



Highly effective flame retarded polystyrene by synergistic effects between expandable graphite and aluminum hypophosphite

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ABSTRACT

Herein, expandable graphite (EG) and aluminum hypophosphite (AP) are used to prepare flame-retardant polystyrene (PS) composites. The flame-retardant properties of the PS composites are investigated by the limiting oxygen index (LOI) test, vertical burning test (UL-94) and cone calorimetry test (CC). With 15 wt% EG or AP incorporated alone, the PS composites show limited improvement in LOI, and fail to pass the UL-94 test. In contrast, with 10 wt% EG and 5 wt% AP added, the sample (PS/10EG/5EG) passes the UL-94 V-0 rating, and its LOI value increases from 17% to 25.5%. CC results show that the PS/10EG/5AP has a significantly depressed peak heat release rate (PHRR) by 77.7%, total heat release (THR) by 39.3%, smoke product rate (SPR) by 78.2% and total smoke product (TSP) by 82.3%. Meanwhile, the flame-retardant mechanism of the PS composites is studied by SEM, XPS, TG-IR and Py-GC/MS, and the results of which indicating a combination of condensed-phase and gaseous-phase activity during combustion.

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1. Introduction

Polystyrene (PS) material is one of the most widely used general thermoplastic. The application areas include electronic appliances, car, packaging and building insulation due to its excellent electrical insulation, dimensional stability, and mechanical durability, etc. [1–3] However, once exposed under a fire, PS material catches fire easily and generates large amounts of black smoke and melt-dripping, which brings severe threat to life and property safety. These shortages limit its application in many fields. It is thus critical to endow PS with good flame retardancy.

Incorporation of flame retardants (FRs) into PS can effectively improve the fire safety of PS. Traditionally, halogenated FRs are effective and economic for PS because of the gaseous-phase mechanism by capturing the free-radicals [4,5]. Nevertheless, the European union have banned the usage of these kinds of halogenated FRs, such as brominated diphenyl oxide and hexabromocyclododecane (HBCD) because of the high toxicity during combustion. At present stage, more and more halogen-free FRs are

developed to replace halogenated ones for polymeric materials.

Among various halogen-free flame retardant (HFFR) additives, intumescent flame retardants (IFRs) are effective to improve the flame retardancy of PS materials. IFRs usually consist of an acid source, a char-forming agent and a blowing agent. For instance, a typical combination of ammonium polyphosphate (acid source), pentaerythritol (char-forming agent) and melamine (blowing agent) is used widely in polyamide-6 [6–8], polypropylene [9–11], ethylene-vinyl acetate copolymer [12,13] and epoxy resin [14,15]. Once a material with IFR is under fire, an intumescent char layer will generate through esterification, carbonization and expansion, which reduces the transfer of heat and oxygen and simultaneously protects the underlying material from further combustion. For flame retarded PS, Lu et al. [16] studied PS/APP/PER/MEL material and revealed condensed-phase mechanism. Yan et al. [17] reported a combination of ammonium polyphosphate (APP) with a new designed char-forming agent (CA). This flame-retardant PS shows a high LOI value of 32.5% and passes UL 94 V-0 rating with only 22.5 wt% APP and 7.5 wt% CA. Moreover, the peak heat release rate (PHRR), the total heat release (THR) and total smoke production (TSP) values of this PS/IFR decreased significantly. However, most IFRs can not avoid the shortage of a high loading amount, which increases cost and more importantly, compromise the physical and

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mechanical properties of the flame retardant products. In addition, typical IFRs have some obvious drawbacks, such as water solubility and moisture absorption. Therefore, it is critical to design more effective FRs for PS materials.

Expandable graphite (EG) is a special type of graphite flake in which sulfuric acid or nitric acid is intercalated between the graphite layers. Expanded graphite can expand and form “worm-like” char layer covering the surface of matrix at a certain temperature, which act as a barrier to restrain the transfer of heat and mass between burning zone and underlying matrix [18]. Shi et al. [19] studied the size effect of EG on the flame retardance of high density PUF and found that flame retardance of high density PUF increased with the particle size of EG. In addition, EG is usually used with other halogen-free FRs to further improve the flame-retardant efficiency. Zhu et al. [20] studied the synergistic effect between EG and APP on poly(lactic acid). The corresponding PLA composite containing both EG and APP showed a LOI value of 36.5% and passed the UL-94 V-0 rating with a condensed-phase flame retardant mechanism. Yuan et al. [21] investigated the synergistic effect of Bis(4-hydroxybutyl) phenylphosphonate (BHPP), melamine-derived polyol (MADP) and EG on the flame retardant rigid PUF and found the synergistic effect between BHPP and MADP could promote the char formation of the rigid PUF/EG. Moreover, EG is also used as a FR for high-impact polystyrene [22,23], rubber [24], ethylene-vinyl acetate copolymer [25,26], etc. However, the flame retardant mechanisms of PS/EG and PS/EG/HFFR need further discussion.

Another effective flame retardant for PS is aluminium hypophosphite (AP). Yan et al. [27] prepared PS/AP composite which presented good flame retardancy. Its LOI value was 25.2% and passed UL-94 V-0 rating with a loading of 25 wt% AP. Moreover, the peak heat release rate (PHRR) and the total heat release (THR) values were reduced significantly. Nonetheless, it is clearly shown that more than 25% of FRs are required to achieve a high flame retardancy (i.e. passing the UL-94 V-0 rating).

