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Influence of zinc borate on the flame retardancy and thermal stability of intumescent flame retardant polypropylene composites

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ABSTRACT

The influence of zinc borate (ZB) on the flame retardancy and thermal stability of intumescent flame retardant polypropylene composites (PP/IFR) containing ammonium polyphosphate (APP) and charring-foaming agent (CNCA-DA) were characterized by limiting oxygen index (LOI), UL-94 measurement, cone calorimeter test (CCT), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS) and thermogravimetry analysis (TGA). The results revealed that a small amount of ZB could effectively improve the LOI value, UL rating of the PP/IFR systems, and reduce the combustion performance of PP/IFR systems from CCT test, including heat release rate (HRR), total heat release (THR), smoke production rate (SPR) and total smoke production (TSP). The catalytic effectivity (CAT-EFF) results showed that when 1% ZB was added to PP/IFR, it had the highest CAT-EFF, and could enhance the LOI value from 27.1 to 30.7. The morphological structures observed by digital photos and SEM indicated that ZB could promote to remain more P and O, and B could participate the connecting reaction to form the more continuous and more compact intumescent char layer on the char surface to hinder heat diffusion and oxygen transmission effectively. The TGA data revealed that ZB could change the degradation behavior of the IFR and PP/IFR, improve the thermal stability of the PP/IFR systems at high temperature and increase the char residue.

1. Introduction

Polypropylene (PP) occupies large part in the polymer consumption duo to its excellent mechanical properties, low cost and easy processing and good chemical resistance, such as automotive parts, architectural materials, furniture, electric shell and packages. However, its further applications have been limited severely by its flammability and burning with dripping. Therefore, it is imperative to enhance the flame retardancy of PP. In recent years, Intumescent flame retardants (IFR) have aroused a great attention and been considered as most promising candidates to substitute halogen-containing flame retardants due to its environmental-friendly properties, halogen-free, and anti-dripping compared with halogenated flame retardants and metal hydroxides [1–7]. The traditional IFR is composed by acid source, charring source and gas source. The most widely reported IFR systems are comprised by ammonium polyphosphate (APP) and pentaerythritol (PER) systems, and the optimal mass fraction of APP/PER is 3 [8–10].

However, the shortcomings of traditional IFR systems have restricted its application, such as poor flame retardant efficiency relatively to bromine-containing flame retardants, poor compatibility with matrix, lower thermal stability, and water-soluble, and these disadvantages are bad for the long-time flame retardancy. To solve these problems, researchers have made great efforts to develop oligomeric or polymeric IFRs with relatively higher molecular weight and synergistic agent have been sued to enhance the flame retardancy of IFR [11–14]. The previous studies showed that some silicon-containing compounds, boron-containing compound, transitional metal oxides, 4A zeotile, metal compounds could serve as synergistic agents to increase the strength and stability of char layer to enhance the flame retardant performance of the composites [15–23] .

The most researches about synergistic effect focused on the traditional IFR systems containing ammonium polyphosphate (APP)/pentaerythritol (PER) or other char forming agent containing hydroxyl group [15–23]. However, the presentation of hydroxyl group in the IFR would deteriorate compatibility between the flame

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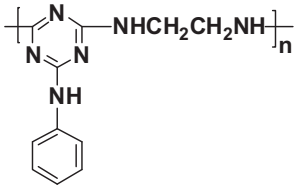

Scheme 1. Structure of CNCA-DA.

retardants and the matrix and increase the moisture sensitivity of the composites. Therefore, it is urgent to develop hydroxyl-free flame retardants and investigate the synergistic effect of between some synergistic agents and the hydroxyl-free flame retardants.

ZB is used as a flame retardant and smoke suppressant, and the combination of zinc borate with some intumescent flame retardant systems could enhance the char formation and improve the char quality, resulting in the improvement of flame retardancy [24–27]. But there are few references about synergistic effect between ZB and IFR systems without hydroxyl group.

In our previously work, a novel oligomeric triazine derivative charring agent (CNCA-DA) containing benzene and triazine ring (Scheme 1), was designed and synthesized in our lab, which was of higher thermal stability, without hydroxyl group and insoluble in water. In our previous work, CNCA-DA has been combined together with APP to form a novel IFR system, which has been proved to have good flame retardancy for PP [28]. Moreover, lanthanum oxide (La_2O_3) and 4A zeotile showed obvious synergistic effects on the flame retardancy of the PP/IFR systems [29,30]. In this work, ZB was selected to investigate the synergistic effect and mechanism with PP/IFR composite. Its effects on the flame retardancy and thermal degradation of PP/IFR systems have been evaluated by limiting oxygen index (LOI), vertical burning test (UL-94), cone calorimeter test (CCT), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), and thermogravimetry analysis (TGA).

