

# Synthesis of novel intumescent flame retardant containing phosphorus, nitrogen and boron and its application in polyethylene

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**Abstract** A novel intumescent flame retardant poly(phenyl phosphamide spirocyclic diethanolamine borate) (PPSDB) containing phosphorus, nitrogen and boron elements was synthesized successfully with diethanolamine borate and phenylphosphonic dichloride. The structure of PPSDB was characterized by infrared spectroscopy with Fourier transformation and nuclear magnetic resonance. As a new intumescent flame retardant, flame-retardant polyethylene (PE) composites were prepared by filling PPSDB with different fractions. The thermal stability of PPSDB and PE/PPSDB composites was investigated by thermogravimetric analysis. The results showed that the thermal stability of PPSDB was fit for processing PE composites, the initial decomposition temperatures of PE/PPSDB composites would decrease and the char residue would increase with an increase in the PPSDB fraction. The PE/PPSDB composite with 30 wt% PPSDB had the best combination properties; the limited oxygen index value was 29.2, and vertical burning reached UL-94 V-0 rating, and the tensile strength and notched impact strength were 18.6 MPa and 12.5 kJ m<sup>-2</sup> respectively. The morphologies of char residue showed a lot of protruding structures consisting of smaller protuberances, which prevented the combustion of composite and enhanced anti-dripping property effectively.

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**Keywords** Intumescent flame retardant · Synthesis · Polyethylene composite · Thermogravimetric analysis · Flame resistance

## Introduction

Polyethylene (PE) is widely used in many fields such as packaging, textiles, household goods and electric cable for its excellent electric insulation, great recyclability, good chemical resistance, ease of processing and low cost, and so on [1, 2]. However, inherent flammability and low limited oxygen index (LOI) have restricted its widespread application in some fields where better flame resistance is required. Therefore, improving the flame resistance of PE has become a recent focus of polymer research. As is well known, flame-retardant PE composite can be prepared by mixing flame-retardant additives with resin granules or powders. In those effective flame retardants for PE, halogen-containing compounds are outstanding flame-retardant additives, especially when compounded with antimony trioxide [3–6]. Unfortunately, some halogen-containing compounds have been forbidden for use in many public places due to the release of toxic and corrosive gases which can choke people exposed to the fumes. The gases also corrode the metal equipment and pollute the environment [7–11]. Environment protectors have resisted the large-scale use of halogen-containing flame retardants and advocated the wide application of alternative chemical products [12]. So, halogen-free flame retardants such as intumescent flame-retardant (IFR) systems have been developed rapidly and widely applied in the field of flame-retardant polymers, especially in polyolefin due to their advantages of low smoke, low toxicity, no corrosion [13–15] and higher flame resistance efficiency. Typically, IFR plays an effective flame resistance role mainly by the condensed-phase mechanism [16–19]. Foam char layers are often formed on the surface of the burning substance during combustion. The char layers act as an insulator and shield the polymers underneath from the heat and also serve as a diffusion barrier to slow down the gasification and vaporization of polymers [20]. Commonly used IFR consists of two or three kinds of flame retardants corresponding to the acid source, carbon source and gas source. It is hard to obtain the best ratio to achieve the best flame resistance; moreover, the mixtures of IFR will deteriorate the mechanical properties due to the poor compatibility. Recently, some new flame retardant containing phosphorus (P) and nitrogen (N) [21–23], or P, N and silicon (Si) [24], was synthesized to improve the flame resistance efficiency and compatibility with the polymer matrix. Other researches [25, 26] have demonstrated that boron (B)-containing compound greatly improves the flame resistance efficiency and reduces the toxicity of halogen-containing flame retardant. However, flame retardants containing P, N and B elements have not been reported until now.

To integrate much more flame resistance elements, a novel intumescent flame retardant of poly(phenylphosphamide spirocyclic diethanolamine borate) (PPSDB) containing P, N and B elements was designed and synthesized successfully by a nucleophilic addition reaction. The structure of PPSDB was characterized by Fourier transform infrared spectrum (FTIR) and nuclear magnetic resonance

( $^1\text{H-NMR}$ ). Acting as an intumescent flame retardant, PPSDB was used to prepare PE/PPSDB composites with different fractions, and the thermal performances, flame resistance, mechanical and residue morphology of those composites were studied in detail.

