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Flame retardancy and toughness modification of flame retardant polycarbonate/acrylonitrile-butadiene-styrene/AHP composites

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ABSTRACT

A kind of flame retardant polycarbonate/acrylonitrile-butadiene-styrene copolymer (FR PC/ABS) composite was prepared by melt extrusion blending using aluminum hypophosphite (AHP) as a flame retardant and ethylene-co-acrylic ester-co-glycidyl methacrylate (EMA) as a compatibilizer. The thermal behavior and flame retardancy of FR PC/ABS composites were investigated by thermogravimetric analysis, the UL-94 vertical burning test, the limiting oxygen index, and the cone calorimeter test. The FR PC/ABS composites showed good flame retardancy, from no vertical rating for PC/ABS, to V-0 rating for FR PC/ABS containing 15 wt% AHP in the UL-94 test. PC/ABS/15wt%AHP/6wt%EMA composite was more efficient in decreasing the peak heat release rate (PHRR) of FR PC/ABS composite in the cone calorimeter test. The same amount of AHP provided equally strong flame inhibition and increased char flame retardancy in PC/ABS/AHP and PC/ABS/AHP/EMA composite. Whereas, the protective compact char layer of PC/ABS/AHP/EMA composite efficiently improved the flame retardancy that of PC/ABS/AHP composite. With the addition of 6 w% of EMA copolymers, the elongation yield at break of the FR PC/ABS composite increased by 6.7 times compared to that of the PC/ABS/AHP composite; and the notched impact strength and unnotched strength improved by approximately 250% and 710%, respectively, compared to those of the PC/ABS/AHP composite. Fourier transformed infrared (FT-IR) and scanning electron measurements (SEM) results indicated that EMA could effectively enhance the interfacial interaction of FR PC/ABS composite.

1. Introduction

Polycarbonate (bisphenol A)/acrylonitrile-butadiene-styrene (PC/ABS) alloy is one of the most important engineering plastics because it has good mechanical properties, excellent chemical resistance, high heat distortion temperature, and good processability. Flame retardant (FR) PC/ABS composites are widely utilized in the electronic devices, automobile and building fields [1,2]. In general, a PC resin achieves V-2 rating in the UL-94 test; however, PC/ABS alloys are easy combustible. The addition of FRs is an effective method to improve the flame retardancy of PC/ABS alloys [3,4]. However, owing to environmental concerns, some high-efficiency halogen-containing FRs have been gradually limited; therefore, halogen-free FRs based on phosphorus and nitrogen have been well developed in recent decades.

Phosphorus-containing compounds are environment-friendly FRs [5–10]. Aromatic phosphates such as triphenyl phosphate (TPP), resorcinol bis(diphenyl phosphate (RDP), bisphenol A bis(diphenyl phosphated) (BDP), tetra-2,6-dimethyl phenyl resorcinol diphosphate (DMP-RDP), and BDP/PTFE and TPP/PTFE mixtures are effective in improving the flame retardancy of PC/ABS alloy [8–12]. BDP and RDP have been already widely commercialized in FR PC/ABS alloy because they are homogenously mixed with PC phase resulting in superior mechanical properties of FR PC/ABS composite. However, different processing of the liquid aromatic phosphates and PC/ABS alloy, low Vicat temperature and thermal stability of FR PC/ABS composites limited their application in some electrical fields. In order to improve the thermal distortion temperature and processability of FR PC/ABS composites, silicon-containing FRs and intumescent FRs (IFR) have been also developed as replacements for halogen-containing FRs [7,13–15]; unfortunately, they bring about some disadvantages such as low compatibility with PC/ABS alloy, low water resistance, and low environmental durability in

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flame retardant PC/ABS composites [16,17]. In addition, the incorporation of a large amount of halogen-free FRs significantly decreases the toughness of thermoplastics. In particular, the inorganic FR in a polymer significantly decreases the impact strength of FR composites. Therefore, reducing the loading of FRs and modifying the compatibility of FRs and the polymer matrix are very important to ensure realistic applications of FR materials. Some compatibilizers have been employed in FR PC/ABS composite to improve the mechanical properties. Three types of compatibilizers-methacrylate-butadiene-styrene (MBS), ethylene-vinyl acetate (EVA), and styrene-maleic anhydride (SMA) were used to improve the toughness of the FR PC/ABS alloy. The results showed that the addition of a small amount of MBS or EVA increased the notched impact strength, and the addition of SMA increased the tensile strength and modulus the FR PC/ABS alloy [18].

Currently, salts of alkyl phosphinic acid and hypophosphite salts have been developed as the new phosphorus-containing effective FRs because they have good flame retardancy, thermal stability, and water resistance [19–21]. Salts of phosphinate and hypophosphite have been used in the flame retardancy applications of many glass-fiber reinforced engineering composites and other polymers, such as glass-fiber reinforced poly(ethylene terephthalate) (GFPET), poly(1,4-butylene terephthalate (GFPBT), polyamide 6 (GFPA6), polyamide 66 (GFPA66), polylactide, poly(vinyl alcohol), poly(-butylene succinate) (PBS), Polyurethane [22–31]. So far, Aluminium hypophosphite (AHP) has rarely been used in flame retarded ABS and PC/ABS alloy because of its disadvantages of a small amount of phosphine production during flame processing and incompatibility of polymer and AHP particles and low flame retardant efficiency. In order to improve the compatibility or restrain the phosphine production during the flame process, some surface modifications of flame retardant have been studied in FR polymers [32–36].