In this study, both EG and AP are used as additive FRs for PS composites. The thermal and flame-retardant properties of the PS composites are well investigated, and the synergistic mechanism in flame retardancy is discussed.

2. Experimental

2.1. Materials

Polystyrene (GP5250) was purchased from Dongguan Plastics & Rubbers materials Co., Ltd (Guangzhou, China). Expandable graphite (EG) (average particle size: 300 μm ; expansion coefficient: 255; setoff temperature: 250 $^{\circ}\text{C}$) was provided from Shijiazhuang ADT Carbonic Material Factory (Shijiazhuang, China). Aluminum hypophosphite (AP) was provided by Jinan Taixing Chemical Co., Ltd. (Shandong, China).

2.2. Sample preparation

Firstly, PS, EG and AP were dried at 80 $^{\circ}\text{C}$ for 8 h through a vacuum oven. Then dried PS blends with different ratios of EG and AP were mixed for about 10 min at 200 $^{\circ}\text{C}$ under 100 rpm via a Banbury mixer (SX300). Finally, these blends were hot-pressed into different samples under 10 MPa for 10 min at 200 $^{\circ}\text{C}$ for combustion tests.

2.3. Measurement

The LOI test was performed on a HC-2C oxygen index meter (Jiangning, China) according to ASTM D2863-97. Samples

dimension was 130 mm \times 6.5 mm \times 3.2 mm.

UL-94 test was performed on a CZF-2 instrument (Jiangning, China) according to ASTM D3801. Samples dimension was 130 mm \times 13 mm \times 3.2 mm.

Combustion behaviors were measured with a cone calorimeter (CC) device (Fire Testing Technology). The samples with a size of 100 mm \times 100 mm \times 3.2 mm were exposed to a radiant cone at a heat flux of 35 kW/m².

Thermogravimetric analysis (TGA) was performed on TG 209 F1 (NETZSCH, Germany). The sample (3–5 mg) was heated from 40 to 700 $^{\circ}\text{C}$ at a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under a the nitrogen flow of 50 mL/min.

Morphology of the char residues of the flame-retardant PS was observed by a JEOL JSM-5900LV scanning electronic microscopy (SEM). The char residues were recorded after gold coating surface treatment under a high vacuum at a voltage of 20 kV.

X-ray photoelectron spectroscopy (XPS) were recorded by a XSAM80 (Kratos Co., UK), using Al Ka excitation radiation ($h\nu = 1486.6 \text{ eV}$).

Thermogravimetric analysis/infrared spectrometry (TG-IR) was performed using a TG 209F1 thermogravimetric analyzer and a Nicolet 6700 FT-IR spectrometer to analyze the gaseous products of samples during the decomposition. About 8 mg of the sample was heated from 40 to 700 $^{\circ}\text{C}$ a heating rate of 10 $^{\circ}\text{C}/\text{min}$ under a the nitrogen flow of 50 mL/min.

Pyrolysis GC/MS test was performed in a CDS 5200 Pyroprobe under a helium atmosphere. The samples (500 μg) was heated from ambient to 600 $^{\circ}\text{C}$ at a rate of 1000 $^{\circ}\text{C}/\text{min}$ and kept for 10 s. The pyrolyzer was coupled with a DANI MASTER GC-TOF-MS systems. The temperature program of the capillary column of GC was as follow: 2 min at 50 $^{\circ}\text{C}$, temperature increased to 300 $^{\circ}\text{C}$ at a rate of 10 $^{\circ}\text{C}/\text{min}$ and kept for 10 min. The injector temperature was 300 $^{\circ}\text{C}$. MS indicator was operated in the electron impact mode at electron energy of 70 eV, and electron source temperature was kept at 180 $^{\circ}\text{C}$. The detection of mass spectra was carried out using a NIST library.

3. Results and discussion

3.1. Flame retardancy of PS composites

Limiting oxygen index (LOI) and UL-94 rating are basic and critical parameters to evaluate the flammability of a polymeric material. The results of LOI values and UL-94 ratings of PS and its flame retarded composites are summarized in Table 1. PS is highly flammable with a LOI value of only 17% and gets no rating in UL-94 tests. Addition of EG or AP alone increases the LOI value of PS composites to a certain extent. For instance, when the addition content of EG is 30%, the LOI value increases to 25%. However, the PS/30EG fails to pass the UL-94 V-0 rating. In contrast, the PS/25AP composite with 25 wt% AP passes UL-94 V-0 rating, and obtains a LOI value of 25.6%. All of the testing samples with 20 wt% of both EG and AP (EG/AP = 1:1, 1:2, 1:3, 1:4, 2:1 and 3:1) can pass V-0 rating. In contrast, PS composites with 20 wt% EG or AP alone can not pass the UL-94 V-0 rating. When the FR content is 15 wt%, the PS/10EG/5AP still passes the UL-94 V-0 rating and possesses a LOI value of 25.5%. These results imply a synergistic effect between EG and AP which impart the PS composites good flame retardancy.

To verify the synergistic efficiency (SE) between EG and AP, the quantitative calculation of synergistic efficiency are calculated by Equation (1) [28]. In the equation, P, A and B represents polymer, flame retardant A and flame retardant B, respectively. Where x and y is the amount of flame retardant A and B in wt%, respectively. Moreover, M is specific parameter in fire property such as LOI, PHRR, THR and Residue. The value of $SE > 1$ indicates a synergistic

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