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Effect of rare earth hypophosphite and melamine cyanurate on fire performance of glass-fiber reinforced poly(1,4-butylene terephthalate) composites

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ABSTRACT

This work mainly deals with a novel flame retardant system for glass-fiber reinforced poly(1,4-butylene terephthalate) (GRPBT) composites using trivalent rare earth hypophosphite (REHP) and melamine cyanurate (MC) through melt blending method. Firstly, two types of REHP, lanthanum hypophosphite and cerium hypophosphite, were synthesized and characterized. Thermal gravimetric analysis (TGA) was employed to investigate the thermal decomposition behavior of REHP and flame retardant treated GRPBT composites. Thermal combustion properties were measured using microscale combustion calorimeter. Fire performance was evaluated by limiting oxygen index, Underwriters Laboratories 94 and cone calorimeter. The results showed that the flammability of GRPBT is significantly reduced by the incorporation of the flame retardant mixture. Mechanism analysis revealed that the addition of MC reduces the condensed phase effect of REHP, but improves the flame inhibition in gas phase.

1. Introduction

Glass-fiber reinforced poly(1,4-butylene terephthalate) (GRPBT) composite is one of most important engineering materials which has been widely used in electronic or electrical equipment, military and civil infrastructure applications, because of its good thermal, mechanical, electrical properties, low weight and low cost. However, the development and application of GRPBT are greatly limited by its flammability when subjected to elevated temperature or combustion. Once ignited, GRPBT can produce amounts of toxic gases, soot, and smoke, seriously harming the human and environment. Fabrication and improvement of the flame retarded GRPBT composites are thus the major concern for academic institutions and industrial laboratories.

Up to now, the most commonly used flame-retardant systems for glass-fiber reinforced polyester composites are mainly composed of halogenated additives. Nevertheless, the toxic and corrosive gases will be released in the increasing temperature condition or combustion process of the halogen-containing polymer composites. The main halogen-free flame retardants are phosphorus-based, nitrogen-based and phosphorus–nitrogen compounds which have been successfully applied in polyesters [1–4]. However, it is difficult to achieve a high flame retarded classification for polyesters with a low loading of these compounds. Recently, one kind of metal phosphinate has been used in polyesters [5–9]. Braun and Schartel [5] prepared a V-0 GRPBT composite using a flame retardant mixture (aluminium diethylphosphinate and melamine cyanurate) at a loading of 20 wt%. Very recently, inorganic compound aluminium hypophosphite has been applied as a flame retardant in glass fiber reinforced polyesters [10–12]. Costanzi and Leonardi [10] found that low fraction of aluminium hypophosphite can provide high fire retardancy properties in GRPBT composites. Nevertheless, the thermal stability and mechanical properties of glass fiber reinforced polyesters is dramatically reduced by the addition of aluminium hypophosphite.

Inspired by the reported flame retardant effects provided by aluminium hypophosphite, another metal hypophosphite was used to improve the fire retardancy performance of GRPBT composites. In this study, two kinds of trivalent rare earth hypophosphite, lanthanum hypophosphite and cerium hypophosphite, will be prepared. As a nitrogen-based flame retardant, melamine cyanurate will be incorporated to establish a novel flame retardant system to further improve the fire retardancy. The aim of this work is to examine the use of rare earth hypophosphite and melamine cyanurate as halogen-free flame retardants for GRPBT composites. Synthesized rare earth hypophosphite will be characterized. The thermal stability and fire retardancy properties for GRPBT composites containing the flame retardants will be studied by thermo-gravimetric analysis, microscale combustion calorimeter, limiting oxygen index, Underwriters Laboratories 94 and cone calorimeter. Moreover, the

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possible mechanism behind the fire retardant behavior will be described and discussed.

2. Experimental

2.1. Materials

Trivalent lanthanum chloride hydrate and cerium chloride heptahydrate (Sinopharm Chemical Reagent Co., Ltd.) were of analytical grade. Sodium hypophosphite (analytical reagent) was supplied by Tianjin Guangfu Fine Chemical Research Institute, China. Poly(1,4-butylene terephthalate) (PBT) (4500) was a product of BASF Chemical Company, Germany. Silane coated short glass fiber (ECS-301CL, fiber diameter of 10 μm and initial fiber length of 3 mm) was supplied by Chongqing Polycomp International Co., Ltd., China. Melamine cyanurate (MC) was a commercial product from Shandong Shouguang Weidong Chemical Engineering Co., Ltd., China. Furthermore, the deionized water (ultrapure water) was used in this work.

2.2. Synthesis of rare earth hypophosphite

In a typical experiment [13], 2.00 g sodium hypophosphite was dissolved in pH 1.4 (KCl–HCl) buffer solution (20 ml). The solvent used for the buffer solution was deionized water. 2.4 g hydrated lanthanide chloride in the buffer solution (20 ml) was added. The reaction mixture was heated to 40 °C under reflux in a nitrogen atmosphere for 3 h. The resulting solids, were collected by suction filtration, washed with deionized water, and dried at the oven. Trivalent lanthanum hypophosphite (LHP) and cerium hypophosphite (CHP) were synthesized via the typical method in this work. The products were analyzed by Fourier transform infrared spectra spectroscopy (Nicolet 6700 FT-IR spectrophotometer) and scanning electron microscope (Hitachi S-4800).

