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A novel flame-retardant acrylonitrile-butadiene-styrene system based on aluminum isobutylphosphinate and red phosphorus: Flame retardance, thermal degradation and pyrolysis behavior

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ABSTRACT

Aluminum isobutylphosphinate (APBu) and its synergistic system with red phosphorus (APBu/RP) were used to flame-retard ABS. With the addition of APBu to ABS, the flame retardance of the material was greatly improved, that LOI value was as high as 29.8%, and a UL-94 V-0 rating was obtained; moreover, heat release parameters obtained from cone calorimetry decreased. However, the smoke release of the material during combustion increased. When RP was added to ABS-APBu system, flame-retardant synergism was gained, and it was helpful to reduce the smoke release of the material. The decomposition behaviors of materials were studied by thermogravimetric analysis (TG), and it was found that the residues of materials at 700 °C increased with the addition of APBu or APBu/RP. The flame-retardant mechanisms of APBu and APBu/RP were analyzed by Fourier transform infrared spectrum (FTIR), scanning electron microscopy (SEM) and pyrolysis-gas chromatograph/mass spectrometer (Py-GC/MS). Results suggested that the addition of RP to ABS-APBu further enhanced the flame retardation of APBu both in the gaseous phase and condensed phase, leading to a high synergistic effect.
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1. Introduction

Acrylonitrile-butadiene-styrene (ABS) consisting of polybutadiene as discrete phase and styrene-acrylonitrile copolymer as continuous phase, is employed widely in automobile parts, toys, washing machines, electric fans, televisions, etc, due to its good mechanical performance, chemical resistance and ease of processing [1–5]. However, ABS is highly combustible, and the combustion always accompanies with the production of toxic gases and smoke, which restricts its wider application, particularly in electronic & electrical equipments and transportations. Consequently, it is necessary to enhance the flame retardance of ABS.

The polymers most difficult to be flame-retarded are those which barely form char after decomposition or combustion, such as polyolefin, styrenics and acrylics [6]. Nowadays, flame retardants in commercial use for ABS are mostly halogen-containing ones, however, halogen-containing flame retardants have been phased out for their proven or suspected adverse effects on the environment and ecological health, thus halogen-free flame retardants now have been gradually developed to meet the constantly changing demand of new regulations, standards and test methods [7].

Aluminum hypophosphite and alkylphosphinates are now widely used to flame-retard polymers containing oxygen, due to its low loading and high flame-retardant efficiency, especially in polyamides [8–13], polylactide [14,15], poly(vinyl alcohol) [16] and poly(butylene terephthalate) [17–22]. Hu and his co-workers [13] reported that glass-fiber-reinforced polyamide 6 easily passed UL-94 V-0 rating with 15 wt% addition of aluminum isobutylphosphinate (APBu); Tang et al. [14] also found that aluminum hypophosphite (AP) was fit to flame-retard polylactide at 20 wt% loading. A 15 wt% loading of AP to PVA was found with V-0 rating and LOI value as high as 28.0% [16]. Braun et al. investigated that glass-fiber-reinforced PBT with 13–20 wt% loading of aluminum diethylphosphinate fulfilled the flame-retardant requirements (UL-94 V-0 and LOI value >42%) [22]. Furthermore, Zhao and his co-workers [9,10] found that the pyrolysis products of AP or APBu both contained high proportion of P_4, indicating that P_4 might have a great effect on the flame retardation of both AP and APBu. It was reported that RP also generated P_4, and in non-polar polyolefin, RP was barely fixed in the condensed phase. In this case phosphorus

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sublimated, resulting a gas-phase mechanism [7]. It was noteworthy that RP was also used as a synergistic additive. Schartel [23] reported that RP combined with magnesium hydroxide were used to flame-retard HIPS. The fire behavior of flame-retardant HIPS were analyzed in detail, and the improvement of fire behavior in terms of heat release was found. Cai [24] also reported that intumescent flame-retardant ABS based on ammonium polyphosphate together with RP, could easily obtain a V-0 rating and high LOI value. Therefore, it should be meaningful to investigate whether APBu had synergistic effect with RP to cause effective gas-phase activity.

However, metal hypophosphite or phosphinates were rarely used to flame-retard ABS [25]. Thus it was meaningful to investigate the flame retardance of APBu in ABS. In this manuscript, APBu and APBu/RP system were used to flame-retard ABS. Flame-retardant properties and combustion behavior of the flame-retardant ABS composites (FR-ABS) were evaluated by limiting oxygen index (LOI), Underwriter Laboratory 94 vertical burning test (UL-94 V) and cone calorimetric analysis. Thermal stability of FR-ABS were investigated by thermogravimetric analysis (TG), and the residues after TG tests at different temperatures were also characterized by FT-IR spectra. The char morphology of the composites after LOI tests were investigated by scanning electronic microscopy (SEM). Moreover, Py-GC/MS was used to study the pyrolysis behaviors of the flame retardants.

