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Enhancement of fire retardancy performance of glass-fibre reinforced poly(ethylene terephthalate) composites with the incorporation of aluminum hypophosphite and melamine cyanurate

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ABSTRACT

This work aims to develop glass-fibre reinforced poly(ethylene terephthalate) (PET/GF) composites with significantly improved flame retardancy using aluminum hypophosphite (AHP) and melamine cyanurate (MC). Microscale combustion calorimetry (MCC) and thermal gravimetric analysis/infrared spectrometry (TG-IR) technique were used to investigate the potential fire hazards of various PET/GF composites. For the PET/GF composites with a low loading of the flame retardant mixture, the heat release capacity (HRC) which is an indicator of a material fire hazard reduced by 47%, meanwhile, the intensities of a variety of combustible or toxic gases detected by TG-IR technique were remarkably decreased. A loading of 10 wt.% AHP alone or its combination with MC could give the PET/GF composites high limited oxygen index and V-0 classification in UL-94 test. Thermal decomposition and residue analysis revealed that the flame retardancy of PET/GF composites is enhanced by the condensed-phase action of AHP and the gas-phase dilution effect of MC.

1. Introduction

Glass-fibre reinforced poly(ethylene terephthalate) (PET/GF) is an excellent composite material broadly applied in building, automotive and electrical equipments, because of its good thermal, mechanical, electrical properties, low weight and low cost in comparison with conventional materials. Nevertheless, PET/GF is susceptible to combustion and fire damage due to the "candlewick effect" which is caused by glass fibres. The interpretation of "candlewick effect" is that in the combustion process of glass-fibre reinforced polymer matrix composites, glass fibres could transfer the flammable pyrolysis products of polymers to the flame zone through capillary action, speed the heat flowing back to polymers and increase the mass loss rate of polymer matrix [1–3]. Once ignited, PET/GF composite hardly extinguishes itself and produces a mass of toxic gases, soot, and smoke, which would harm the human and environment.

The flame-retardant systems which have been most commonly used for glass-fibre reinforced polyester composites consist of halogenated additives. But the application of halogen-containing additives has been forbidden in many countries due to the release of toxic and corrosive gases. As a result, the development of halogen-free flame retarded glass-fibre reinforced polyester composites is strongly demanded. Traditional phosphorus-based additives have been successfully applied in these composites, but they need 20–30 wt.% loading to achieve a V-0 classification in UL-94 tests [4–7]. However, high loadings of flame retardants would cause harmful effects to the mechanical properties of the polymer composites.

Recently, a variety of nanoparticles, including nanoclay, carbon nanotubes, carbon nanofibers, and polyhedral oligomeric silsesquioxanes (POSS), have been used to fabricate flame retarded nanocomposites. Hapuarachchi and Peijs [8] studied the use of multiwalled carbon nanotubes (MWNTs) and sepiolite nanoclays as flame retardants for polylactide (PLA) and its natural fibre reinforced composites. A noticeable reduction of heat release capacity (HRC) for the PLA ternary system based on nanoclays and MWNTs was reported in this work. Gou et al. [9] fabricated flame retarded glass fibre reinforced polyester composites using carbon nanofiber sheets (CNS) through resin transfer molding (RTM) process. Significant improvement was achieved in the fire retardancy of

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composite laminates due to the incorporation of CNS. Although many nanoparticles have been confirmed to be particularly efficient to reduce the fire hazards of polymeric materials, few articles reported the polymer nanocomposites with a UL-94, V-0 rating and high LOI using nanoparticles alone.

Metal salts of alkylphosphinic acid have been found to be especially effective in polyesters [10–14]. Braun and Schartel [10] investigated the flame retardancy mechanisms of aluminum diethylphosphinate and its combination with melamine cyanurate in glass-fibre reinforced poly(butylene terephthalate) composites. Both the gas-phase and solid-phase actions caused by aluminum diethylphosphinate were revealed in this work, and a UL-94, V-0 rating composite material was achieved at a loading of 20 wt.%. Nevertheless, the preparation of these organic phosphinate salts on an industrial scale is relatively complex and expensive, thereby limiting greatly the possibilities of using the products as flame retardants [14].

