sodium hydroxide (0.13 g, 3.25×10^{-3} mol) was added into the above system followed by stirring for 2 h at 30 ^{o}C. Subsequently, allyl chloride (0.24 ml, 4.4×10^{-3} mol) was mixed into the above system. The temperature of reaction mixture was maintained at 105 ^{o}C for 6 h. Deionized water and ethyl acetate were added to extract product into ethyl acetate. After the solvent was evaporated off under vacuum, the desired product as pale yellow liquid was obtained (Scheme 1 shows the synthesis route of APP.).



Scheme 1 synthetic route of APP

2.5 Preparation of P-DBMI resins

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DBA (25g), BBE (5g) and BDM (40g) were mixed homogeneously in a 150ml beaker. Then APP were added to the above system at 140 °C with stirring for 30 min. After getting rid of bubbles by a vacuum drying oven, the reaction mixtures were cured at 180 °C, 200 °C and 240 °C for 2 h respectively, and post cured at 250 °C for 4 h. Then P-DBMI resins were successfully prepared (Table 1).

Table 1 The content of APP in P-DBMI resins.

Sample Code	Formulation (wt %)	
	APP Content	P-loading
DBMI	0.0	0.000
2.0wt%-P-DBMI	2.0	0.159
4.0wt%-P-DBMI	4.0	0.318
6.0wt%-P-DBMI	6.0	0.477
8.0wt%-P-DBMI	8.0	0.636

2.6 Measurements

Fourier-transform infrared spectra (FTIR) were recorded on PberkinElmer-283B FT-IR Spectrometer. The samples were pressed into a pellet with KBr and scanned from 400-4000cm^{-1}.

^{1}H NMR, ^{13}C NMR and ^{31}P NMR spectra were recorded with an AVANCE 400 Bruker spectrometer using $CDCl_3$ or DMSO-d_6 as a solvent.

Impact strength and flexural strength were obtained according to GB/T2571-1981. In each system, more than 5 specimens were tested.

TG analyses were performed using TGAQ50 at a heating rate of 20 °C·min^{-1} in nitrogen atmosphere from 40 °C to 800 °C

The flammability of all the samples was determined using the vertical test according to the UL-94 standard (sample size is 127 × 12.7 × 3.6 mm^3) and limited oxygen index (LOI) values measurement by a Stanton Redcraft Flame Meter (UK) according to ASTM D2863/77 (sample size is 100 × 6.5 × 3 mm^3).

The surface morphologies of samples were observed using a scanning electronic microscope (SEM, Hitachi S-570). The samples were sputter coated with a thin layer (about 10 nm) of gold.

A sample (10.0mm×10.0mm×3.6mm) was put on the central place of the heating platform in a muffle furnace and maintained at 600 °C for 5 min. Then FTIR spectra and element analysis of external char layer were recorded.

3. Results and discussion

3.1 Characterization of APP

The chemical structure of APP was characterized with FTIR, ^{1}H ^{13}C and ^{31}P NMR. Figure 1

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presents the FTIR spectrum of APP. The absorption band at about 3080 cm^{-1} corresponds to vibration of benzene ring, and the peaks at 2900 cm^{-1} and 2860 cm^{-1} are assigned to =C-H, -C-H stretching band. The three absorption bands at about 1647 cm^{-1}, 1600 cm^{-1} and 1500 cm^{-1} correspond to the skeleton vibration of benzene ring. The absorption band at about 1450 cm^{-1} corresponds to vibration of P-C. The sharp bonds at 1268 cm^{-1} is attributed to C-O-C. The absorption bands at 1180 cm^{-1} are for P=O. The absorptions at 935 cm^{-1} and 834 cm^{-1} are assigned to stretching vibration and flexural vibration of P-O-C, respectively. It initially demonstrated that APP was synthesized successfully.

