

Preparation, fire behavior and thermal stability of a novel flame retardant polypropylene system

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Abstract In this study, a novel spirocyclic pentaerythritol bisphosphorate disphosphoryl-di-prop-2-en-1-amine (SPSA) compound containing a functional double bond (C=C) was synthesized and characterized by Fourier transform infrared spectroscopy and ¹H nuclear magnetic resonance spectroscopy (¹H NMR). In this paper, a new intumescent flame retardant (IFR) was designed by combining ammonium polyphosphate (APP) and SPSA (mass ratio of APP and SPSA was 2:1) and this IFR was mixed with polypropylene (PP) via twin-screw extruder to prepare a series of flame retardant PP composites. The thermal stability and fire behaviors of these flame retardant PP composites were investigated by thermogravimetric analysis, limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimeter test. Furthermore, the morphology of the char residues of flame retardant PP composites after cone calorimeter test was studied by scanning electron microscopy with energy dispersive X-ray analysis (EDS). Aiming to further improve the thermal stability of the composites, electron beam irradiation has been used to treat these composites. The results showed that LOI value of flame retardant PP composite containing 30 % IFR was 24.0 and passed UL 94 V-0. In the cone calorimeter test, both peak heat release rate and total heat release results of PP/IFR system were lower than those of PP/APP system. In addition, this IFR provided relatively good quality of char residue in the

combustion. Moreover, electron beam treatment of the composites improved the thermal stability of these designed flame retardant PP composites.

Keywords Polypropylene · Flame retardancy · Fire behavior · Thermal stability · Electron beam irradiation

Introduction

Polypropylene (PP) has excellent mechanical and physicochemical properties. Thus, it is used in a wide range of applications, but its inherent combustibility limits its broader application [1–3]. Thus, the flame retardancy of PP has to be improved. The use of intumescent flame retardants (IFR) is established in polymeric materials since it is regarded as a safe and friendly flame retardant method [4]. IFR is generally made of three constituents: acid source (e.g., ammonium polyphosphate, etc.), carbon source (e.g., pentaerythritol, sorbitol, etc.) and foaming agent (e.g., melamine, etc.).

Many researches have shown that synergistic agents can effectively increase the strength and stability of char layer as well as promote catalyzing the reactions among IFR components in IFR-PP systems. Wang et al. [5] proposed to use the catalytic action of phosphotungstic acid in the synthesis of melamine salts of pentaerythritol phosphate in order to solve the problems of conventional preparation methods. Nie et al. [6] suggested the synthesis of a char-forming agent and microencapsulated ammonium polyphosphate was incorporated in PP via an intumescence mechanism. Wang reported [7, 8] the synthesis of a novel char former for intumescent system based on a charring agent and ammonium polyphosphate. Bourbigot et al. [9] investigated charring polyamide-6 clay nanocomposite

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Fig. 1 Synthesis of new phosphorus-containing flame retardant (SPSA)

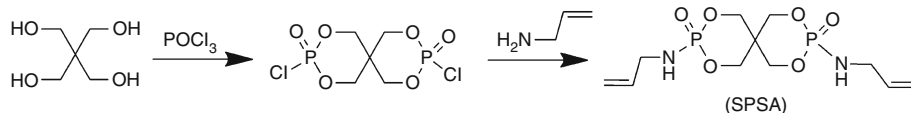


Table 1 Formulation of PP and flame retardant PP composites

Sample	PP/mass%	IFR	
		APP/mass%	SPSA/mass%
PP0	100	0	0
PP1	80	13.3	6.7
PP2	75	16.7	8.3
PP3	70	20	10
PP4	70	30	0

hybrid (PA-6-nano) as a carbonization agent. Some phosphorus and nitrogen-containing intumescent agents were synthesized, such as spiro and caged bicyclic phosphate (SBCPO) [10], spirocyclic pentaerythritol bisphosphorite disphosphoryl melamine (SPDPM) [11], poly(4,4-diaminodiphenyl methane spirocyclic pentaerythritol bisphosphonate) (PDSPB) [12] and poly(2-hydroxy propylene spirocyclic pentaerythritol bisphosphonate) (PPPBP) [13]. Recently, Wang et al. [14, 15] found that P–O–C and P–N–C structures could greatly improve the residues layer during combustion. Since traditional IFR is non-reactive type compounds to polymers, it may result in the low thermal stability of flame retardant polymer due to the initial decomposition of the components in IFR.

It is well known that electron beam (EB) technology is an environment-friendly method [16–18]. It can be used to chemically modify polymer [19]. Its main advantage is the spatial and temporal precise generation of free radicals in accordance with the requirement of the chemical reaction without any use of chemicals as well as without any dependence on the temperature and the state of aggregation [20]. Formed the cross-linked structure may be used to improve the thermal stability of polymers.