## Experimental

### Materials

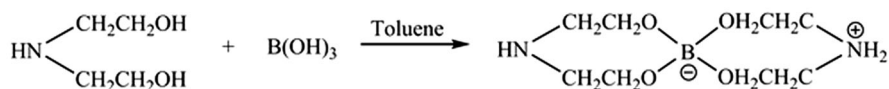
Polyethylene (PE) was provided by CSPC Petroleum Chemical Industry CO., LTD (Guangdong, China); diethanolamine was purchased from Chinese Medicine Group Chemical Reagent Corp. (Shanghai, China); toluene, acetonitrile, tetrahydrofuran and dichloromethane were supplied by Tianjin Damao Chemical Reagent Factory (Tianjin, China); boric acid was obtained from Shantou Xilong Chemical Co., LTD (Guangdong, China); phenylphosphonic dichloride (PPC) was supplied by Rizhao Lideshi Chemical Co., LTD (Shandong, China).

### Synthesis of DEAB

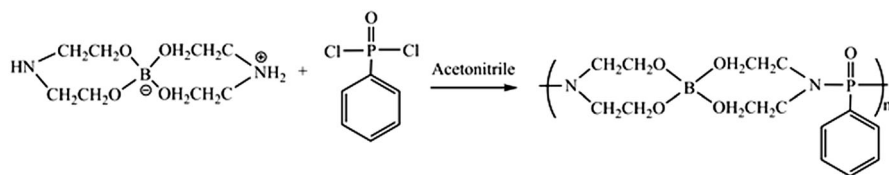
A 250 ml three-necked round bottom flask equipped with a magnetic stirrer, reflux condenser, thermometer and water knockout vessel was placed into a water bath. 24.7 g (0.4 mol) boric acid, 92.5 g (0.88 mol) diethanolamine and 100 ml toluene were added and stirred at 110 °C until no water was generated in the reaction system. Then, the reaction mixture was cooled to room temperature slowly, toluene was removed by vacuum distillation and a pale yellow viscous liquid was obtained. Finally, the yellow liquid was refined by washing with tetrahydrofuran (THF) repeatedly. After the refined product was dried at 50 °C in vacuum for 12 h, a white liquid was obtained and named as diethanolamine borate (DEAB). The yield of the DEAB product was 85.3 %. The whole reaction equation is illustrated in Scheme 1.

### Synthesis of PPSDB

21.8 g DEAB (0.1 mol) and 150 ml acetonitrile were taken in a 250 ml flask equipped with a stirrer, thermometer, dropping funnel and circumference condenser. 19.5 g phenylphosphonic dichloride (0.1 mol) was dissolved in acetonitrile to form a homogeneous solution. The solution was poured into the flask and reacted for 1 h at a temperature of 15–20 °C. After the reaction was complete, the final mixture was refluxed for 6 h, followed by cooling, filtering, washing and drying. White powders



**Scheme 1** Synthesis route of DEAB



**Scheme 2** Synthesis route of PPSDB

were obtained and the yield was 65.34 %. The specific reaction equation is shown in Scheme 2.

### Preparation of flame-retardant PE/PPSDB composites

All the composite samples were prepared by mixing PE and PPSDB in an open mill at 170 °C for 15 min. After the composites were mixed uniformly, the composite samples were hot pressed under 10 MPa at 170 °C for 5 min and cold pressed under 10 MPa at room temperature for 3 min, then cooled to room temperature. The specimens were prepared finally.