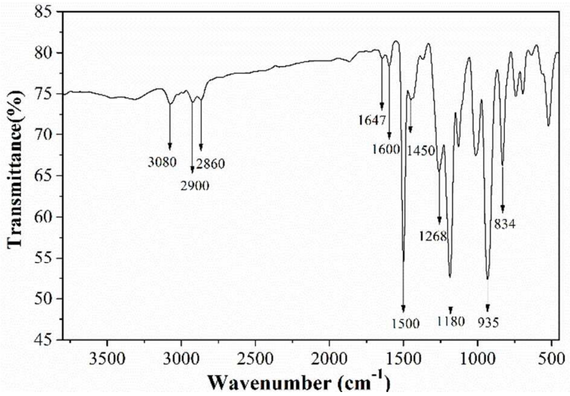

Figure 1 FTIR spectrum of APP.

In order to study the structure of APP further, ^{1}H NMR, ^{13}C NMR and ^{31}P NMR were employed. Figure 2 and Figure 3 illustrate the ^{1}H NMR and ^{13}C NMR spectra of APP, respectively. Compared with ^{1}H NMR spectrum of HPP, the chemical shifts attributing to the protons of allyl (6.00 ppm, 5.37 ppm, 5.25 ppm and 4.45 ppm) appear in the ^{1}H NMR spectrum of APP, and the signal of HO-Ph at 9.42 ppm disappears. Similarly, the peaks at 133.05 ppm, 115.53 ppm and 69.14 ppm in ^{13}C NMR spectrum support the existence of allyl. In order to confirm the symmetric molecular structure, ^{31}P NMR spectrum was recorded (Figure 4). One sharp signal is observed at 12.29 ppm. The results indicate that the target product has been synthesized successfully.

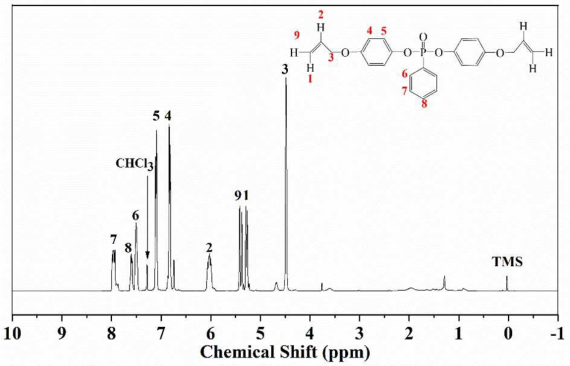

Figure 2 ^{1}H NMR spectrum of APP.

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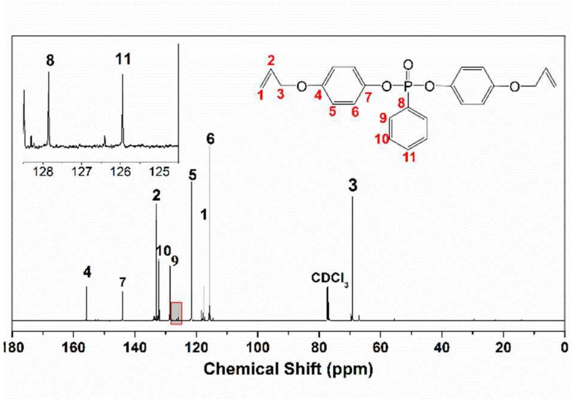

Figure 3 ^{13}C NMR spectrum of APP.

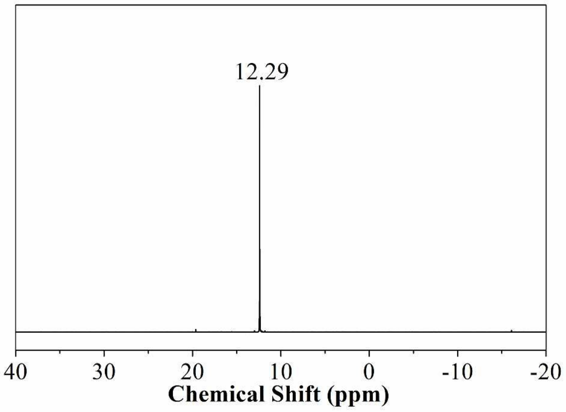

Figure 4 ^{31}P NMR spectrum of APP.