2. Experimental

2.1. Materials

Polypropylene (PP) resin (T30S, melt flow rate: 2–5 g/10 min) used in this work was produced by Maoming Petroleum Chemical Company. Zinc borate (ZB: $2ZnO{\cdot}3B_2O_3{\cdot}3.5H_2O$) was offered by Sinopharm Chemical Reagent Co., Ltd., China. Ammonium polyphosphate (APP) was offered by Shenzhen Anzheng Chemicals Company, China. Antioxidant 1010 was produced by Ciba Specialty Chemicals, Switzerland. The charring-foaming agent (CNCA-DA) was synthesized in our laboratory.

2.2. Preparation of flame retardant PP composites

The intumescent flame retardant polypropylene composites were fabricated by melt compounding of PP, APP and CNCA-DA or a small amount of ZB at 180 °C in a two- roll mill with a rotor speed of 60 rpm, and a mixing time of 8 min for each sample. Then the composites were pressed on a curing machine for 4 min to produce various thick sheets, which were used to produce various dimension sheets in all tests. For comparison, the pure PP sample was also prepared with the same procedures.

2.3. Flame retardancy tests

The flame retardancy of all samples was characterized by limited oxygen index (LOI) and UL-94 methods. LOI data of all samples were carried out in a DRK304B oxygen index instrument (Jinan Deruike Instrument Factory) at room temperature with the sample dimension of 130 × 10 × 4 mm according to the ISO4589-1984 standard. Vertical burning rates of all samples were measured on a CZF-2 instrument (Jiangning Analysis Instrument Factory), with sample dimensions of 125 × 12.5 × 3.2 mm according to the American National Standard UL-94.

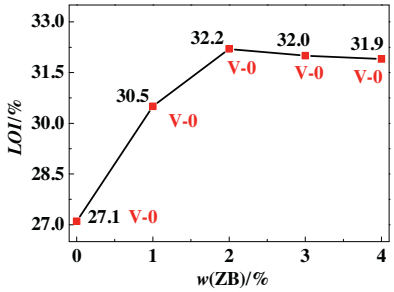

Fig. 1. Effect of ZB on the flame retardant properties of PP/IFR composites.

2.4. Cone calorimeter test (CCT)

The cone data were evaluated by a cone calorimeter performed in an Fire Testing Technology (UK) device in thickness and an incident flux of 35 $kW{\cdot}m^{-2}$ according to ISO 5660-1. All samples ($100 \times 100 \times 4\,mm^3$) were laid on a horizontal sample holder. The experimental error for all the mentioned parameters is ±10%.

2.5. Thermogravimetry analysis (TGA) tests

Thermogravimetric analysis (TGA) was performed on a TA Q500 thermogravimetric analyzer at a heating rate of 10 °C/min with a scan range from room temperature to 800 °C. In each case, 4–5 mg of the sample was examined under a N_2 or air with a flowing rate of 40 mL/min. All thermal degradation data were obtained from the TG and DTG curves.

2.6. Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) and energy dispersive spectrometry (EDS) were performed by using a FEI Quanta 400 SEM with accelerating voltage was 15 kV. The surface of the char residues which were obtained after cone calorimeter tests was sputter-coated with gold layer before examination.

3. Results and discussions

3.1. Flame retardancy of PP/IFR/ZB composites and catalytic effects of ZB

LOI and UL-94 rating are common flammability measure methods. Fig. 1 presents the LOI values and UL rating of PP/IFR composites with 20% IFR and different ZB loading. The LOI value of PP, PP/1%ZB, and PP/IFR is 17.0% [28], 17.5% and 27.1%, respectively. The LOI value of PP/IFR composite is 27.1%, and reaches the UL-94 V-O rating. It can be found that the LOI values firstly increases rapidly with increasing the amount of ZB in the PP/IFR composites, but these values decreases slightly with more than 2% ZB loading. When the ZB loading is 2%, the LOI value of the PP/IFR composite reaches the maximum of 32.2%, and passes the UL-94 V-0 rating. When the concentration of ZB is 4%, the LOI value reduces slightly to 31.9%, and still reaches V-0 rating with higher LOI value than that of PP/IFR composite. The LOI and UL-94 rating results reveal that a proper amount of ZB could improve the flame retardant performance of PP/IFR, and clearly exhibit synergistic effect between