In this work, a novel halogen-free intumescent flame retardant containing a functional double bond (C=C) that may form cross-linking structure with PP in the electron beam treatment, spirocyclic pentaerythritol bisphosphorite disphosphoryl-di-prop-2-en-1-amine (SPSA), was developed and mixed in the PP system via melt compounding. The thermal stability and fire behavior of these flame retardant PP composites were investigated by thermogravimetric analysis (TG), limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimeter test. Furthermore, the morphology of the char residues of flame retardant PP composites after cone calorimeter test was

studied by scanning electron microscopy (SEM) with energy dispersive X-ray analysis (EDS). In the end, the thermal stability of non-irradiated and electron beam irradiated flame retardant PP composites was investigated.

Experimental

Materials

Pentaerythritol, phosphoryl chloride, triethylamine, prop-2-en-1-amine, trichloromethane, sodium hydroxide and tetrahydrofuran were supplied by Sigma-Aldrich Chemical Reagent Co., Ltd. and used without further purification. Polypropylene (PP, homopolymer, HD 120MO) was supplied by Borealis, Porvoo, Finland. Ammonium polyphosphate (APP) was supplied by Budenheim Company. Spirocyclic pentaerythritol bisphosphorite disphosphoryl-di-prop-2-en-1-amine (SPSA) was prepared from pentaerythritol and phosphoryl chloride, leading to spirocyclic pentaerythritol bisphosphorite disphosphoryl chloride, which was then reacted with prop-2-en-1-amine, as shown in Fig. 1.

Synthesis of spirocyclic pentaerythritol bisphosphorite disphosphoryl chloride [21]

In a 500-mL glass flask equipped with a magnetic stirrer, a thermometer, a heating bath and circumference condenser, pentaerythritol (68 g, 0.5 mol) and phosphoryl chloride (618 g, 4.0 mol) were mixed. The mixture was stirred

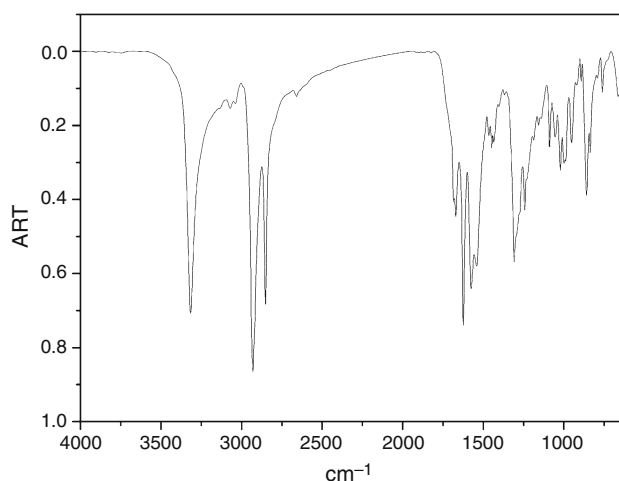


Fig. 2 FTIR spectra of SPSA

about 100 °C until HCl evolution subsided. Then, the mixture was gradually heated and refluxed until no HCl gas was emitted. The raw product obtained was filtered and purified using a filter with chloroform sequentially. The product was dried to constant mass at 55 °C in vacuum. Thus, spirocyclic pentaerythritol bisphosphorate disphosphoryl chloride, a white solid powder, was obtained (108 g, yield: 73 %).

Characterization: ^1H NMR (500 MHz, d_6 -DMSO) (ppm): 4.23–4.20 (d, $-\text{CCH}_2\text{O}-\text{PO}-$, 8H). FTIR (cm^{-1}): 1305 (vs, P=O), 1025 (vs, P–O–C).

Synthesis of new phosphorus-containing flame retardant (SPSA)

A mixture of prop-2-en-1-amine (28.5 g, 0.5 mol) and triethylamine (70 mL, 0.5 mol) was added dropwise to a stirred solution of spirocyclic pentaerythritol bisphosphorate disphosphoryl chloride (60 g, 0.2 mol) in anhydrous tetrahydrofuran (100 mL) under nitrogen gas at 0–5 °C. The resulting mixture was allowed to warm to room temperature and left stirring for 12 h. Then, the mixture was filtered off. Finally, the filtrate was concentrated at reduced pressure. Thus, the product SPSA (57 g, yield: 85 %) was distilled under reduced pressure to provide the desired compounds. The reactions are shown in Fig. 1.