3.2 Mechanical properties of P-DBMI resins

The data for the tensile strength (a) and impact strength (b) of P-DBMI resins were obtained from the universal tensile and impact testing machine controlled by computer. The results of flexural strength and impact strength are shown in Figure 5. It can be seen that the incorporation of APP gives slight reduction to both flexural strength and impact strength of DBMI resin. In details, the flexural strength and impact strength of P-DBMI resin with 8.0 wt% of APP decrease 13.6% and 20.4% compared with DBMI resin, respectively. As is known, the phosphorus-containing flame retardant at high content usually cause a negative influence on the mechanical properties of the polymer matrix [14, 17]. Compared with previous reports [6, 18] that the flexural and impact strength of the common BDM resin are about 125-135 MPa and 11.5-13.5 kJ/m^2 respectively, those of P-DBMI resin are still much higher. It can be attributed to the following reasons: (1) the synthesized APP, like DBA [19], maybe react with BDM (as shown in Scheme 2), which enhanced compatibility of APP with bismaleimide resin to some extent. (2) In P-DBMI resin, BBE was incorporated as active dilute and toughing agent. At low temperature, BBE can decrease viscosity of system, and thus dispersion of APP improved. Besides, at high temperature, it can rearranged into DBA, which can enhance toughness of DBMI resin greatly [16].

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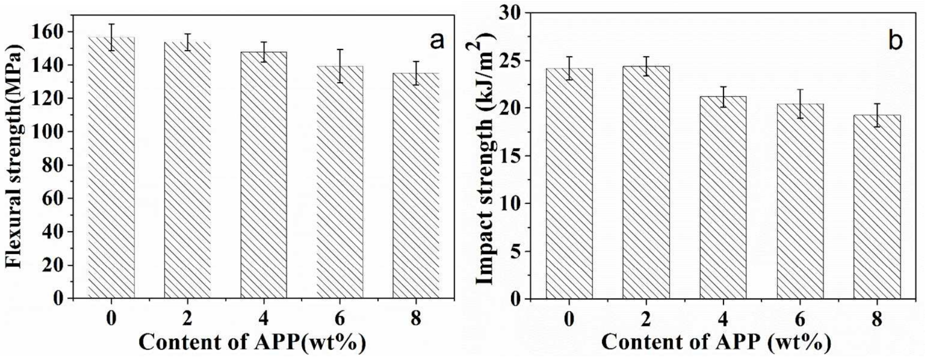
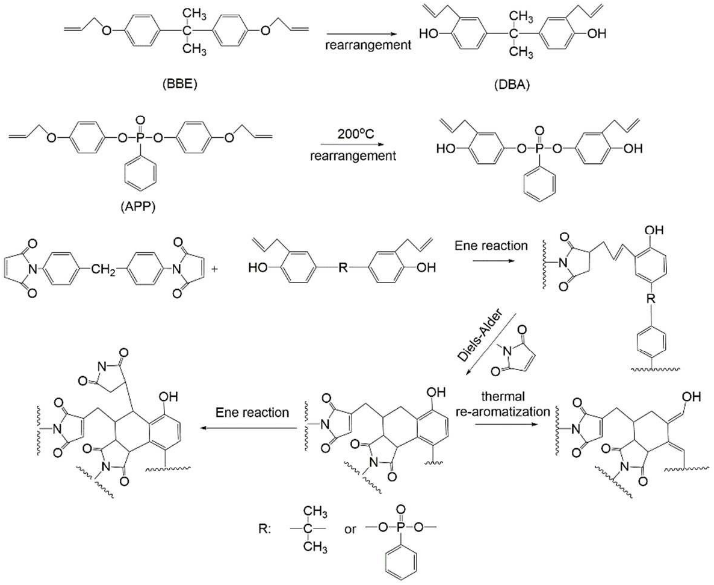


Figure 5 Dependence of the content of APP on the flexural strength (a) and impact strength (b) of DBMI resin.