2. Experimental

2.1. Materials

ABS resin (MFI: 19 g/10 min, product code: PA-757K) was purchased from CHIMEI chemical Co., Ltd, Zhenjiang, China. Aluminum isobutylphosphinate (APBu), a mixture of aluminum mono-isobutylphosphinate (58 wt%) and aluminum di-isobutylphosphinate (42 wt%), was prepared in our laboratory [9], and red phosphorus (RP) without treatment was provided from Kelong Chemical Co., Ltd, Chengdu, China.

2.2. Preparation of FR-ABS

ABS resin was dried in a vacuum oven at 80 °C for 2 h, and APBu together with RP were dried in a vacuum oven at 80 °C for 8 h prior to processing. ABS resin and flame retardants were mixed uniformity according to the corresponding mass ratio, then the mixtures were fed into twin-screw extruder ($L/D = 20$) which was operated with rotation speed of 100 rpm at 190, 200, 210, 210, 200 and 190 °C from feed inlet to die, respectively; next the extrudates were cut into pellets, finally the pellets were compression-molded in 10 MPa at 220 °C, cut into standard testing bars for UL-94, LOI and cone calorimeter tests, respectively.

2.3. Measurement

The measurement of melt flow index (MFI) was carried out through melt flow rate meter (XNR-400AM, Chengde Shipeng Detection Equipment, China) under the pressure of 10 kg weight at 220 °C according to ISO 1133-2011.

Flame retardance of FR-ABS was measured by LOI, and UL-94 vertical burning test. LOI values were evaluated according to ASTM D2863-97 with the three-dimensional size of 130 mm × 6.5 mm × 3.2 mm; UL-94 vertical burning ratings were assessed according to ASTM D3801 with the three-dimensional size of 130 mm × 13 mm × 3.2 mm. Combustion behavior of the samples with three-dimensional size of 100.0 mm × 100.0 mm × 3.0 mm were measured with a cone calorimeter device (Fire Testing Technology, East Grinstead, UK) exposing to a radiant cone at a heat flux of 35 kW/m^2 according to ISO 5660-1. Tests were duplicated up to three times, depending on whether the deviation between the results was <10%.

Thermogravimetric analysis (TGA) were experimented by using NETZSCH 209 F1 apparatus in nitrogen and air atmosphere with a flow rate of 60 mL/min. Samples (4–5 mg) placed in the Al_2O_3 pans were heated from 40 to 700 °C at a heating rate of 10 °C/min.

The samples (8–10 mg) suspended at different temperatures during TGA were characterized by Fourier transform infrared spectrum (FTIR), which was performed on a Nicolet FTIR 170SX infrared spectrometer with KBr pellets.

Scanning electron microscopy (SEM) was used to study the surface morphology of the burning residue after LOI tests on a JEOL JSM-5900LV microscope under an accelerating voltage of 20 kV. A thin layer of gold was sprayed on the surface prior to SEM observation.

Py-GC/MS tests were performed in a pyrolyzer (CDS5200). The pyrolysis chamber was full of helium; the relevant samples (300 μg) were heated from ambient to 600 °C at a heating rate of 1000 °C/min and kept for 20 s. The pyrolyzer was coupled with DANI MASTER GC-TOF-MS Systems, and the carrier gas was also helium. For the operation, the temperature program of the capillary column (DN-1701 FAST 10 m 0.10 mm 0.10 mm) of GC was as following: 2 min at 45 °C, temperature increased to 280 °C at a rate of 15 °C/min then kept at 280 °C for 5 min. The injector temperature was 300 °C. MS indicator was operated in the electron impact mode at electron energy of 70 eV, and the ion source temperature was kept at 180 °C. The components detected from py-GC/MS are contrasted with NIST mass spectral database.

3. Results and discussion

3.1. Melt flow index of FR-ABS

MFI was often used to assess the melt flow behavior of thermoplastic materials, and the higher MFI value of a material showed, the better the flowability it exhibited. In this work, MFI values of ABS, ABS-20 wt% APBu, ABS-30 wt% APBu and ABS-20 wt% 3APBu/1RP were listed in Table 1. It was found that, with the addition of 30 wt% APBu, MFI of flame-retardant ABS composite decreased, and the flowability of composite was restricted due to the filling effect of APBu. While MFI of ABS-20 wt% APBu and ABS-20wt% 3APBu/1RP was reduced by a little, and it would not affect the melt flowability of ABS remarkably.

3.2. Flame retardance of FR-ABS

UL-94 V and LOI were always used to evaluate the flame retardance of materials, and the experimental results were listed in Table 2. When total dosage of APBu was 20 wt% in ABS, though UL-94 was still no rate (NR), LOI value increased from 18.2 to 26.0%. With the loading of APBu further increased to 25 wt%, a V-0 rating was achieved, but the LOI value was not much improved (26.9%). The best flame retardance was obtained at the 30 wt% loading of APBu, which the LOI value further increased to 29.8%. In addition, P_4

Table 1
Melt flow indexes of ABS and FR-ABS.

Samples	MFI (g/10 min)
ABS	18.8
ABS-20 wt% APBu	14.2
ABS-30 wt% APBu	7.0
ABS-20 wt% 3APBu/1RP	13.2

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