Preparation of flame retardant PP composites

APP and SPSA were dried in a vacuum oven at 80 °C for 12 h. Then, PP and IFR (mass ratio of APP and SPSA at 2:1) were compounded by a twin-screw extruder (KETSE 20/40 EC, Brabender) (compositions see Table 1) with a rotational speed of 150 rpm at a fixed temperature protocol

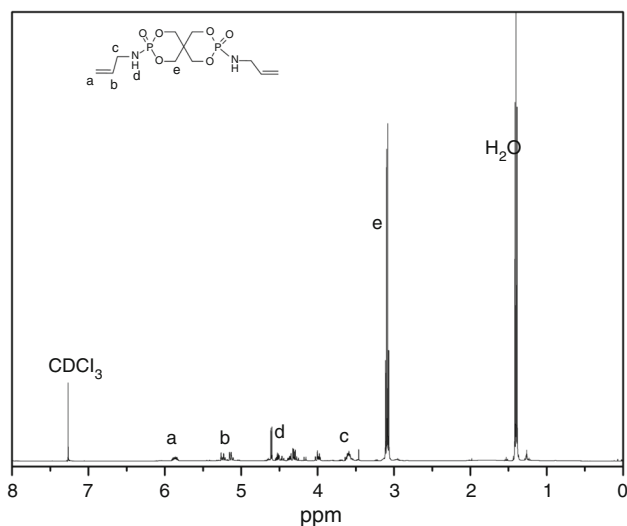


Fig. 3 ^1H NMR spectra of SPSA

Table 2 LOI values and UL94 results of PP and flame retardant PP composites

Sample	LOI	UL94	Dripping in UL94 test
PP0	17.6	N.R.	Yes
PP1	21.0	N.R.	Yes
PP2	22.5	N.R.	Yes
PP3	24.0	V-0	No
PP4	20.4	N.R.	Yes

N.R. no rating

for the feed zone to the die: 175, 180, 190, 185, 180 and 170 °C. Finally, the specimens were applied for LOI, UL-94, and cone calorimeter test was carried out by injection molding (Arburg 320 C) at a processing temperature around 200 °C.

Electron beam irradiation

Flame retardant PP composites were irradiated at room temperature in nitrogen atmosphere with an average dose 32 kGy using an ELV-2 electron accelerator (BINP, Novosibirsk, Russia). The electron energy was 1.5 MeV, and the electron current amounted to 4 mA.

Experimental devices description

The Fourier transform infrared (FTIR) spectrum of SPSA sample was recorded using the Bruker Vertex 80 V spectrometer in the wave number range of 600–4000 cm^{-1} .

^1H nuclear magnetic resonance (^1H NMR) was obtained on a Bruker spectrometer using CDCl_3 as a solvent.

The thermogravimetric analysis (TG) was carried out using a TA Instruments TGA Q 5000 in the range between

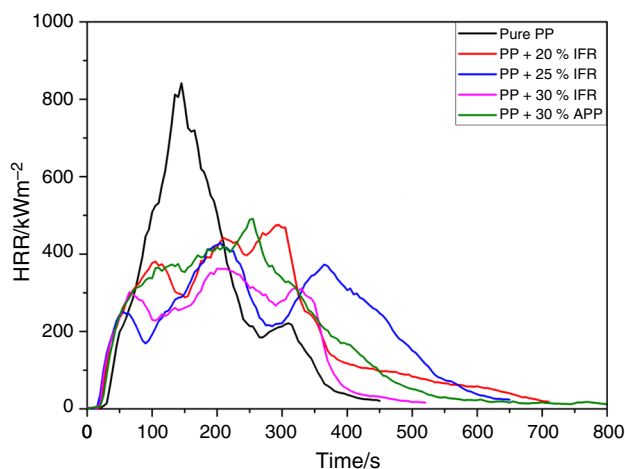


Fig. 4 Heat release rate plots of pure PP and its composites

room temperature and 700 °C. The experiments were done in nitrogen atmosphere at heating rate of 10 K min⁻¹, and the flow rate of the nitrogen was 60 mL min⁻¹.

The UL-94 test was performed using a vertical burning instrument (Fire Testing Technology, UK), and the specimens in this work for testing were of dimensions 130 mm × 13 mm × 3.2 mm.

Limiting oxygen index (LOI) was measured on sheets (120 mm × 6.5 mm × 3.2 mm) according to the standard DIN EN ISO 4589-1 and 4589-2. It describes the minimum concentration of oxygen in nitrogen that supports the combustion of a polymer. The unit of concentration is percentage.

The cone calorimeter tests (CC) were carried out on a cone calorimeter (FTT, UK). The squared specimens (100 mm × 100 mm × 4 mm) were wrapped with aluminum foil and placed in a frame without grid. The specimens were irradiated at a heat flux of 50 kW m⁻². Each sample was tested three times.