Scheme 2 The curing reaction of P-DBMI resins.

3.3 Thermal property of P-DBMI resins

TGA is an effective method to characterize the thermal property of materials. Figure 6 shows TG and DTG curves of DBMI and 4.0 wt%-P-DBMI resins under N_2 atmosphere. The temperature of initial decomposition ($T_{initial}$), the temperature of 5 wt % weight loss ($T_{d,\ 5\%}$), the midpoint temperature of degradation ($T_{d,\ 50\%}$), the maximum degradation rate temperature (T_{max}), and the fraction of char residue at 800 ^{o}C were obtained from the TGA curves. And all of these data are presented in Table 1.

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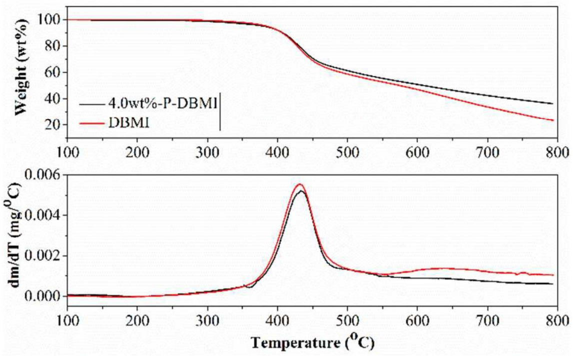

Figure 6 TG and DTG curves of cured of neat DBMI and 4.0 wt%-P-DBMI resins under N_2 atmosphere.

From the Table 2, we can found that both $T_{d,\ 50\%}$ and char residual at 800 °C of 4.0wt%-P-DBMI are much higher than those of DBMI resin. This reason was probably that the phosphorous-containing flame retardant-APP-can accelerate the formation of char layer on surface of polymer, which can prevent the inner part of resin from degradation. Some researchers [20] have reported that a thick charred layer is a good thermal barrier that can delay and prevent the thermal degradation of the resin; therefore, a high char residue will give the resin system excellent flame-retardant properties.

Table 2 TGA Data for the Samples in Nitrogen.

Sample Code	**$T_{initial}$ (°C)**	**$T_{d,5\%}$ (°C)**	**$T_{d,50\%}$ (°C)**	**T_{max} (°C)**	**Char residue at 800 °C (%)**
DBMI	399	381.6	576.1	432.5	23.48
4.0 wt%-P-DBMI	395	381.3	611.0	436.1	36.45

3.4 Flame retardancy of P-DBMI resins

UL-94 test and LOI is often used to evaluate the flame retardancy of BDM resin. And the results are given in Table 3 for all of the investigated samples. It can be seen that the UL-94 rating of DBMI resin is V-1 indicating that the DBMI resin possesses a certain degree of flame retardancy. This can be attributed to that nitrogen in DBMI resin can produce nonflammable gases during burning, which can dilute flammable gases supporting combustion and thereby suppress combustion. From Table 3, we can see that the duration of flaming gets much shorter with increase of APP content, which suggests that APP had good flame retarding effect on DBMI resin. With the addition of 8.0 wt% APP, the UL-94 rating of DBMI resin improved from V-1 to V-0. Besides, as APP is incorporated, the LOI value increases from 26.5 to 34.7. It is generally acknowledged that when the LOI is below 22%, the materials can burn in air. The LOI of pristine DBMI resin is 26.3, which also indicates that DBMI resin possesses a certain degree of flame retardancy.

Table 3 Results of UL-94 tests and LOI of the investigated formulations.

