

Comparative study on the flame retarded efficiency of melamine phosphate, melamine phosphite and melamine hypophosphite on poly(butylene succinate) composites



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ABSTRACT

The main aim of this work was to investigate the flame retarded efficiency of melamine phosphate (MP), melamine phosphite (MPi) and melamine hypophosphite (MHP) on poly(butylene succinate) (PBS) composites. The flame retardant, thermal degradation and combustion properties of PBS composites were characterized by limiting oxygen index (LOI) test, vertical burning (UL-94) test, thermogravimetric analysis (TGA) and cone calorimeter (Cone), respectively. The LOI results showed that the LOI values followed the sequence of PBS/MP < PBS/MHP < PBS/MPi at the same additive loadings. TGA results indicated that the initial decomposition temperature of PBS composites decreased with the decrease of phosphorus valence state and the incorporation of all three compounds could promote the char formation. Adding these three compounds into PBS matrix can decrease the peak heat release rate (PHRR) obviously from cone calorimeter results. Scanning electron microscopy (SEM) was employed to characterize the morphology and structure of the char residues. The flame-retardant mechanism in gaseous phase and condensed phase were investigated by thermogravimetric analysis/infrared spectrometry (TG-IR) and in situ Fourier transform infrared spectroscopy (in situ FTIR), respectively, and the possible flame-retardant mechanism was proposed.

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1. Introduction

Phosphorus-containing flame retardants as a species of halogen-free flame retardants have been widely used to impart polymer composites with flame retardancy due to their high efficiency. According to previous literature [1–8], many kinds of phosphorus-containing flame retardants have been investigated, such as red phosphorus (Pr), hypophosphites, phosphites, phosphates, etc. These compounds function in gaseous phase, condensed phase or both. In the gaseous phase [9,10], some phosphorus-containing compounds play a role in flame inhibition through radical trapping; in the condensed phase [11,12], they

promote the formation of carbon char or inorganic residue and then acts as a barrier, which decreases the mass loss rate and heat release. In general, the phosphorus-containing compounds (act as acid source) are combined with carbon source (or char forming agent) and gas source (or blowing agent) to form an intumescent flame retardant system [13]. Because of the formation of intumescent compact char layer during combustion, which can effectively protect the polymer matrix, the intumescent system exhibits high flame retardant efficiency.

Recently, hypophosphites such as aluminum hypophosphite (AHP), rare earth hypophosphite (REHP) have been used as effective flame retardant for poly (1,4-butylene terephthalate) (PBT) [14], Polyamide (PA) [15], Polylactide (PLA) [16], etc. Phosphites, such as trimethyl phosphite is a good flame retardant additive used in the electrolyte [17]. Phosphates [18–20], including ammonium polyphosphate (APP), melamine phosphate (MP), melamine polyphosphate (MPP), etc. are the most common flame retardants on the market. However, the flame-retardant mechanisms of these

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compounds above are not the same. Some compounds mainly function in condensed phase, while others mainly act in gaseous phase. The largest difference among these compounds is the phosphorus valency.

Therefore, to explore the flame-retardant mechanism of several typical phosphorus flame retardants with varied valence state of phosphorus on improving the fire retardancy of polymer materials is necessary and important. Braun et al. [21], systemically investigated the influence of the oxidation state of phosphorus on the decomposition and fire behavior of flame-retarded epoxy resin composites by using different hardeners such as phosphine oxide, phosphinate, phosphonate and phosphate-based ones. Modesti et al. [22], reported decomposition/pyrolysis studies of polyurethane (PU) rigid foams containing phosphinate, phosphonate or phosphate as flame retardant. Wilkie et al. [23] studied the influence of oxidation state of phosphorus on the thermal and flammability of polyurea and epoxy resin. Since deep understanding of the actual mechanisms is rather in its infancy, further systemically studying the structure property relationships of phosphorus-containing compounds on other polymers like polyester, polyolefin, etc. is required.

As a kind of biodegradable aliphatic polyesters, poly(butylene succinate) (PBS) has been widely used in many fields (such as agricultural films, packing materials, injection-molded products). Be conscious of the inherent flammability of PBS which severely restricted its potential applications, Chen et al. [24] and Wang [25] recently researched the intumescent flame retardant poly(butylene succinate) using ammonium polyphosphate as acid source, melamine as source gas, fumed silica and graphene as synergistic agent, respectively. Notable intumescent char can be observed in the optimal proportion of their LOI results, indicating that PBS itself can serve as carbon source in intumescent flame retardant PBS composite system.