Scanning electron microscopy (SEM) (microscope model: Ultra Plus, Carl Zeiss SMT) with energy dispersive X-ray analysis (EDS) was used to study morphological features of the powdered samples. The samples were placed on a sample holder using conducting copper tape and then coated with a thin layer of platinum (layer thickness 3 nm) using a sputter coater (BAL-TEC SCD 500 sputter coater).

Results and discussion

Structure characterization of SPSA

FTIR spectroscopy

In order to identify the structure of SPSA, firstly, FTIR spectroscopy was used to characterize SPSA, as shown in

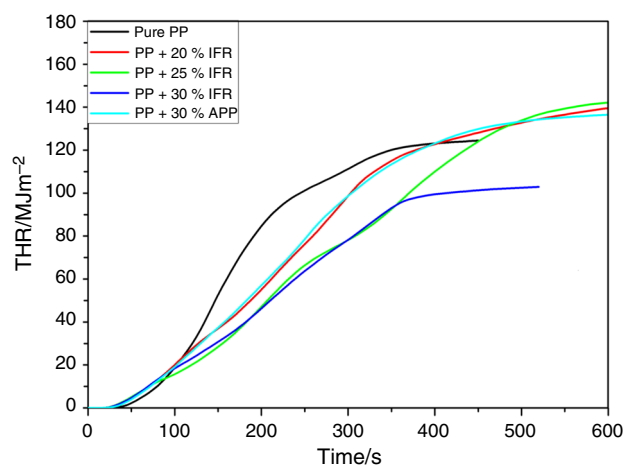


Fig. 5 Total heat release (THR) of PP and flame retardant PP composites

Fig. 2. The characteristic absorption peak at 3311 cm⁻¹ was attributed to the N–H bond segments in structure of SPSA. Also, the characteristic absorption peaks for carbon–carbon double bonds (1635 cm⁻¹) were clearly observed. The peak at 987 cm⁻¹ was assigned to P–O–C bond on the structure of SPSA segments.

¹H NMR spectroscopy

Further structural conformation for SPSA was made by means of ¹H NMR spectroscopy. As shown in Fig. 3, the peak groups at 5.80–5.11 ppm could be assigned to the protons on the carbon–carbon double bond on the structure of SPSA segments (corresponding to a, b in Fig. 3). The peak groups at 4.51–3.00 ppm could be assigned to the protons on methylene groups of the structure of SPSA segments (corresponding to d, e in Fig. 3).

Fire behaviors

In the following, polypropylene (PP)/intumescent flame retardant (IFR) composites have been prepared in different compositions as given in Table 2 and the composites have been compared with pure PP in the fire behavior. Ammonium polyphosphate (APP) alone and together with SPSA in a 2:1 ratio were used as IFR.

LOI and UL94

Aiming to evaluate flammability of PP and flame retardant PP composites, usually, LOI and UL-94 tests are used [22–24]. In this study, both LOI and UL94 were used to investigate the flammability of the composites and the results are given in Table 2. Obviously, LOI value of virgin PP was only 17.6 %, showing high flammability. At a load of 30 mass% of APP, the LOI value of PP/APP composite increased to 20.4 %, but there was no rating in the UL 94 test. It meant that APP alone was not an efficient flame retardant to PP. In comparison, the LOI values of PP/IFR composites containing 20, 25 and 30 mass% IFR were 21.0, 22.5 and 24.0, respectively. More importantly, PP + 30 % IFR passed UL 94 V-0, indicating that this IFR was more efficient than APP alone.

Cone calorimeter test

While the LOI and UL 94 tests are widely used to evaluate the flame retardation of materials, especially for screening flame retarded formulations of polymers, the cone calorimeter provides a wealth of information on the combustion behavior [25]. Some cone calorimeter results correlate well with those obtained from large-scale fire tests and can be used to predict the behavior of materials in real

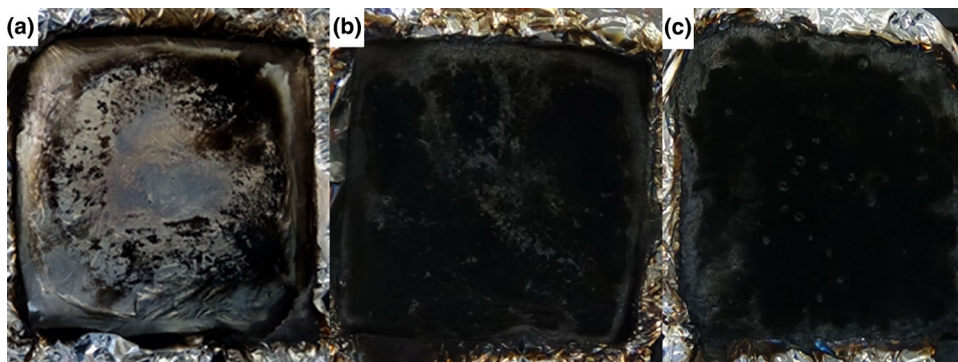


Fig. 6 Digital photographs of residue char for PP (a), PP composite with 30 % APP (b), PP composite with 30 % IFR (c)

