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Flame retardance and thermal degradation mechanism of polystyrene modified with aluminum hypophosphite

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ABSTRACT

A phosphorus-containing inorganic compound, aluminum hypophosphite (AP), was used to prepare flame-retardant polystyrene (PS). The flammability of the PS/AP composites was investigated by the limiting oxygen index (LOI), vertical burning test (UL-94) and cone calorimeter test. When the content of AP reaches 25 wt%, the LOI of PS/AP is 25.6% and it passes UL-94 V-0 rating. The results of cone calorimeter test show that the heat release rate (HRR), the total heat release (THR) and the mass loss rate (MLR) of PS/AP composites are significantly reduced. The thermal degradation mechanism of PS/AP was investigated by thermogravimetric analysis (TGA), Fourier transform infrared spectrometry (FTIR), thermal gravimetric-Fourier transform infrared spectrometry (TG-FTIR), pyrolysis gas chromatography-mass spectrometry (Py-GC/MS), and X-ray photoelectron analysis (XPS) tests. The results indicate that PS/AP has a combined gas-phase and condensed-phase activity in the combustion and degradation of the composites. Consequently, a possible flame-retardant mechanism of PS/AP composites is proposed.

1. Introduction

Polystyrene (PS) is a widely used plastic because of its outstanding properties, such as thermal resistance, low density, excellent mechanical durability and convenience of processing and molding. However, its high flammability and severe melt-dripping during combustion greatly limit the application in some areas [1,2]. To solve this problem, some halogen-containing and halogen-free flame retardants have been used to obtain flame-retardant PS [3–9] with desired UL-94 rating and high oxygen index.

Phosphorus-containing compounds are known as the effective and promising flame retardants for PS. Many commercial phosphorus-containing flame retardants, such as red phosphorus, tris (2,4-di-ter-butylphenyl) phosphate (TBP), polyphosphoric acid (PPA) and ammonium polyphosphate (APP), are used to improve the flame retardance of PS [9–11]. However, a single phosphorus-based additive or combinations of phosphorus with other traditional synergists can only result in a V-2 or V-1 rating in UL-94 test and some improvement in the oxygen index (OI).

Intumescent flame retardants (IFRs) are very effective for PS because of their typical condensed-phase activity. In our previous work, PS/IFR composites exhibited excellent flame retardance [9]. In addition, inorganic nanofillers are usually used as synergists to enhance the flame-retardant efficiency of PS/IFR composites [12–14], but the cost of IFR is often too high.

Inorganic compounds are the most cost-effective and environmentally friendly. Hydroxides such as $Mg(OH)_2$ and $Al(OH)_3$ can alter the decomposition pathways of PS during the combustion, promote incomplete combustion and decrease combustibility of PS [15]. However, phosphorus-containing compounds such as red phosphorus are usually added as synergists for PS/hydroxide composites because of the low flame-retardant efficiency of hydroxides (40 wt% nano-modified ATH cannot make PS pass UL-94 rating) [16]. A small number of layered double hydroxide (LDH) (usually less than 10 wt%) can significantly improve the thermal stability and flammability property of PS [17–19], but it is difficult to achieve a desired UL-94 rating for PS/LDH composites. Metal salts of alkylphosphonic or dialkylphosphinic acids are also found efficient in improving the flame retardance of styrenic polymers. For example, 11 wt% loading of the aluminum salt of methyl methylphosphonic acid which was in commercial development in the early 1990s gives a V-2 rating and increases 2–4% of LOI for PS [20]. Ethylenediamine phosphate which is commercially available was also reported to give a V-2 rating in styrenic polymers [21]. In summary, V-0 rating is hard to reach for PS/inorganic flame retardant composites when the additive amount is low.

Recently, aluminum hypophosphite (AP) has attracted a lot of attention of researchers because of its cost-effective and high-

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efficiency in flame retardance [22–25]. However, the flame-retardant properties and mechanism of PS/AP composite are seldom reported in literature. In the present paper, AP was used as a flame retardant of PS. The flammability and thermal degradation behaviors of PS/AP composites were studied and the flame-retardant mechanism of PS/AP was also investigated.

2. Experimental

2.1. Materials

Polystyrene (GP5250) was purchased from Formosa Chemicals & Fibre Corporation (Taipei, Taiwan), which was dried in the oven at 80 °C for 8 h prior to blending. Aluminum hypophosphite was prepared according to the previous literature [26].

2.2. Sample preparation

Dried PS and AP with different weight ratios (20 wt%, 25 wt% and 30 wt%) were fed into the twin-screw extruder at 205 °C with the *L*/*D* ratio of 44 and a rotation speed of 100 RPM to obtain PS/AP extrudates. Then the extrudates were comminuted into pellets and the pellets were compression molded into standard testing bars.

2.3. Measurement

The LOI values were measured on an HC-2C oxygen index meter (Jiangning, China) according to ASTM D2863-97 and the dimension of all samples is 130 mm × 6.5 mm × 3.2 mm.

The UL-94 test was performed on a CZF-2 instrument (Jiangning, China) according to ASTM D3801 and dimension of all samples is 130 mm × 13 mm × 3.2 mm.