In this work, three simple salts with different phosphorus valency including melamine hypophosphite (MHP), melamine phosphite (MPi) and melamine phosphate (MP) were prepared and blended with poly(butylene succinate) (PBS) to obtain a series of flame retardant PBS composites. The flammability and thermal properties of flame retardant PBS composites were evaluated by limiting oxygen index test, UL-94, cone calorimeter (Cone), and thermogravimetric analysis (TGA). In order to further understand their flame-retardant mechanism, selective samples have been studied by thermogravimetric analysis-infrared spectrometry (TG-IR) technique and in situ Fourier transform infrared spectroscopy (in situ FTIR).

2. Experimental section

2.1. Materials

Poly(butylene succinate) (PBS, weight-average molecular weight: 170,000, hydroxyl end-capped) was purchased from Anqing Hexing Chemicals Co. Ltd. (Anhui, China). Melamine (CP), phosphoric acid (AR, $\geq 85\%$), phosphorous acid (AR, $\geq 99\%$) and hypophosphorous acid (GR, 50% aqueous solution) were purchased from Sinopharm Chemical Reagent Co. (Shanghai, China).

2.2. Synthesis of melamine phosphate (MP), melamine phosphite (MPi) and melamine hypophosphite (MHP)

In typical experiment, 37.84 g (0.3 mol) melamine was dissolved in 750 ml deionized water in a 1000 ml three-necked, round-bottomed flask fitted with a mechanical stirrer, flux condenser and dropping funnel, and stirred at 95 °C for 30 min. 34.6 g (0.3 mol) phosphoric acid was added dropwise to the above reaction flask and then kept at 95 °C for 1 h. After cooling to room temperature, the precipitate was filtered, washed with cold water and then dried to a constant weight. The obtained white solid was melamine phosphate (MP). For MPi, 37.84 g (0.3 mol) melamine was dissolved in 750 ml deionized water in a 1000 ml three-necked, round-bottomed flask fitted with a mechanical stirrer, flux condenser and dropping funnel, and stirred at 95 °C for 30 min. 24.8 g (0.3 mol) phosphorous acid which dissolved in 50 ml deionized water was added dropwise to the above reaction flask and then kept at 95 °C for 1 h. After cooling to room temperature, the precipitate was filtered, washed with cold water and then dried to a constant weight. The synthesis of MHP was similar to that of MPi. In this procedure, to react with 0.3 mol melamine, 39.6 g (0.3 mol) hypophosphorous acid (50% aqueous solution) was added. All of these three compounds are white powder as can be seen from digital images in Fig. 1.

2.3. Preparation of the PBS samples

All samples were prepared on a two-roll mill at a temperature range of 120–125 °C for 15 min. After mixing, the samples were hot-pressed under 10 MPa for 10 min at about 125 °C into sheets of suitable thickness and size for analysis. The composition of the PBS composites is listed in Table 1.

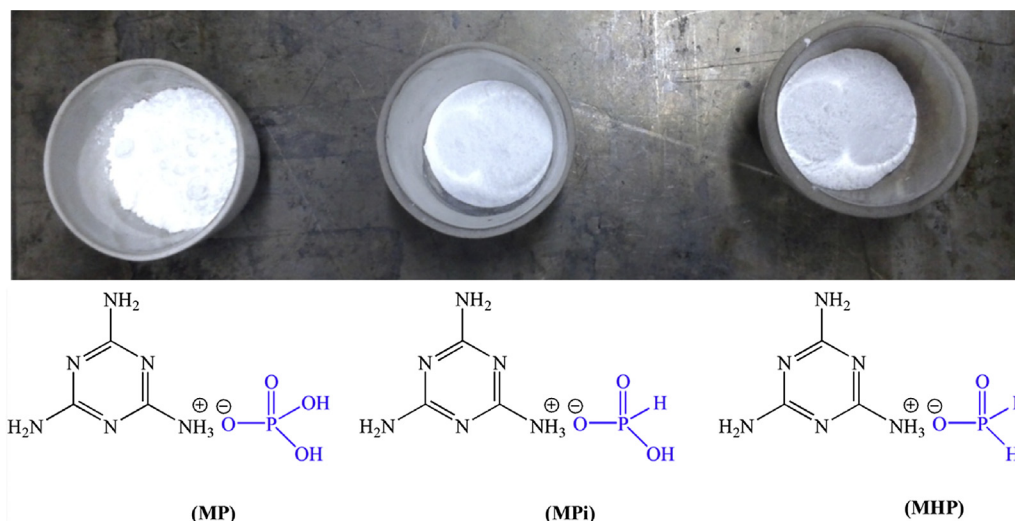


Fig. 1. The digital images and chemical structure of MP, MPi and MHP.

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