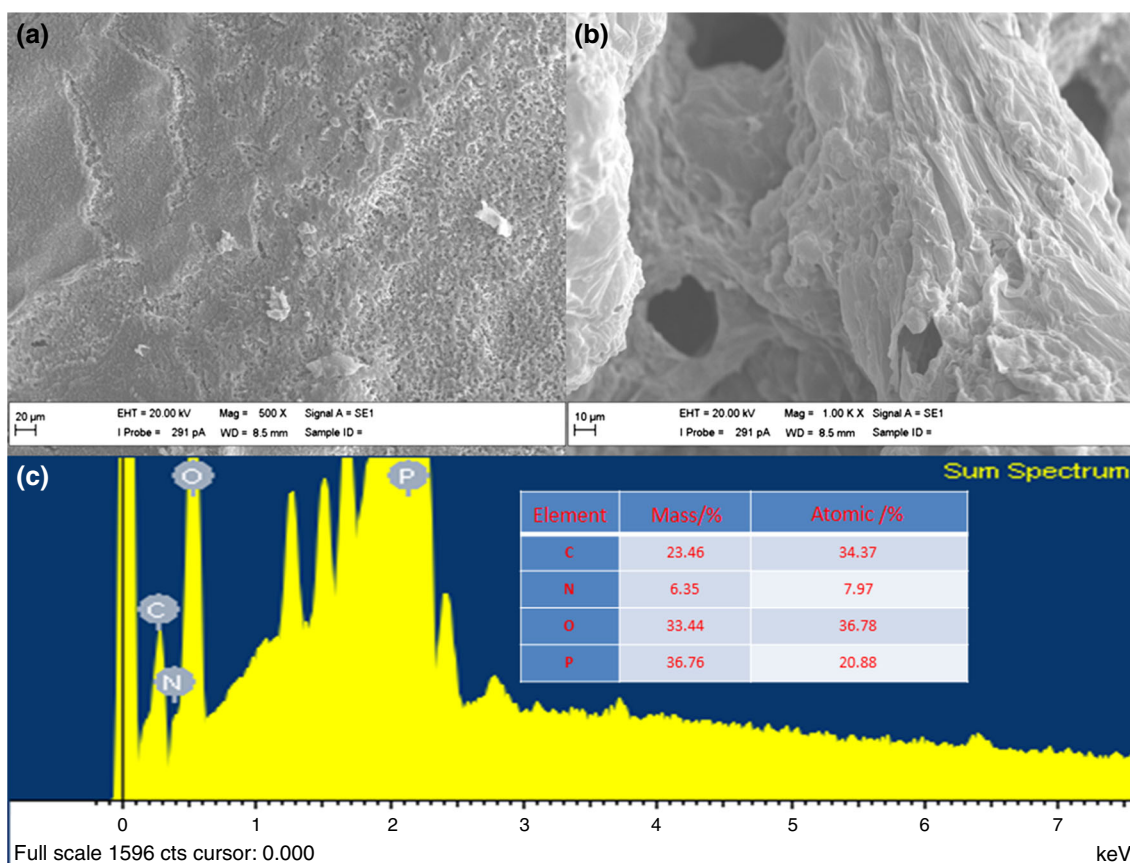


Fig. 7 a SEM images of the residues for outer residues surface of PP/30 % IFR; b SEM images of the inner residues surface of PP/30 % IFR; c EDS spectra of the char residues of PP/30 % IFR

fires [26]. The heat release rate (HRR) has come to be recognized as one of the most important fire properties of a material [27], and it is a measure of the heat release per

unit of surface area of burning materials. Figure 4 shows the HRR curves of the pure PP and flame retardant PP composites. It was noted that the pure PP resin burned very