Sample Code	**t_{max} (s)^a**	**t (s)^b**	**Dripping**	**UL-94 rating**	**LOI**

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DBMI	29.2	201.5	No	V-1	26.3
2.0wt%-P-DBMI	20.7	150.3	No	V-1	28.4
4.0wt%-P-DBMI	15.8	120.7	No	V-1	31.2
6.0wt%-P-DBMI	9.0	87.9	No	V-1	32.8
8.0wt%-P-DBMI	6.5	37.6	No	V-0	34.7

a Maximum of combustion time.

b Total combustion time of 10 times

It is known that compact and thick char layer can prevent resin from contact with flame and release of combustible gases. And thereby flame retardancy of resin can be improved greatly. So it's necessary to investigate the morphology of char residual. The photographs of DBMI (A) and 8.0wt%-P-DBMI (B) after being maintained at 600 °C for 5 min in a muffle furnace are shown in Figure 7. It can be seen that 8.0wt%-P-DBMI resin can retain its shape after being maintained at 600 °C, but DBMI resin cannot. Besides, the char layer of DBMI is thin and intumescent, and that of 8.0wt%-P-DBMI is thick and compact. Acting as an excellent barrier of mass transport and thermal insulation, these compact charred layers can protect the underlying materials from further burning and retain its shape during combustion. SEM micrographs of the residual chars for external structure of DBMI and 8.0wt%-P-DBMI (Figure 7a, 7b) verify the above speculation. The internal structure of 8.0wt%-P-DBMI residual (Figure 7c) distributes uniform holes resulting from wrapping gases produced during decomposition of resin under external char layer, for which combustible gases can't be released to support combustion.

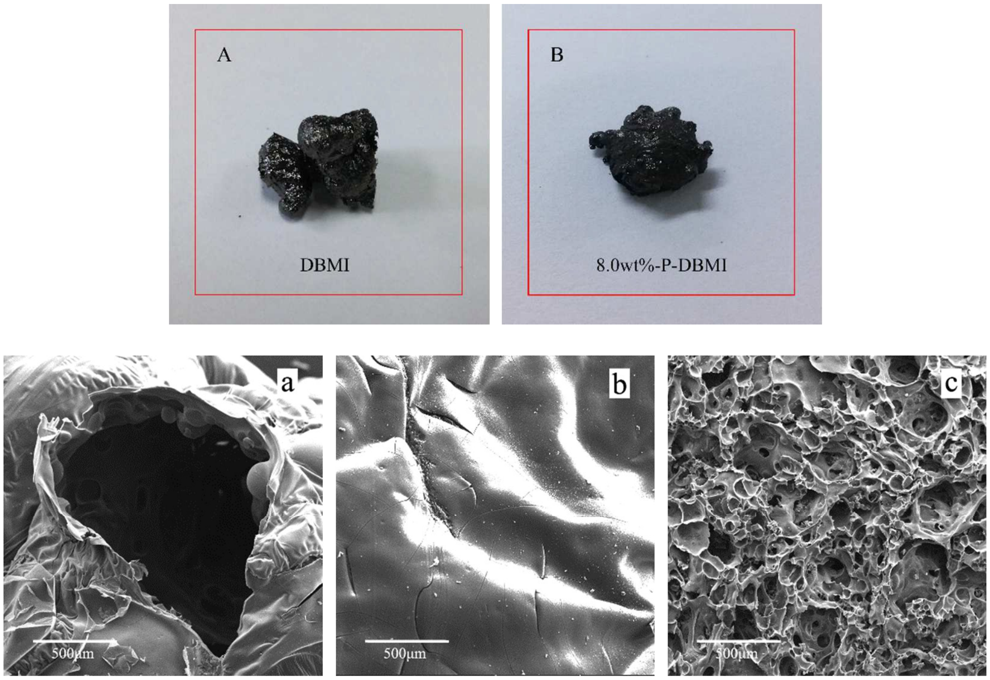

Figure 7 Photographs of DBMI resin (A) and 8.0wt%-P-DBMI resin (B) after being maintained at 600

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°C for 5 min, and SEM micrographs of external char structure of DBMI resin (a), external and internal char structures of 8.0wt%-P-DBMI resin (b, c).