The present study chooses aluminum hypophosphite (AHP) and melamine cyanurate (MC) to develop a glass-fibre reinforced poly(ethylene terephthalate) (PET/GF) composite with enhanced flame retardancy. The chemical formula of AHP is $Al(H_2PO_2)_3$, which has been synthesized on an industrial scale. MC is used as a synergist in this work, which has been applied in flame retardant polyesters [10]. The aim of this research is to combine the fire retarded potential of AHP and MC to significantly improve the flame retardancy of PET/GF composites. The formulations in this work will be investigated for the contributions to possible fire hazards using microscale combustion calorimetry (MCC) and thermal gravimetric analysis/infrared spectrometry (TG-IR) technique. Furthermore, the flame retardancy mechanism of an optimized formulation will be studied in this work.

2. Experimental

2.1. Materials

In this work, poly(ethylene terephthalate) was supplied by Wuhu Keyan Chemical Material Technology Co., Ltd., China. Silane coated short glass fibre (ECS-301CL, fibre diameter of 10 μm and initial fibre 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. Aluminum phosphinate (AHP) was supplied by Qingzhou Yichao Chemical Co., Ltd., China.

2.2. Processing

PET and all additives were dried at 100 °C overnight before use. PET was blended with additives using a twin-roll mill (XK-160, made in Jiangsu, China) at 265 °C for 10 min. The roller speed was 100 rpm for the preparation of all the samples. They were then molded using a hot press at 265 °C in order to obtain 3.2 mm thick plaques. Four different formulations of PET with 30 wt.% glass fibres (GF) were prepared: PET/GF as a non-flame retardant composite, PET/GF-MC and PET/GF-AHP as single flame retardant composites, PET/GF-AHP-MC as a combined flame retardant composite. In single flame retardant composites, the content of MC and AHP were both kept at 10 wt.%. PET/GF-AHP-MC contains a total of 10 wt.% of flame retardant mixture, and the ratio between AHP and MC is 2:1.

2.3. Pyrolysis analysis

Thermal gravimetric analysis (TGA) was carried out using a Q5000 IR thermal gravimetric analyzer (TA Instruments Waters, China) at a linear heating rate of 20 °C/min under both nitrogen and air conditions. The weight of all the samples were kept at 5–10 mg. Composites in an open Pt pan were tested under an flow rate of 6×10^{-5} m^3/min at temperature ranging from room temperature to 650 °C.

Thermal gravimetric analysis/infrared spectrometry (TG-IR) of all composites had been performed using the TGA Q5000 IR thermal gravimetric analyzer interfaced to the Nicolet 6700 FT-IR spectrophotometer. About 5.0 mg of each composite was put in an alumina crucible and heated from 30 to 650 °C with a heating rate of 20 °C/min in a nitrogen atmosphere with a flow rate of 45 ml/min.

2.4. Combustion testing

Thermal combustion properties of plastics were measured using a microscale combustion calorimetry (MCC, Govmark) according to ASTM D 7309-07. 4–8 mg of each sample was heated at 1 °C/s 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). All MCC data obtained were reproducible to about ±3%.

The flammability properties of studied formulations were determined by limited oxygen index (LOI) test according to ASTM D2863 and UL-94 test according to ASTM D3801. An HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) was used in the LOI test. The specimens used for the test were of dimensions $100 \times 6.5 \times 3.2$ mm^3. UL-94 test was carried out on a CFZ-2-type instrument (Jiangning Analysis Instrument Company, China). The specimens used were of dimensions $130 \times 13 \times 3.2$ mm^3.

2.5. Residue analysis

Fourier transform infrared spectra spectroscopy (Nicolet 6700 FT-IR spectrophotometer) was employed to characterize the residues collected in LOI tests using thin KBr disc. The transition mode was used and the wavenumber range was set from 4000 to 500 cm^{-1}. The residues after LOI tests were treated in muffle furnace at 700 °C under air condition for 30 min. They were then analyzed by FTIR again.

The residues collected in LOI tests were further analyzed by the scanning electron microscope (SEM). The SEM micrographs of the PET composites were obtained with a scanning electron microscope Inspect S at an accelerating voltage of 10 kV. The specimens were sputter-coated with a conductive layer.

3. Results and discussion

3.1. Thermal decomposition

Aluminum phosphinate (AHP) and melamine cyanurate (MC) were analyzed by thermogravimetry in a nitrogen atmosphere. The thermal decomposition of AHP is characterized by two steps with two maximal mass loss rates at 332 °C and 450 °C (Fig. 1a). The decomposition process of AHP could be represented by the two equations as detailed below:

$$2Al(H_2PO_2)_3 \xrightarrow{\Delta} Al_2(HPO_4)_3 + 3PH_3$$

$$2Al_2(HPO_4)_3 \xrightarrow{\Delta} Al_4(P_2O_7)_3 + 3H_2O$$