A novel branched phosphorus-containing flame retardant: synthesis and its application

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Abstract. A novel branched polyphosphonate flame retardant (BPDD) has been synthesized through melt polycondensation and end-capping reaction. The chemical structure of BPDD was characterized by fourier transform infrared (FTIR) spectra and nuclear magnetic resonance (NMR) spectra. The test results of the vertical burning test (UL-94), limiting oxygen index (LOI) and cone calorimeter (CONE) measurements reveal that BPDD can effectively enhance flame-retardant properties of EP. The LOI values of EP/BPDD composites increased from 23.9 % of pure EP to 33.6% and UL-94 V-0 was obtained with the 20 wt% BPDD loading. Besides, the peak heat release rate (PHRR) and total heat release (THR) of EP/BPDD composites were reduced significantly compared with the pure EP. When 20 wt% BPDD was incorporated, the PHRR and THR were decreased 66.2 % and 37.3%, respectively. The comprehensive test results shows that the improvement of flame retardancy of the EP/BPDD composites was attributed to the synergistic action of the condensed phase and gas phases.

1. Introduction
Epoyx resins (EP) is a type of typical thermosetting resins. It is widely used in adhesives, composites and electronic packaging material owing to its outstanding adhesive, mechanical and electrical properties[1-3]. However, epoxy resins perform very poorly in a fire, most of them burn easily and violently, which limits its application in some fields where rigorously flame-retardant grade is needed[4]. As a result, much effort has been made to improve the flame-retardant properties of EP[5].

Traditionally, halogen-containing compounds in conjunction with antimony oxide was considered to be the high-performance flame retardant additives to overcome the flammability of EP [4]. However, those halogen-containing flame-retardant systems are often accompanied by a release of toxic, potentially carcinogenic brominated furans and dioxins during combustion[6]. Thus, halogen-containing flame-retardant was banned by European regulations.

In this article, a halogen-free and eco-friendly flame retardant of branched polyphosphonate (BPDD) was synthesis by the melt polymerization, its molecular structure was confirmed by FTIR and 1H NMR tests. BPDD was incorporated into EP and cured by m-phenylenediamine (m-PDA) to prepare EP/BPDD composites, the thermal properties and fire behaviour of EP/BPDD composites were investigate in detail.
2. Experimental

2.1. Materials
Phosphorus oxychloride and 4,4-Dihydroxybenzophenone (DHBP) were supplied by Shanghai Aladdin Bio-Chef Technology Co., Ltd. DOPO, aniline, m-PDA, ethanol and acetone were supplied by Sinopharm Chemical Reagents Beijing Co., Ltd. Epoxy resin (DGEBA, E-44, epoxy value = 0.44 mol/100g) was purchased from Sinopec Baling Company (Zhengzhou, China). Phosphorus oxychloride and aniline were purified before use.

2.2. Synthesis of DOPO-PhOH
As shown in Scheme 1, DOPO-PhOH was synthesized by the method according to a published procedure [7].

![Figure 1. Synthetic route of DOPO-PhOH](image)

2.3. Synthesis of branched polyphosphonate (BPDD)
As shown in Scheme 2, the preparation process of BPDD was divided into two steps. Firstly, DOPO-PhOH (0.15mol) and phosphorus oxychloride (0.10mol) were mixed in a 250 mL round-bottom glass flask equipped with a mechanical stirrer and a temperature controller. The temperature of the reaction mixture was increased to 180 °C and keep reaction to no HCl gas was emitted (approximately 2h). When the reaction system temperature drops to 50°C, a mixture of aniline (0.02mol) and 100 mL of acetone was added dropwise into the round-bottom glass flask. After 1h, the brown solid was obtained.

![Figure 2. Synthetic route of BPDD](image)

2.4. Preparation of the pure EP and EP/BPDD composites
BPDD was grinding to more than 300 mesh size and dried under vacuum at 100°C for 2h before using. The EP, m-PDA and BPDD were mixed with a mechanical stirrer at 80°C for 10 min according to the formulas presented in Table 1. Then the mixture was poured into the molds and cured in oven.

| Sample | DGEBA (g) | m-PDA (g) | BPDD (g) | BPDD (wt.%) | LOI (%) | UL-94 |
|--------|-----------|-----------|-----------|-------------|---------|-------|
| EP     | 100.0     | 50.0      | 0         | 0           | 23.9    | -     |
| EP-1   | 100.0     | 50.0      | 7.90      | 5.0         | 28.1    | V-2   |
| EP-2   | 100.0     | 50.0      | 16.66     | 10.0        | 30.4    | V-1   |
| EP-3   | 100.0     | 50.0      | 26.48     | 15.0        | 32.7    | V-1   |
| EP-4   | 100.0     | 50.0      | 37.50     | 20.0        | 33.6    | V-0   |
2.5. Characterization
The chemical structure of PDDP was characterized by FTIR and NMR. The flame-retardant performance of EP/BPDD was evaluated by UL-94, LOI, and CONE test.