In order to make it clear that how compact and thick char layer can be developed, the composition of external char was investigated. Figure 8 shows FTIR spectra of DBMI (a) and 8.0wt%-P-DBMI (b) external chars degraded at 600 °C in muffle furnace for 5 min. Except -CH_3 (2962 cm^{-1}), -CH_2- (2924 cm^{-1}), -CH- (2853 cm^{-1}), C-N (1383 cm^{-1}), C-O-C (1090 cm^{-1}), many peaks attributing to organic groups have vanished in both of the spectra, which resulted from the decomposition of resin. Besides characteristic absorptions of the above organic bonds appearing in FTIR spectrum of DBMI, there are also absorptions reflecting P-N (1040 cm^{-1}), P-O-C (1002 cm^{-1}) and P-O (933 cm^{-1}) in FTIR spectrum of 8.0wt%-P-DBMI [3, 21]. But on account of the porous structure of char residual, water produced during decomposition of resin is wrapped easily in residual. So the strong absorptions at about 3453 cm^{-1} and 1638 cm^{-1} attributed to stretching vibration band and bending vibration band of H-O-H arose. Char formation is generally companied by generation of water. The water generated will evaporate for high temperature and thereby bring down ambient temperature. Simultaneously, water vapor can also dilute combustible gases supporting combustion. Therefore, water wrapped in char layer contributes to combustion suppression.

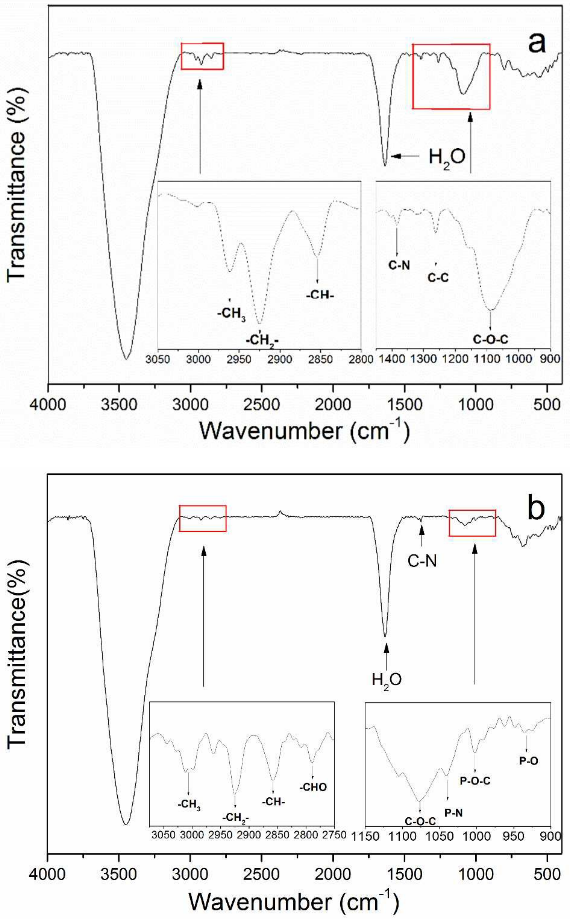

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Figure 8 FTIR spectra of DBMI (a) and 8.0wt%-P-DBMI (b) external chars degraded at 600 °C for 5 min.

In addition, the elemental analysis results of DBMI and 8.0wt%-P-DBMI external residue after retaining at 600 ^{o}C for 5 min are summarized in Table 4. Compared with phosphorus content of DBMI resin shown in Table 1, the char layer of 8.0wt%-P-DBMI resin contains much higher phosphorus content, suggesting that phosphorus was enriched in condensed phase during combustion [22]. On the other hand, the results of elemental analysis show that the content of oxygen and nitrogen in char residual of 8.0wt%-P-DBMI are both higher than those of DBMI, which can be attributed to generation of P-O-P, P-O-C, P-N bonds during the combustion [23]. According to results of FTIR spectra and element analysis, phosphorus can migrate towards surface of resin during burning and promote formation of compact and thick char layer to suppress combustion.

