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Synergistic effect of zinc hydroxystannate with intumescent flame-retardants on fire retardancy and thermal behavior of polypropylene

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ABSTRACT

The flammability and thermal degradation properties of polypropylene (PP) composites containing zinc hydroxystannate (ZHS) and intumescent flame retardant additives (IFR), i.e. ammonium polyphosphate (APP) and pentaerythritol (PER) were characterized respectively by limiting oxygen index (LOI), UL-94 measurements, Cone calorimeter test (CCT) and Thermogravimetry analysis (TGA) in this work. A synergistic effect in flame retardancy was observed when ZHS was used in combination with APP and PER. The experimental data indicated that ZHS enhanced the LOI value, UL-94 ratings and restricted the dripping of the composites. The PP/IFR composites passed the UL-94 V-0 rating test in the presence of 1 wt% ZHS. The CCT tests indicated that the heat release rate (HRR), peak rate of heat release (PHRR) and mass loss rate (MLR) values of the PP/IFR/ZHS samples were much lower than those of the PP/IFR and pure PP samples. The TGA results showed that ZHS could accelerate the char formation of IFR, therefore, greatly increase the thermal stability of PP composites. The Fourier transformed infrared spectra (FTIR) revealed that the flame retardant mechanism of ZHS could be ascribed to its catalysis degradation of the PP resin, which promoted the formation of charred layers with the P–O–P and P–O–C complexes in the condensed phase. SEM observation further indicated that ZHS could promote forming stable and compact intumescent char layer and effectively protect the underlying polymer from burning.

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1. Introduction

Very recently, polypropylene (PP), as one of the three most common general plastics, is wildly used in industry and our daily life such as automotive and electrical engineering materials [1]. However, due to its poor flame-resistance, the applications of polypropylene have been very limited [2,3].

Thus, several kinds of flame retardant additives, such as bromide, chloride, phosphorus, antimony, aluminum and boron-containing compounds have been used to reduce the flammability of PP [4,5]. However, the use of halogenated organic compounds has been limited due to the environmental concerns. Therefore, low toxic environmental friendly flame retardant such as the intumescent flame retardant has found an important place in the flame retardant markets [6]. The proposed mechanism of intumescent flame retardant materials is the foamed cellular layer, which is formed during heating process, on their surface protects the underlying materials from the action of heat flux and flame. The formed charred layer will act as a physical barrier that slows down heat and mass transfer between the gas and condensed phase and protects the underlying material from flux or flame [7–9].

The most widely reported intumescent flame retardant system are ammonium polyphosphate (APP) and pentaerythritol (PER), which when the ratio of APP/PER is 3 the system performs the maximum flame retardancy [10]. However, there is a poor flame retardant efficiency when the IFR additives are at a low concentration. Therefore, the use of synergistic agents to the PP/IFR system represents a good way to solve the above problems. Some authors have shown that 4A zeolites, some transitional metal oxides and metal compounds can act as synergist to effectively promote the strength and stability of char layer [11–14]. Zinc hydroxystannate has a variety of application in replace of antimony trioxide in polyester resins containing halogenated flame retardants [15,16]. Meanwhile the Zn^{2+} ion can be used as a Lewis acid for catalyzing esterification and dehydrogenation [17], as a result forming a compact residue layer, and then a positive to the flame retardancy in halogen free systems is found. However, there are few reports about zinc hydroxystannate used in IFR polypropylene composites. In this work, synthesized zinc hydroxystannate (ZHS) as a synergistic agent was used to improve the flame retardancy of

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intumescent PP composites. The effects of ZHS on the flame retardancy and thermal behavior of polypropylene were evaluated by LOI, UL-94 standard, CCT and TGA. FTIR was used to identify the composition of the residue char obtained from CONE test, which could explain how this synergistic effect happened. SEM observation further indicated the synergistic effect of ZHS on flame retardant PP composites. Thermal degradation kinetics of the flame retardant PP composites was also investigated.

2. Experimental

2.1. Materials

The matrix polymer used in this study was polypropylene, PP (1215-c, pellets products). Pentaerythritol (PER, white powder, AR grade) was provided by Sinopharm Chemical Reagent Co. Ltd. Ammonium polyphosphate, APP, was supplied by Xingxing flame retardant Co. Ltd. Zinc oxide, ZnO, and tin oxide, SnO_2, were purchased from Sinopharm Chemical Reagent Co. Ltd. Zinc hydroxystannate (ZHS) and zinc stannate (ZS) was synthesized in our laboratory.

2.2. Preparation of samples

2.2.1. Synthesis of zinc hydroxystannate and zinc stannate

The zinc hydroxystannate (ZHS) was obtained by adding dropwise of 100 ml zinc chloride (0.034 mol) aqueous solution into 250 ml of sodium stannate (0.037 mol) aqueous solution, vigorous stirred at 60 °C for 1 h. Then, the precipitate was filtered, washed with distilled water until pH value was 7, and finally vacuum dried in oven at 60 °C for 24 h. After the ZHS was calcined at 320 °C for 10 h, zinc stannate (ZS) was obtained.