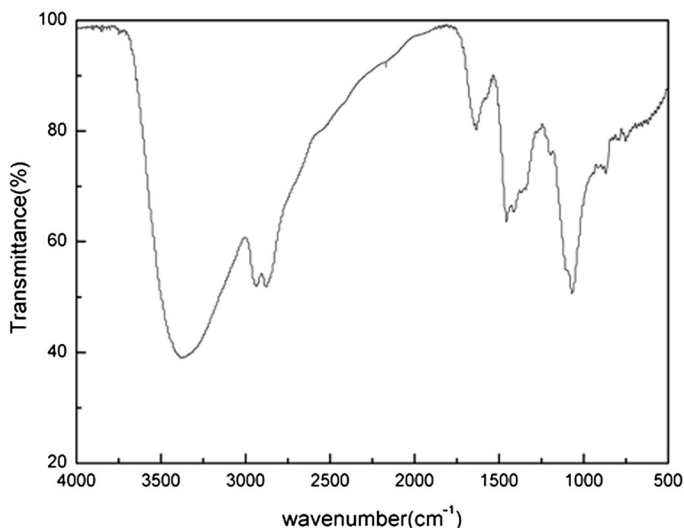
### Characterization

FTIR (NICOLET 470) was used to characterize the chemical structure of DEAB and PPSDB. The  $^1\text{H}$  NMR (BRUKER AVANCE III) was applied to characterize DEAB and PPSDB with DMSO as a solvent. Thermogravimetric analyzer (STA 449C) was used, and the test temperature ranged from ambient to 800 °C at a heating rate of 10 °C  $\text{min}^{-1}$  under nitrogen, and the sample's weight was about 10 mg in each test. Scanning electron microscopy (SEM JSM-6360LV) was used to investigate the char surface of flame-retardant PE. The surface of char residues was clad with gold before SEM scanning, and the char residues were obtained from the burned samples in the vertical burning test. Oxygen index instrument (JF-3) was used to measure the limited oxygen index (LOI) of samples with the dimensions of  $130 \times 6.5 \times 3 \text{ mm}^3$  according to ASTM D2863-97. The vertical burning tests (UL-94) were performed in CZF-3 horizontal and vertical burning test instrument with sample dimension of  $130 \times 13 \times 3 \text{ mm}^3$  according to ASTM D3801. The tensile and impact behavior tests were carried out in TCS-2000 tensile test equipment and GT-7045-MDL digital impact tester according to ASTM D638 and ASTM D256, respectively, and the listed data were the mean of five samples.

## Results and discussion

### Characterization of DEAB and PPSDB

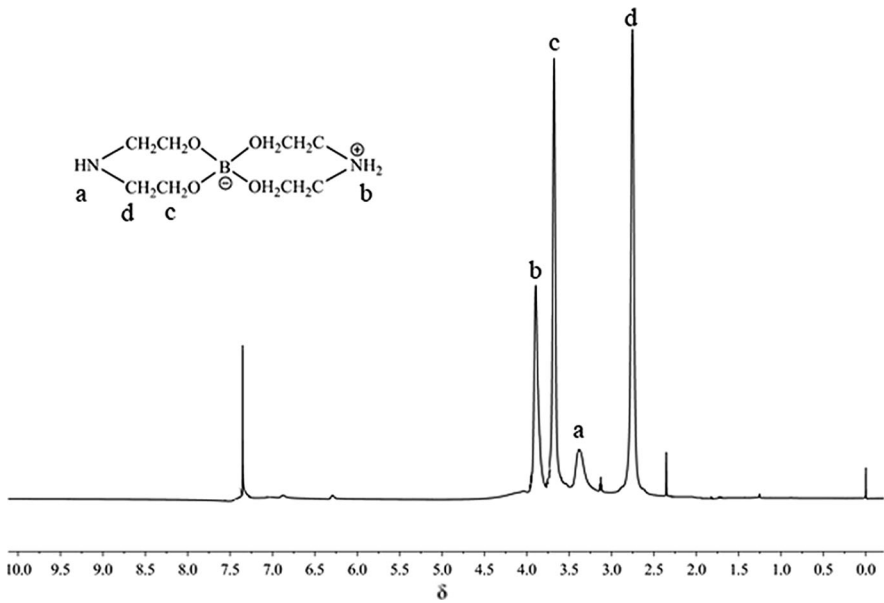
The structure of DEAB was characterized by FTIR and shown in Fig. 1. The peaks at 3382 and 1637  $\text{cm}^{-1}$  corresponded to the stretching vibration and bending