The combustion behaviors were measured with a cone calorimeter device (Fire Testing Technology). The samples with a size of 100 mm × 100 mm × 6 mm were exposed to a radiant cone at a heat flux of 35 kW/m^2.

Thermogravimetric analysis (TGA) was carried on a TG 209F1 (NETZSCH, Germany) thermogravimetric analyzer at a heating rate of 10 °C/min under N_2 and air, respectively.

FT-IR spectra were recorded using an FT-IR spectrometer (Nicolet 6700) using KBr pellets.

Thermogravimetric analysis-infrared spectrometry (TG-IR) was performed using TG 209F1 (NETZSCH, Germany) thermogravimetric analyzer and FT-IR spectrometer (Nicolet 6700) to determine the vapor products of the sample during the decomposition. The sample was heated from 40 to 700 °C with a heating rate of 10 °C/min under N_2.

Pyrolysis GC/MS test was performed in a Pyroprobe (CDS 5000). The pyrolysis chamber with the relevant sample (AP, 500 μg) was heated from ambient to 600 °C at a rate of 1000 °C/min and kept for 10 s. The pyrolyzer was coupled with a GC/MS operation (6890N-5975). The temperature program of the capillary column of GC was as follow: 2 min at 40 °C, temperature increased to 300 °C at a rate of 10 °C/min and kept for 10 min. The injector temperature was 250 °C. MS indicator was operated in the electron impact mode at electron energy of 70 eV with the electron source being kept at about 180 °C. The detection of mass spectra was carried out using a NIST library.

XPS spectra were recorded by a XSAM80 (Kratos Co., UK), using Al Kα excitation radiation ($h\nu$ − 1486.6 eV). The morphologies of the char residues collected after the cone calorimeter tests, were observed using scanning electron microscopy (JEOL JSM 5900LV).

Table 1
The LOI test and UL-94 test results of PS with different content of AP.

Sample	PS (wt%)	AP (wt%)	LOI (%)	UL-94
PS	100	0	17.0	NR
PS/20AP	80	20	24.5	V-2
PS/25AP	75	25	25.6	V-0
PS/30AP	70	30	26.0	V-0

3. Results and discussion

3.1. Flammability of PS/AP composites

3.1.1. LOI and UL-94 tests

The LOI tests and vertical burning tests (UL-94) were carried out at the room temperature to investigate the flame retardance of the PS/AP composites. The detailed data are listed in Table 1. Neat PS is a highly flammable thermoplastic with very low LOI value (17.0%), no UL-94 rating and serious melt-dripping during burning. The LOI of PS composites is obviously increased with the addition of AP. When the addition of AP is increased to 25 wt%, the LOI of PS/AP is increased to 25.6%. Meanwhile, UL-94 rating is enhanced to V-0 of PS/25AP from V-2 of PS/20AP. LOI value of PS/30AP is further increased to 26.0% and V-0 can be achieved. The results indicate that the flame retardance of PS composites is increased significantly with the addition of AP.

3.1.2. Cone calorimetric analysis

Cone calorimetry is one of the most widely used techniques to evaluate the flammability of polymeric materials. The combustion environment of the sample in the test is similar to the real scale fire, so the fire performance of the materials can be evaluated by the results of the cone calorimeter [27–32]. The detailed cone calorimetric parameters of neat PS and PS/AP composites at an incident heat flux of 35 kW/m^2 are listed in Table 2. The data include the time to ignition (TTI), the peak of heat release rate (PHRR), the time to PHRR (t_p), the total heat release (THR), the mass loss rate (MLR), and the value of the residual char. Compared with the TTI of 67 s for neat PS, the TTI of the PS/30AP is decreased to 37 s which may be caused by the comparatively low thermal stability of AP. However, the initial decomposition of AP can play a role in the flame retardance of the composites [33] during combustion.

Fig. 1a shows the HRR of PS and flame-retardant PS/30AP. The PHRR of PS/30AP composite is decreased by 84%, which means the flame retardance of the system is improved significantly. Moreover, the curves show that the total burning time of PS/30AP is increased largely compared with that of neat PS, which is typical for a residue-forming material [34]. The t_p of PS/30AP is decreased, it is also because of the comparatively low thermal stability of AP. An obvious decrease of THR of PS/30AP is observed compared with that of neat PS (Table 2 and Fig. 1b). The THR of PS/30AP is decreased to 69 MJ/m^2, while that of neat PS is 188 MJ/m^2. Fig. 2 shows the mass loss as a function of the combustion time for the samples. Adding AP increases the burning residues of PS/AP system and decreases the mass loss rate remarkably. The mass loss rate of pure PS is 0.128 g/s (Table 4), and the value decreases to 0.0026 g/s

Table 2
Cone calorimetric data of PS and PS/30AP.

Sample	TTI (s)	PHRR (kW/m^2)	t_p (s)	THR (MJ/m^2)	MLR (g/s)	Residual char (%)
PS	67	743	305	188	0.128	0
PS/30AP	37	122	80	69	0.026	65.1