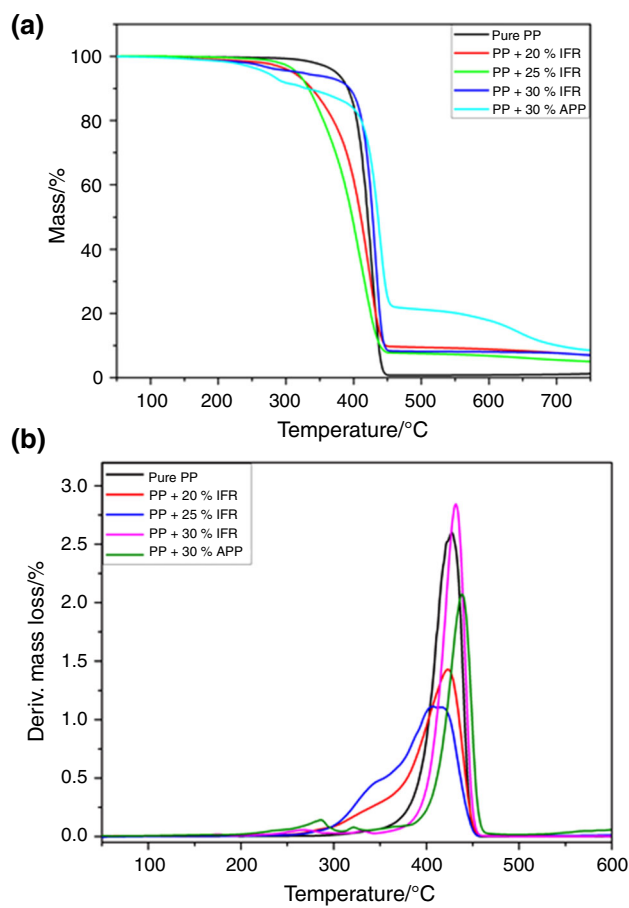


Fig. 8 TG (a) and DTG (b) curves of PP and its composites

fast after ignition and a sharp HRR peak appears with a peak PHRR of 842 kW m^{-2} . In the case of PP with 30 mass% of APP, the PHRR decreased to 489 kW m^{-2} . However, the PHRR of PP/IFR containing 20, 25, and 30 mass% of IFR was 473, 349 and 430 kW m^{-2} , respectively. It confirmed that this IFR was a more efficient flame retardant to PP compared to APP.

Table 3 Data obtained from TG and DTG curves

Samples	$T_{\text{onset}}/^{\circ}\text{C}$	$T_{\text{max}}/^{\circ}\text{C}$	$R_{\text{max}}/ \%^{\circ}\text{C}^{-1}$	Residue/%	
				500 $^{\circ}\text{C}$	750 $^{\circ}\text{C}$
PP	374	427	2.5	1.1	1.0
PP + 30 % APP	265	439	2.0	21.2	8.6
PP + 20 % IFR	315	425	1.4	6.6	6.5
PP + 25 % IFR	314	414	1.1	7.3	7.2
PP + 30 % IFR	309	430	2.8	7.6	7.5
EB PP + 20 % IFR*	340	440	1.9	10.9	10.8
EB PP + 25 % IFR*	337	438	1.8	7.3	7.2
EB PP + 30 % IFR*	325	437	1.8	7.5	7.4

* The composites were irradiated with a dose of 32 kGy

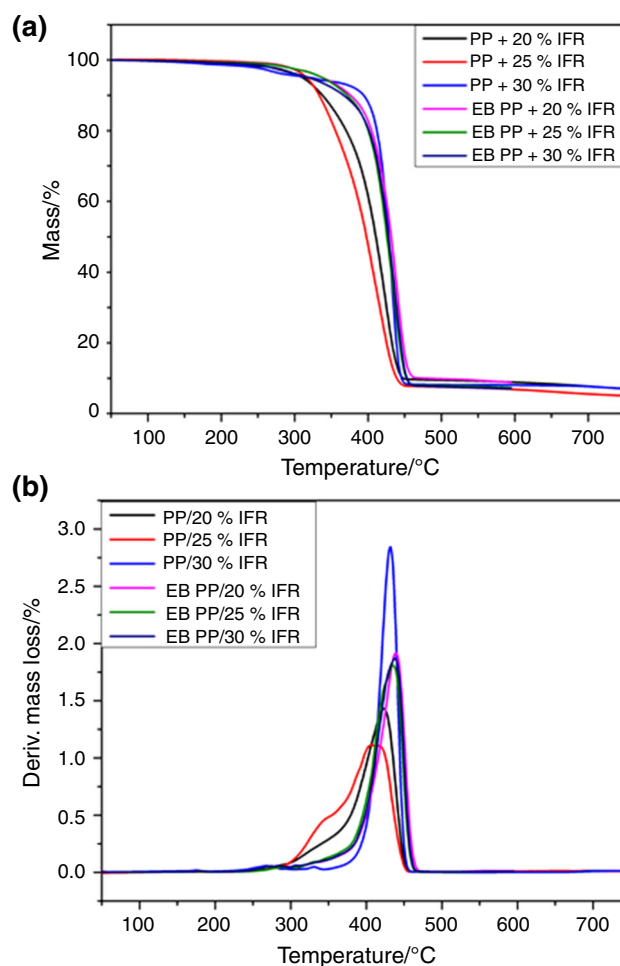


Fig. 9 TG (a) and DTG (b) curves of non-irradiated and irradiated flame retardant PP composites at 32 kGy

The total heat release (THR) is another important parameter for fire hazard evaluation. THR value of pure PP, PP/APP and PP/IFR composites are shown in Fig. 5. In comparison with pure PP, all the flame retardant PP composites (PP1,

PP2, PP3 and PP4, see Table 1) showed lower THR within the first 350 s. Consequently, these flame retardant PP composites showed a lower heat release during the combustion compared to that of pure PP. Further, the difference in the THR between PP3 and PP4 indicates that SPSA acts as an excellent flame retardant synergist to traditional APP since both composites contain 30 mass% flame retardant additives.