It is very practical and meaningful to develop a kind of halogen-free FR PC/ABS composite with a high impact toughness, good flame retardancy, and good thermal stability and processability. In this study, we employed aluminum hypophosphite (AHP) as a FR and Ethylene-acrylic ester-glycidyl methacrylate (EMA) as a modifier agent in order to improve the compatibility of the PC and ABS and AHP particles. The weight ratio of PC and ABS of PC/ABS alloy is set as 50/50 (w/w). The effects of the compatibilizer on the mechanical properties and flame retardancy of the FR PC/ABS composites were systematically investigated. The thermal behaviors, flame retardancy, and flame retardant mechanism of FR PC/ABS composites were studied using thermal gravimetric analysis (TGA), the limiting oxygen index (LOI), the UL-94 vertical burning test, and the cone calorimeter test.

2. Experimental section

2.1. Materials

Polycarbonate (PC) resin was purchased from Japan Mitsubishi Chemical Company (LS1010). ABS resin (GP22, BASF, Germany (A:B:S = 20:30:50) in granular form was purchased from Qingdao Laiken Corp. Company in China. AHP (Purity≥99.0%, average size ≤5 μm) was purchased from Qingdao Fusilin Chemical and technology Corp in China. Ethylene-acrylic ester-glycidyl methacrylate was purchased from French Arkema Company (AX8900). The melt index at 190 °C is 6 g/min; Methyl acrylate content and glycidyl methacrylate content are 24wt% and 8wt%, respectively.

2.2. Preparation of flame retardant PC/ABS composites

PC, ABS, AHP were dried in a vacuum oven at 80 °C for 4 h before use, respectively. PC, ABS, flame retardant and modifier were premixed in room temperature, and then the mixtures were melt-extruded in a CTE-20 type twin-extruder (Nanjing Kebeilong machinery Co., Ltd, China); the temperature range was from 220 °C to 240 °C, and rotation speed of the twin-screw was 50 rpm. The extrudates were cooled and cut into pellets. The pellets were dried at 80 °C for 4 h. The pellets were hot-pressed under 10 MPa for 10 min at 220 °C to obtain 3.2 mm thick plaques, and the plaques were cut into standard size. The samples for mechanical property measurements were prepared by injection molding at temperature from 240 to 260 °C. A amount of the decomposition product including water or phosphine (PH_3) of PC/ABS/AHP has some influence on the average molecular weight of PC on the processing temperature because PC is quite sensitive to acids and water during processing.

2.3. Measurements

2.3.1. Mechanical properties measurements

Tensile properties were measured by ASTM D882 standard using a screw-driven universal testing machine equipped with an electronic load cell and mechanical grips (AL-7000M, Taiwan Gotech Testing Machines Inc.). The extensometer size is 25 KN. The tests were conducted at room temperature using a cross-head rate of 20 mm/min. At least five specimens were tested for each sample.

The izod impact tests were carried out according to GB/T1043.1-2008 using an impact tester (Suzhou Ligao Detection Equipment Co. LTD) on the standard sized rectangular bars at room temperature. The depth of the nick was 2 mm. At least five specimens were tested for each sample to get an average value.

Thermogravimetric Analysis. TGA measurement was carried out using a TGA-7 type thermo-analysis instrument (Perkin–Elmer Company, USA). Samples were measured in an alumina crucible with a mass of about 5.5 ± 0.3 mg from room temperature to 800 °C at a heating rate of 10 °C/min under N_2 atmosphere.

Limited Oxygen Index (LOI). LOI was measured using a HC-2 oxygen index meter (Jiangning Analysis Instrument Company, China) according to the standard oxygen index test ASTM D2863. The specimen dimension was 130 × 6.5 × 3.2 mm^3.

UL94 Vertical Burning Test. The vertical burning test was performed using a vertical burning instrument (CFZ-1 type, Jiangning Analysis Instrument Co., China) according to UL94 test ASTM D3801-2010. The dimensions of samples were 130 × 13 × 3.2 mm^3.

Cone Calorimeter Test. The Cone Calorimeter Test was performed on the cone calorimeter (Fire Testing Technology, U.K.) according to ASTM E1354/ISO 5660. The dimensions of samples were 100 × 100 × 3.2 mm^3. Each specimen was wrapped in an aluminum foil and exposed horizontally to 50 kW/m^2 external heat flux.

Fourier transformed infrared measurement (FT-IR). FT-IR spectra of the thin films were measured with a Bruker Tensor 27 spectrometer using transmission mode in the wavenumber range of 400–4000 cm^{-1}. The thin film sample was prepared by direct hot pressing of melt-blending sample at 200 °C. The thickness is about 20–40 μm.

Scanning electron microscopy (SEM). The surface morphologies of char residue samples obtained from the cone calorimeter test were observed using scanning electron microscopy (JSM-6700F, Japan Electronics Corp.) The specimens were previously coated with a conductive layer of gold.

3. Results and discussion

3.1. Flame retardancy and mechanical properties of FR PC/ABS composite

The FR PC/ABS (PC/ABS = 50:50, w/w) composites were