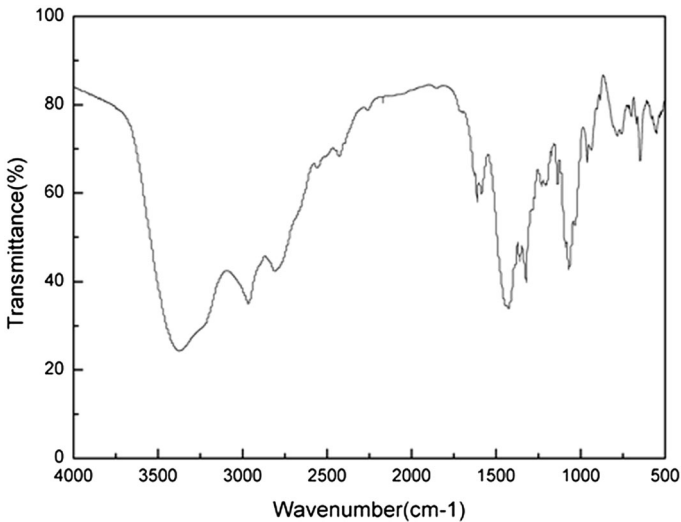
**Fig. 1** FTIR spectrum of DEAB

vibration of  $\text{-NH}$ , respectively. The stretching vibration of  $\text{-CH}_2$  is observed at 2937 and 2877  $\text{cm}^{-1}$ . The peak at 1455  $\text{cm}^{-1}$  is assigned to  $\text{-CH}$  bending vibration. Furthermore, the peak at 869  $\text{cm}^{-1}$  is the characteristic absorption peak of the B–O bond. In addition, the structure of DEAB is also characterized by  $^1\text{H-NMR}$  spectrum and illustrated in Fig. 2. The peak at 3.38 and 3.89 ppm are assigned to the proton of  $\text{-NH}$  and  $\text{-NH}_2$ , respectively. The peak at 3.68 ppm is associated with  $\text{-CH}_2$  protons near the spirocyclic boron. The peak at 2.75 ppm is assigned to the proton of  $\text{-CH}_2$  out of the spirocyclic boron. The peak at 7.24 ppm comes from the solvent. These results confirm that the chemical reaction takes place as in Scheme 1.

The structure of PPSDB was characterized by FTIR and is illustrated in Fig. 3. The stretching vibration of  $\text{-NH}$  is observed at 3375  $\text{cm}^{-1}$ . The absorption at 2965 and 2809  $\text{cm}^{-1}$  is assigned to the stretching vibration of  $\text{-CH}_2$ . The peak at 1359  $\text{cm}^{-1}$  is associated with the stretching vibration of  $\text{-CN}$ . The peaks at 1613, 1586 and 1425  $\text{cm}^{-1}$  are assigned to the skeleton vibration from the benzene ring. The absorption peak of  $\text{P=O}$  is observed at 1247  $\text{cm}^{-1}$ . Moreover, the peak of 961  $\text{cm}^{-1}$  is associated with the stretching vibration of  $\text{P-N}$ , which indicates that the final product was obtained successfully. The  $^1\text{H-NMR}$  spectrum of PPSDB is shown in Fig. 4. The multiple peaks between 7.54 and 7.81 ppm belong to the benzene ring. The signal at 3.65 ppm is attributed to the  $\text{-CH}_2$  protons adjacent to the spirocyclic boron. The peak of  $\text{-CH}_2$  protons out of the spirocyclic boron is observed at 2.98 ppm. The peak at 8.66 ppm is associated with  $\text{P-NH}$ , which confirms the final structure of PPSDB. The peaks at 3.36 and 2.48 ppm belong to the water protons and protons of the DMSO solvent, respectively. The chemical shifts of the absorption peaks and the area ratios of the peak integration are identical to the expected chemical structure.