Morphology and structure of the char residues

From the digital photographs (as shown in Fig. 6) of the specimens after cone calorimeter test, there was almost no residue for pure PP. In comparison, after adding the flame retardant to PP, more char residues remained in the sample holder. In particular, by introducing IFR into PP, the quantity was increased and quality of formed char was improved. These improved char layers will act as good barrier to prevent the transmission of fuel and oxygen.

In order to further understand the relationship between the microstructure of intumescent chars and flame retardancy of PP composites, SEM micrographs of the char residues of the outer surface (Fig. 7a) and inner surface (Fig. 7b) of PP/30 % IFR were imaged. It is noted that the char morphology on the outer surface of PP/30 % IFR showed the formation of a continuous and compact char layer, which would act as an insulating barrier to heat and would prevent the access of oxygen during combustion. Aiming to further understand elements distribution on the char residues, energy dispersive spectrometry (EDS) was employed to characterize the residue. The results are shown in Fig. 7c. It is noted that in the elemental composition of the char residue of the PP/30 % IFR, the content of C, O, N, P were 34.37, 7.97, 36.78, 20.88 mass%, respectively. This means that rich P and N-based compounds are formed on the surface via varied decomposition and reconstruction approaches.

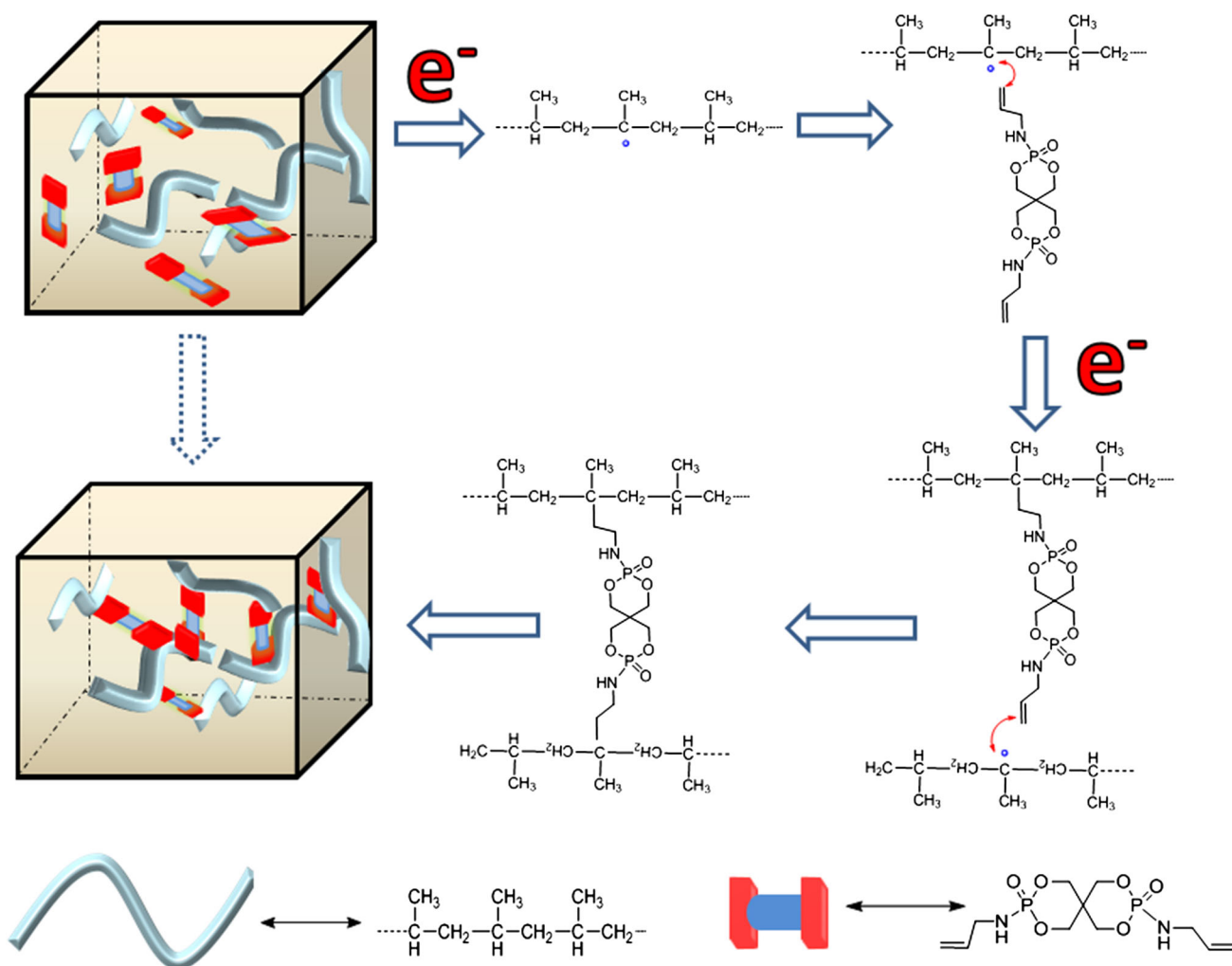


Fig. 10 Possible cross-linking mechanism

Thermal stability of flame retardant PP composites

The effect of IFR on the thermal stability of PP composites was revealed through TG test. TG and DTG curves of PP and its composites are shown in Fig. 8. The corresponding data are given in Table 3. From Fig. 8, it was observed that all samples studied showed only one degradation step within the experimental temperature range. It was clear from Fig. 8 and Table 3 that the addition of IFR had an obvious effect on the thermal stability of PP. The onset degradation temperature of pure PP, T_{onset} , defined as the temperature at which 5 % mass loss occurred, was 374 °C. In the case of PP with 30 mass% of APP, the onset degradation temperature decreased to 265 °C. In contrast, the T_{onset} of flame retardant PP composites containing 20, 25 and 30 % IFR were 315, 314 and 309 °C, respectively. This indicates that the addition of IFR decreased the thermal stability of PP-based composites. However, as given in Table 3, T_{max} of PP amounts to 427 °C, while the maximal decomposition temperature T_{max} of PP with 20, 25 and 30 % IFR was 425, 414 and 430 °C. Consequently, there is only a small impact on the T_{max} of PP after adding IFR.

Effect of electron beam irradiation on the thermal stability of flame retardant PP composites