2.3. Preparation of flame retarded glass fiber reinforced PBT composites

PBT, LHP, CHP, MC and glass fiber were dried at 80 °C overnight before use. PBT was blended with additives using a twin-roll mill (XK-160, made in Jiangsu, China) at 235 °C for 10 min. The roller speed was 100 rpm for the preparation of all the samples. They were then molded by using a hot press at 235 °C under 5–10 MPa for 10 min in order to obtain 3.2 or 1.6 mm thick plaques. The formulations of these composites were shown in Table 1.

2.4. Pyrolysis analysis

Thermogravimetric analysis (TGA) was carried out using a Q5000 IR thermogravimetric analyzer (TA Instruments Waters, China) at a linear heating rate of 20 °C/min under nitrogen atmosphere. The weight of all the samples were kept within 5–10 mg. Composites in an open Pt pan were tested under an airflow rate of 6×10^{-5} m^3 min^{-1} at temperature ranging from room temperature to 700 °C.

2.5. Thermal combustion properties

Thermal combustion properties of plastics were measured using a microscale combustion calorimeter (MCC, Govmark) according to ASTM D 7309-07. 5 (±0.1) mg of each sample was heated at 1 °C s^{-1} from 90 to 600 °C and held there for 30 s. During pyrolysis, the volatilized decomposition products are transferred in the stream of nitrogen to a high-temperature combustion furnace where pure oxygen is added and the decomposition products are completely combusted. The amount of oxygen consumed is measured with an oxygen analyzer and used to calculate a heat release rate (HRR).

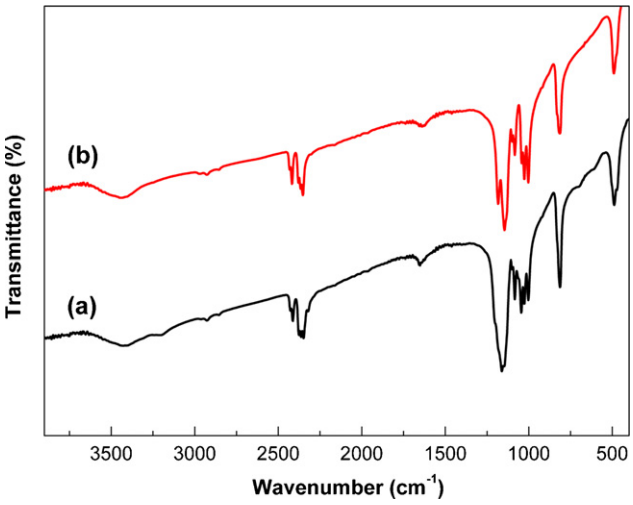

Fig. 1. FTIR spectra of LHP (a) and CHP (b).

2.6. Combustion testing

One group of combustion experiments were determined by limiting oxygen index (LOI) and Underwriters Laboratories (UL) 94 testing according to ASTM D2863 and the standard [14] respectively. An HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) was used in the LOI testing. The specimens used for the test were of dimensions 100 mm × 6.5 mm × 3.2 mm. UL 94 testing was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China). The specimens used were of dimensions 130 mm × 13 mm × 3.2(or 1.6) mm.

The other combustion experiments were performed in a cone calorimeter (Fire Testing Technology) according to ASTM E 1354/ISO 5660. Each specimen (100 mm × 100mm × 3.2 mm) was wrapped in an aluminium foil and exposed horizontally to 35 kW/m^2 external heat flux. Some residues collected in the cone testing were further analyzed by means of the scanning electron microscope (SEM). The SEM micrographs were obtained with a scanning electron microscope AMRAY1000B at an accelerating voltage of 20 kV. The specimens were sputter-coated with a conductive layer.

3. Results and discussion

3.1. Characterization of rare earth hypophosphite

Infrared spectra of lanthanum hypophosphite (LHP) and CHP are shown in Fig. 1. The bands in the region of 2300–2450 cm^{-1} observed in the two compounds are attributed to PH_2 stretching modes [15]. The bands between 1100 cm^{-1} and 1250 cm^{-1} correspond to the bending modes of PH_2 [16]. The medium intensity peak at 809 cm^{-1} is assigned to the rocking mode of PH_2. The weak peak at 1079 cm^{-1} is attributed to P–O modes. The absence of characteristic bands of water molecules in the infrared spectra indicates that the two compounds are anhydrous.

The SEM micrographs of the two compounds are shown in Fig. 2. Both the two micrographs illustrate the rod-like crystals, while having nonuniform sizes. The small rod-like crystals of LHP have sizes of about 1.0–6.0 μm in length and 0.3–0.7 μm in width, while the large ones have sizes of about 8.0–24.0 μm in length and 0.6–4.2 μm in width. The fragments of CHP are smaller than those of LHP, having irregular morphology. The large rod-like crystals of