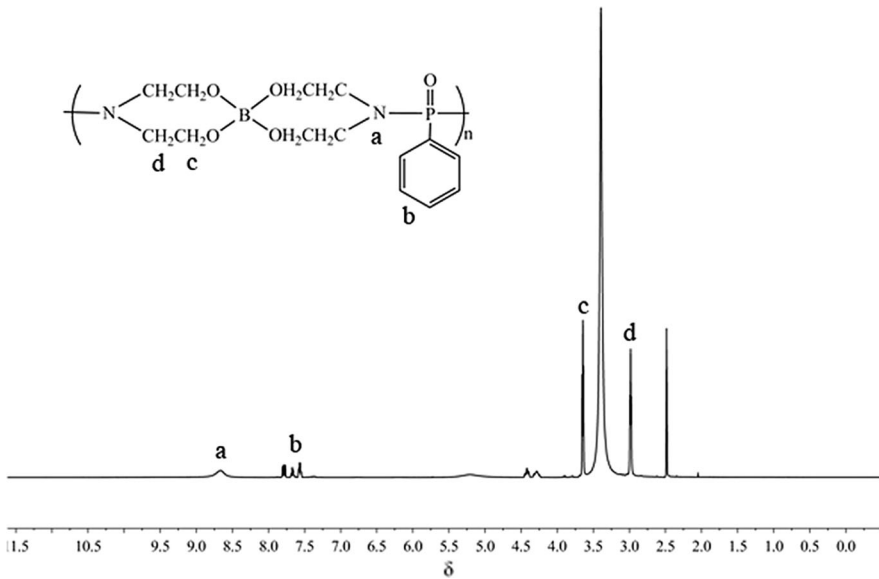
**Fig. 2** <sup>1</sup>H-NMR spectrum of DEAB



**Fig. 3** FTIR spectrum of PPSDB

### Flame resistance of PE/PPSDB composites

Limiting oxygen index (LOI) and vertical burning test (UL-94) are widely used to evaluate the flame resistance of polymer composites. LOI is defined as the minimum



**Fig. 4** <sup>1</sup>H-NMR spectrum of PPSDB

**Table 1** Flame resistance of PE and PE/PPSDB composites

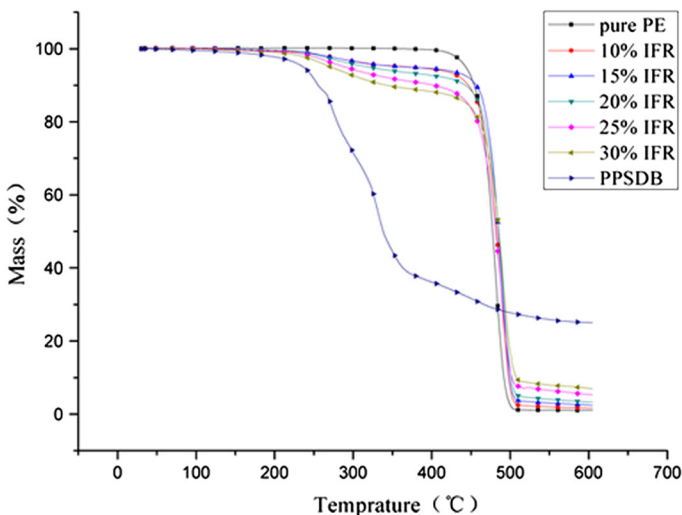
Samples	LOI (%)	UL94 rating	
		Ratings	Dripping
PE	17.4	Fail	Yes
PE/10 % IFR	21.3	Fail	Yes
PE/15 % IFR	23.1	Fail	Yes
PE/20 % IFR	24.9	V-2	Yes
PE/25 % IFR	27.5	V-1	No
PE/30 % IFR	29.2	V-0	No

percentage of oxygen in an oxygen–nitrogen mixture, which is just sufficient to sustain combustion (after ignition) of the specimen. The sample can be considered as a flame-retardant material when the LOI value is more than 26. UL-94 test results fall into three categories, with burning ratings V-0, V-1 and V-2, and the V-0 rating corresponds to the highest level of flame resistance. The LOI values and vertical burning ratings of pure PE and PE/PPSDB composites are shown in Table 1. Pure PE is highly combustible with molten drips, the LOI value is only 17.4 and UL-94 cannot reach any rating. Compared with pure PE, the PE/PPSDB composites show a better flame resistance performance. The LOI values of flame-retardant PE/PPSDB composites improve obviously with an increase of the PPSDB fraction. When the PPSDB fraction is 30 wt% in composite, the LOI value is 29.2, the increment of LOI ( $\Delta$ LOI) is 11.8 when compared with pure PE, the UL-94 V-0 rating can be achieved, and there are no molten drips during vertical burning (UL-94 test) when

the PPSDB content is more than 25 wt% in the composite. So the novel IFR PPSDB shows higher flame resistance efficiency and excellent anti-dripping property. The reason for PPSDB's better flame resistance is attributed to the combination of P, N and B elements and the special molecular structure in Scheme 2. When PE/PPSDB composite burns at a lower temperature, the P=O bonds provide the acid resource, the rigid phenyl groups connecting P=O play an anti-burning effect to a certain extent, the N element would turn into incombustible  $\text{NH}_3$  and the B element will be changed into  $\text{B}_2\text{O}_3$  or boric acid. The intermediate or final products of P, N and B elements prevent the composite from burning further, and the synergetic effect of three effective elements can be achieved to improve the flame resistance efficiency of PE/PPSDB composites prominently.