Figure 9 presents the TG and DTG curves of non-irradiated and irradiated flame retardant PP composites, and the corresponding values are listed in Table 3.

Obviously, the thermal stability of flame retardant PP composites was remarkably improved via electron beam (EB) treatment. For example, T_{onset} of PP + 20 % IFR was increased from 315 to 340 °C after EB treatment. For the other flame retardant PP composites, a similar trend was shown. Moreover, the maximal decomposition temperatures (T_{max}) of flame retardant PP composites were also increased via EB treatment. Herein, a possible grafting and/or cross-linking mechanism between the novel flame retardant PP was proposed, as shown in Fig. 10. Firstly, electron beam treatment resulted in the generation of PP macroradicals. Then, the macroradical reacts with the C=C group presented in the SPSA to generate the first grafting reaction. The same reaction can be induced by the macroradicals at the second C=C group of SPSA. Finally, a cross-linked structure was generated in the flame retardant PP composites.

Conclusions

In order to develop high-performance flame retardant PP composites, in this article, a novel flame retardant, spirocyclic pentaerythritol bisphosphorate disphosphoryl-di-prop-2-en-1-amine (SPSA), containing two functional

double bond (C=C) that may form cross-linked structure with PP in the electron beam treatment was synthesized and characterized successfully. Then, an intumescent flame retardant (IFR) based on aluminum polyphosphate (APP) and SPSA (mass ratio of APP and SPSA at 2:1) was developed and used in PP system to prepare fire retardant PP composites. LOI value of flame retardant PP composite containing 30 % IFR was 24.0, while the LOI value of PP + 30 % APP was only 20.4. More importantly, PP + 30 % IFR passed UL 94 V-0, indicating that this IFR was more efficient than APP alone. In the cone calorimeter test, both PHRR and THR results of PP/IFR system were lower than those of PP/APP system. It proved that this IFR was a more efficient flame retardant to PP compared to APP. In addition, the analysis of char residues proved that this IFR provided relatively good quality of char residue in the combustion that acted as good barrier to prevent the transmission of fuel and oxygen. Moreover, it could be shown that electron beam treatment of the composites is an efficient approach to improve the thermal stability of these designed flame retardant PP composites. Further investigations on the optimized dose of electron beam irradiation will be reported in the future. This irradiated flame retardant PP system might be a promising formulation for the industrial application such as insulated material of wire, cable, etc.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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