Table 4 Element compositions of DBMI and 8.0 wt%-P-DBMI external residue after retaining at 600 ^{o}C for 5 min.

Samples	C	O	N	P
DBMI	86.44	10.69	2.87	0.00
8.0wt%-P-DBMI	81.72	12.17	3.91	2.20

All the above evidences demonstrate that the flame retardancy of DBMI was enhanced greatly for the incorporation of APP, which can migrate towards the surface of resin and promote formation of compact and thick char layer.

4 Conclusion

A novel phosphorus-containing flame retardanct with active double bonds APP was successfully synthesized. A new kind of flame-retardant bismaleimide resin with APP (P-DBMI resin) exhibits significantly improved mechanical properties, thermal stability as well as flame retardancy. The impact and flexural strength of P-DBMI resin enhanced greatly for synergistic effect of BBE and DBA. The char residue at 800 ^{o}C of 4.0wt%-P-DBMI resin is 55.24% higher than that of DBMI resin, while thermal decomposition rate of 4.0wt%-P-DBMI resin is much lower than that of DBMI resin. When the content of phosphorus is as low as 0.64 wt%, the UL-94 rating of P-DBMI can reach V-0 and LOI is 34.7. Furthermore, SEM micrographs, FTIR spectra and elemental analysis of residues revealed the flame-retardant mechanism that phosphorus can enrich in condensed phase during combustion and promote formation of thick and porous char layer, which can act as an excellent barrier of mass transport and thermal insulation.

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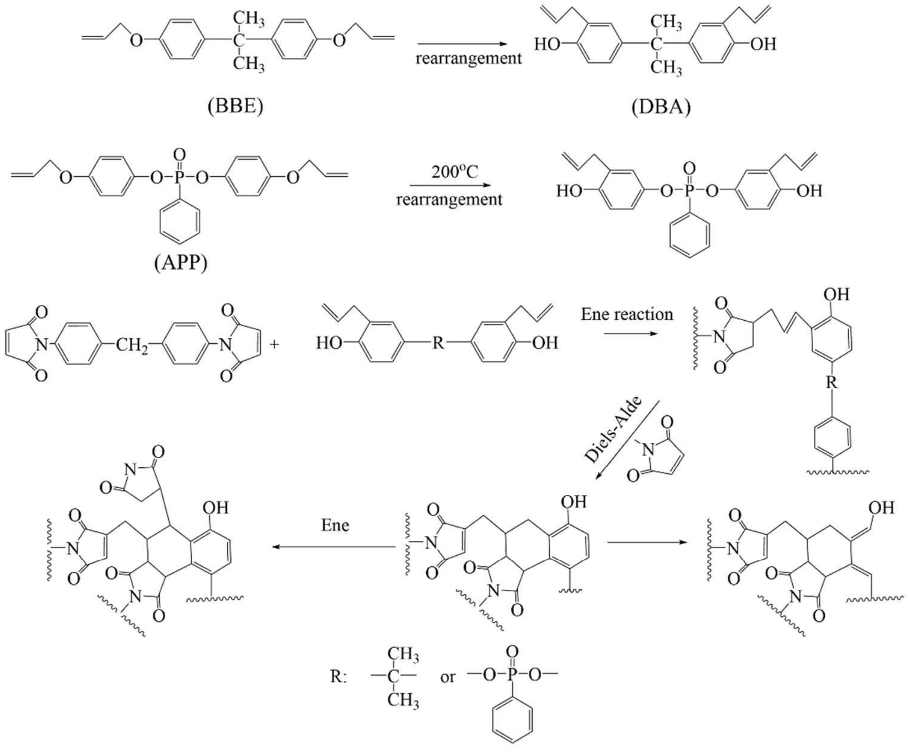
Graphical Abstract



A novel phosphorus-containing flame retardant with double bonds was synthesized and incorporated into bismaleimide resin subsequently. According to investigation, the modified bismaleimide resin has good mechanical properties, thermal stability and flame retardancy simultaneously.

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