### Thermal stability

Thermogravimetric analysis (TGA) is a common technique for evaluating the thermal stability of various polymers, and it also indicate the decomposition behaviors of the polymer at various temperatures [27, 28]. The TGA curves of PPSDB and PE/PPSDB composites are shown in Fig. 5, and the corresponding data are listed in Table 2. The initial decomposition temperature of PPSDB is 254 °C; the weight loss increases rapidly with an increase of temperature. The initial decomposition of PPSDB at a lower temperature is assigned to the weak boron spiro bonds. Two degradation steps of PPSDB are observed at about 260 and 350 °C, respectively. The major degradation between 260 and 350 °C is attributed to the scission of boron spiro bonds. The subsequent minor degradation is observed at a temperature ranging from 350 to 470 °C, which is considered as that for the formation of residue char. The weight loss slows down when the temperature is higher than 500 °C, and the final residue is 25.1 % at 800 °C. Generally speaking,



**Fig. 5** TGA curves of the PPSDB and PE/PPSDB composites



**Table 2** Date of TGA curves for PPSDB and PE/PPSDB at a heating rate of  $10^\circ \text{ min}^{-1}$ 

Samples	$T_i$ ( $^\circ$ )	$T_{50}$ % ( $^\circ$ )	Residue at $800^\circ$ (%)
PE	420	470	1.00
PPSDB	254	339	25.1
PE-10 % IFR	343	475	1.52
PE-15 % IFR	310	478	2.43
PE-20 % IFR	286	476	3.21
PE-25 % IFR	266	473	5.21
PE-30 % IFR	250	475	6.87

$T_i$  the initial decomposition temperature,  $T_{50}$  % the temperature of 50 wt% weight loss

the common processing temperature of PE is about  $200^\circ \text{C}$ , and the initial decomposition temperature and thermal stability of PPSDB can meet the requirement for fabricating the PE/PPSDB composite sufficiently.

For pure PE, the initial degradation temperature and the maximum decomposition temperature is 420 and about  $470^\circ \text{C}$ , respectively. When the temperature is higher than  $500^\circ \text{C}$ , the weight will not decrease any longer and the char residue is negligible (only 1.0 %). For the PE/PPSDB composites with different fractions of flame retardant, all the initial degradation temperatures are lower than pure PE, which is attributed to the weaker thermal stability of PPSDB, as the B–O, P=O and C–N bonds in PPSDB are less stable than uniform C–C bonds in PE. For the PE/PPSDB composites, the decomposition curves are similar in shape, the initial decomposition temperatures are higher than  $250^\circ \text{C}$ , and the maximum weight loss temperatures range from 450 to  $500^\circ \text{C}$ . When the temperature is higher than  $510^\circ \text{C}$ , the weight loss shows no obvious change, which indicates that the char residues remain constant and the composites decompose completely. We can also find that the char residues of PE/PPSDB composites increase with an increase of the PPSDB fraction, which is attributed to the formation of the char layer induced by PPSDB.

According to the thermal decomposition curves and the molecular structure of PPSDB, we attempt to illustrate the flame resistance mechanism of PPSDB in the composite. At a lower temperature, the P=O bonds or B–O bonds of PPSDB will decompose and generate inorganic acid, such as phosphoric acid, metaphosphoric acid or boric acid. Esterification reaction would take place between inorganic acid and carbon source, and the carbon source would turn into the char layer after the dehydration reaction. Then, at a higher temperature, the polymer matrix will be molten, and the polymer melt expands by bubbles formed by the water vapor or  $\text{NH}_3$  from gas source (C–N bonds). The inflammable gas can also serve as catalyst for the esterification reaction. Finally, the whole system changes from gel into compact porous char layers on the surface of the sample, which prevents the composite from decomposing further and isolates the heat and oxygen from the surroundings. That is the condensed-phase mechanism of flame resistance.