2.2.2. Preparation of PP composites

All flame retarded PP composites were prepared using the CM reciprocating single-screw extruder (CM-30). The temperature range of the single-screw extruder was set at 160–200 °C. Compositions are listed in Table 1. The resulting compounds were subsequently dried in an oven and were further injection molded into bars with an injection molding machine (HTF86X1) for fire properties characterizations. The composites were injected into standard testing bars for the tests of combustibility.

2.3. Characterization

2.3.1. Limiting oxygen index (LOI) and UL-94 testing

Limiting oxygen index (LOI) was carried in an HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) with samples measurement 120 × 10 × 4 mm, following the procedure described in the ASTM D2863 standard. UL-94 tests were performed on vertical testing apparatus (CZF-2, Jiangning Analysis Instrument Factory, China), with sample dimensions of 130 × 13 × 3 mm according to the UL-94 test standard.

Table 1
Formulation of the flame retardant PP composites.

Sample	PP (wt%)	IFR[a] (wt%)	ZHS (wt%)	ZnO (wt%)	SnO_2 (wt%)	ZS (wt%)
Pure PP	100	–	–	–	–	–
PP/IFR	75	25	–	–	–	–
PP/IFR/ZHS1	75	24	1	–	–	–
PP/IFR/ZHS2	75	23	2	–	–	–
PP/IFR/ZHS3	75	22	3	–	–	–
PP/IFR/ZHS4	75	21	4	–	–	–
PP/IFR/ZnO	75	24	–	1	–	–
PP/IFR/SnO_2	75	24	–	–	1	–
PP/IFR/ZS	75	24	–	–	–	1

[a] IFR: APP/PER = 3/1, by weight.

2.3.2. Cone calorimeter test

All cone data were taken from a low oxygen standard cone calorimeter (manufactured by fire testing technology) at an incident heat flux of 50 kW/m^2 according to ISO 5660-1 standard. All samples (100 × 100 × 3 mm^3) were laid on a horizontal sample holder.

2.3.3. Thermal analysis measurements

Thermogravimetric analysis (TGA) was carried out in nitrogen at a heating rate of 10 °C/min using a NETZSCH STA409 PC thermo-analyzer instrument. In each case, 10 mg sample was examined under a nitrogen flow rate of 20 ml/min from 40 to 600 °C. The thermal degradation kinetic of PP composites was investigated with a heating rate of 5, 10, 15 and 20 °C/min in the temperature range of 30–700 °C under a nitrogen flow.

2.3.4. Scanning electron microscopy

Scanning electron microscopy (SEM) was used to examine the morphology of the residue char obtained from CONE test by using a SUPRA 55/55VP SEM, whose accelerating voltage was 15 kV. The surface of residue char was sputter-coated with gold layer before examination.

2.3.5. FTIR

Samples for FTIR measurements, which obtained from the residue char after CONE test, were mixed with KBr powders and pressed into a tablet. The FTIR spectra were obtained using an FTIR spectrophotometer (NEXUS 670) in the range from 390 to 3700 cm^{-1}.

3. Results and discussion

3.1. LOI and UL-94 rating

Fig. 1 gives the XRD diagram of ZHS and ZS. According to XRD result, ZHS has body centered cubic structure with the unit cell parameters of $a = b = c = 7.80$ Å, which is in full agreement with the ICSD card no: 20-1455; ZS has hexagonal structure with the unit cell parameters of $a = 5.28$ Å, $c = 14.09$ Å, which is corresponding with the ICSD card no: 89-0095. Fig. 2 gives the SEM image of ZHS, it shows that the ZHS particle has a regular cubic sharps and its

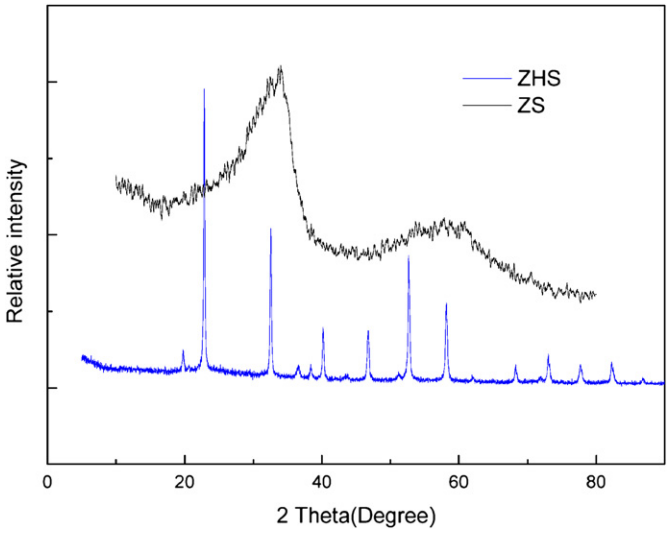

Fig. 1. XRD pattern of ZHS and ZS.

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