3. Results and discussion

3.1. Structural characterizations of BPDD
The chemical structure of BPDD was characterized by FTIR and ¹H NMR. Figure 3 shows FTIR spectra of the BPDD. The characteristic bands at 3430 cm⁻¹ is assigned to the O−H and N−H, the bands at 3062, 1593 and 1485 cm⁻¹ are assigned to the benzene ring. The bands at 1203 and 947 cm⁻¹ are assigned to the P=O and P-O-C, respectively [8-10]. Figure 4 shows ¹H NMR spectra of the BPDD, the characteristic bands between 6.63 ppm and 8.31 ppm correspond to the protons of benzene ring. The characteristic bands at 5.71 ppm correspond to the protons of ph-N(H)-P. Therefore, the chemical structure of BPDD was verified.

Figure 3. FTIR spectra of BPDD
Figure 4. ¹H NMR spectra of BPDD

3.2. Flame-retardant properties of EP/BPDD composites

3.2.1. LOI and UL-94 tests.
The flame-retardant properties of EP/BPDD composites were evaluated by LOI and UL-94 tests. The test results are listed in Table 1. As shown in Table 1, the pure EP burns very easily, with a low LOI value of 23.9% and a no rating in the UL-94 test. When flame retardant of BPDD was incorporated, the LOI values and UL-94 level of EP/BPDD composites increased obviously. When 20 wt% BPDD was incorporated, the LOI value increased to 33.6% and the UL-94 tests increased to V-0 level. These results reveal that BPDD can effectively improve the flame retardant performance of EP.

3.2.2. Cone calorimetry test. The Cone calorimetry (CONE) was used to further investigate the flame-retardancy performance of pure EP and EP/BPDD composites. Many important parameters, including heat release rate (HRR), total heat release (THR), time to ignition (TTI) and char yield (CY) were obtained from CONE test. The detailed experimental parameters of pure EP, EP-2 and EP-4 are summarized in table 2.

Table 2. Cone calorimetry test parameters of pure EP and EP/BPDD composites

| Sample | TTI (s) | PHRR (kW/m²) | THR (MJ/m²) | CY (%) |
|--------|--------|--------------|-------------|-------|
| EP     | 49     | 931          | 38.9        | 5.1   |
| EP-2   | 36     | 559          | 31.8        | 13.8  |
| EP-4   | 34     | 468          | 29.7        | 23.6  |
As shown in Table 2, the ignition time of pure EP sample was 49s. When BPDD was loading, the ignition time of EP/BPDD composites occurred earlier than pure EP. This result can be explained in two ways: (1) When BPDD was introduction into EP, the crosslinking density of EP/BPDD composites was reduce than pure EP, which reduce the thermal-stability of EP. (2) The thermal stability of flame retardant (BPDD) is lower than EP, when the EP/BPDD composites was heated, the flame retardant decomposition first, the decomposition products of BPDD can promote the degradation of EP. Therefor, the ignition time of EP/BPDD composites is shorter than pure EP.

The heat release rate (HRR) and total heat release (THR) curves of EP, EP-2 and EP-4 are presented in Figure 5. As shown in Figure 5, when the pure EP was ignited, its burns rapidly and reaches the peak of heat release quickly, giving a peak of heat release rate and a total heat release values of 931kW/m² and 38.9 MJ/m², respectively. The introduction of BPDD obviously decreased the PHRR and THR values of composites. When 20 wt.% BPDD loading, the values of THR and HRR were decreased by 49.7 % and 23.7% respectively.

![Figure 5. The HRR (a) and THR (b) curves of EP, EP-2 and EP-4 (50 kW/m²)](image)

3.3. BPDD flame-retardant mechanism analysis

3.3.1 Flame-retardant mechanism of condensed phase. The macroscopic and microscopic morphologies of EP, EP-2 and EP-4 after CONE tests are shown in Figure 6. As shown in Figure 6, the residual chars of pure EP was loose and little. When BPDD was introduction into EP, The residual chars of EP/BPDD composites increased greatly after CONE test, and it shows a continuous and dense microstructure. This type of residual chars can effectively inhibit the spread of combustible gas and heat, and provide flame-retardant protection to EP from condensed phase.
3.3.2. Flame-retardant mechanism of gas phase. In order to investigate the flame-retardant effect by gas phase, we used TGA-FTIR to analysis the thermal decomposition products of EP and EP-4. The FTIR 3D spectra of the thermal decomposition products of epoxy resin are shown in Figure 7. It can be found that the FTIR absorption strength of the thermal decomposition products of EP decreased with the addition of BPDD, which proved that the addition of BPDD can affect the thermal decomposition process of EP and reduce the formation of combustible gas.

4. Conclusions
In this study, a novel branched polyphosphonate flame retardant (BPDD) has been synthesized. The chemical structure of BPDD was characterized by FTIR and 1H NMR. The test results of the UL-94, LOI and CONE tests reveal that BPDD can effectively enhanced flame-retardant properties of EP. The LOI values of EP/BPDD composites increased from 23.9% of pure EP to 33.6% and UL-94 V-0 was
obtained with the 20 wt% was incorporated. Besides, the peak heat release rate (PHRR) and total heat release (THR) of EP/BPDD composites were reduced significantly compared with the pure EP. The comprehensive test results shows that the improvement of flame retardancy of the EP/BPDD composites was attributed to the synergistic action of the condensed phase and gas phases.

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