## Mechanical properties

The mechanical properties of PE and PE/PPSDB composites are shown in Table 3. The results show that the mechanical properties of composites decrease with an

**Table 3** Mechanical properties of PE and PE/PPSDB composites

Samples	Tensile strength (MPa)	Impact strength (kJ m <sup>-2</sup> )
PE	25.5	15.5
PE/PPSDB-10 %	26.2	10.9
PE/PPSDB-15 %	25.3	9.4
PE/PPSDB-20 %	24.9	11.2
PE/PPSDB-25 %	20.8	12.1
PE/PPSDB-30 %	18.6	12.5

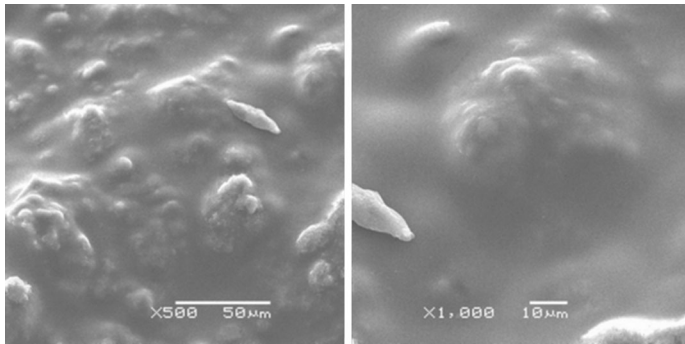
increase of the PPSDB fraction. It can be seen that the tensile strength of the PE/PPSDB composite with 10 wt% PPSDB increases to 26.2 from 25.5 MPa of pure PE, and the corresponding impact strength drops to 10.9 from 15.5 kJ m<sup>-2</sup> of pure PE. When the fraction of PPSDB is more than 10 wt%, the tensile strength decreases and the notched impact strength of composites improves with an increase of the PPSDB fraction. Considering the flame resistance, the PE/PPSDB composite with 30 wt% PPSDB has much more practical significance, and the tensile strength and notched impact strength are 18.6 MPa and 12.5 kJ m<sup>-2</sup>, respectively. Compared with metal hydroxide or mixtures of intumescent flame retardants, the PPSDB integrates the P, N and B elements by forming the non-polar phenyl and spirocyclic groups, which play a positive effect in improving the flame resistance efficiency and compatibility between the flame retardant and PE matrix [5].

### Morphologies of the char residue

Figure 6 shows the microscopic morphologies of char layers. The specimen for SEM is the final residue of the sample PE/PPSDB-30 wt%. There are some protruding structures on the smooth char layer surface. After the sample is magnified by 1000 times, the protruding structure is composed of many small protuberances, which are just generated by the bubbles of inflammable gas. The special structure with lots of protuberances in the char layer prevents the composites from burning further and enhances the anti-dripping property effectively, which proves the condensed-phase mechanism of novel flame resistance PPSDB.

### Conclusions

A novel flame retardant (PPSDB) containing phosphorus, nitrogen and boron was synthesized successfully and its chemical structure was confirmed by FTIR and <sup>1</sup>H-NMR. The thermal stability of PPSDB was confirmed to meet the requirement for fabricating PE composites by TGA, and the initial decomposition temperatures of PE/PPSDB composites decreased and the char residue increased with an increase of PPSDB fraction. PE/PPSDB composites showed good flame resistance, anti-dripping properties and compatibility. When the PPSDB fraction was 30 wt% in the PE/PPSDB composite, the LOI value was 29.2, vertical burning reached UL-94 V-0



**Fig. 6** SEM micrographs for the char residue after vertical burning of PE/PPSDB-30 %

rating, and the tensile strength and notched impact strength were 18.6 MPa and 12.5 kJ m<sup>-2</sup>, respectively. The morphologies of char residue showed a lot of protruding structures consisting of smaller protuberances, which prevented the combustion of the composite and enhanced the anti-dripping property effectively. The PPSDB integrated the P, N and B elements by forming the non-polar phenyl and spirocyclic groups, which has a positive effect in improving the flame resistance efficiency and the compatibility between the flame retardant and PE matrix. This has a potential to be industrialized in the near future.

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