



Full Length Article

Multi-functional carbon microspheres with double shell layers for flame retardant poly (ethylene terephthalate)

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ARTICLE INFO

Article history:

Received 29 June 2017

Received in revised form 30 October 2017

Accepted 18 November 2017

Available online 21 November 2017

Keywords:

Carbon microspheres

Microencapsulation

Poly (ethylene terephthalate)

Magnesium hydroxide

Interface binding

Flame retardant

ABSTRACT

Carbon microspheres (CMSs) as a core material had been coated by two capsule walls: an inorganic material of magnesium hydroxide (MH) as inner shell layer and an organic material of poly (ethylene terephthalate) (PET) as outer shell layer. MH coating CMSs (MCMs) were fabricated by liquid phase deposition method, then grafted 3-Aminopropyltriethoxysilane (APTS) to obtain the Si-MCMs. Microencapsulated Si-MCMs (PMCMs) was prepared by in situ polymerization method. Morphology structure, dispersion, flame retardant and other properties of PMCMs have been investigated. A series of PET blends were prepared by melt compounding. The results showed that MH and PET as two layers were coated on CMSs surface with the optimal thickness of about 70 nm. The PMCMs owned better dispersion in PET matrix. Compared with MCMs/PET composites, the mechanical property of PMCMs/PET composites had significantly increased because of the strong interface binding force between PMCMs and PET matrix. Moreover, PMCMs was proved to be an effective flame retardant. For PMCMs/PET with 2 wt% PMCMs, the limiting oxygen index (LOI) value increased from 21.0% (pristine PET) to 27.2%, and the peak heat release rate (pk-HRR) decreased from 513.22 kW/m² to 352.14 kW/m². The decreased smoke production rate (SPR) and total smoke production (TSP) values demonstrated PMCMs suppressed the smoke production. The increased Fire performance index (FPI) value illustrated PMCMs significantly reduced the fire risk of PET. Overall, the two capsular walls endowed the PMCMs/PET composites with good mechanical and flame-retardant properties.

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1. Introduction

Carbon microspheres, a spherical carbonaceous material with a fullerene-like cage structure, can be seen as grown onion-like fullerenes (OLFs) with diameters ranging from 100 nm to 1 μm. The unique structure of CMSs determines its excellent physical and chemical properties, such as chemical stability, thermal sta-

bility, low density and excellent electrical conductivity [1], etc. Functionalized CMSs own special properties and have been widely used in catalytic carriers, photovoltaic and supercapacitor electrode materials [2–4], etc. CMSs were also promising for flame retardant. CMSs can not only reduce the heat release rate, but also effectively improve the LOI value of poly (ethylene terephthalate) (PET) [5]. Compared with other carbon materials [6–11], CMSs (glucose as raw material, obtained by hydrothermal method) were easy to be functionalized because of the rich oxygen-containing groups on the surface (the amount of groups was about 15%). However, carbon materials as flame retardant, the common flaw is that large amount of black smoke will produce during the combustion. With the continuous improvement of environmental law, the flame retardant should be in the development trend of halogen-free, nano, smoke suppression and the reduction of harmful gases. Among environ-

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mentally friendly flame retardants, magnesium hydroxide (MH) is a representative of green flame retardant and has the dual effects of smoke suppression and flame retardancy.

The multi-component composite flame retardant (MFR) owns the ability to form a complementary or synergistic effect among the components. MFR has the unique advantages in improving the physical, chemical and flame-retardant properties of the polymer composites, so it is one of the most important ways to improve the flame retardant of polymer [12–14]. In the preliminary work, the synergistic flame-retardant effect of CMSs and MH has been proved in (PET) [14,15]. According to the conventional compounding method, directly adding diverse fillers into polymer will lead to many interface problems between every filler and polymer matrix. In order to simplify the encountered interface problems, in the present work, MH was coated on the CMSs surface to form a whole core-shell structure (MCMSs). This step can avoid the interface problem between CMSs and PET matrix. Only solve one interface problem between MH and PET matrix can satisfy the requirement for mechanical property. However, although MCMSs can improve the flame retardant of PET, MCMSs existed in aggregated state because of intensive Van der Waals attractive force and high surface energy of MH on the MCMSs surface. In addition, the MCMSs surface contained large amounts of hydroxyl and turned out to be hydrophilic state [16]. The difference in the surface polarity between MCMSs and polymer PET (hydrophobic) was very large, leading to the weak interface binding force, which brought about a decrease in other properties of the polymer composites. Therefore, MCMSs should be effectively modified to improve dispersion and interface binding with the PET matrix to meet the requirement of use.

The microencapsulation of the filler-type flame retardant lies in coating a homogeneous film with a certain thickness on the flame retardant surface [17–19]. The microencapsulated flame retardant owns core-shell structure. In order to improve the dispersion and compatibility of flame retardant, the surface polarity of shell material is often similar to the polymer matrix. The interface binding force between the flame retardant and polymer matrix ultimately affected the flame retardancy of polymer composites. In this work, on the basis of MH coating CMSs (MCMSs), silane coupling agent (APTS) as a bridge link was firstly grafted on the MCMSs surface (Si-MCMSs). Then Poly (ethylene terephthalate) microencapsulated PMCMSs were successfully prepared by in situ polymerization. The CMSs were coated by two layers to form core-shell PMCMSs. The effects of shell thickness on the structure and dispersion of PMCMSs were discussed. It was investigated systematically the effects of PMCMSs on the distribution in PET matrix as well as mechanical and flame retardant properties of PMCMSs/PET composites.

2. Materials and methods

2.1. Materials

CMSs with about 500 nm in diameter were synthesized by hydrothermal method. Glucose ($C_6H_{12}O_6$), Magnesium chloride ($MgCl_2 \cdot 6H_2O$), sodium hydroxide (NaOH), Polyethylene glycol (PEG6000), Dimethyl terephthalate (DMT), Ethylene glycol (EG), Zinc acetate ($Zn(Ac)_2$), antimony oxide (Sb_2O_3), Trimethyl phosphate (TMP), were all AR grade and obtained from Beijing Chemical Indstires Co, Ltd. (China). 3-Aminopropyltriethoxysilane (APTS) was purchased by Sigma-Aldrich Trading Co, Ltd. PET chips (SD500) with a viscosity index of 0.68 dL/g, were produced by Sinopec Yizheng Co., Ltd. (China).

2.2. Preparation of MH coating CMSs (MCMSs) flame retardant

Ionization treatment: 50 mL of NaOH solution (1 mol/L) was added into a beaker containing 2 g of CMSs. After the mixture was stirred at 45 °C for 3 h, the ionized CMSs was obtained by filtering, washing with distilled water and drying at 80 °C for 12 h.

Preparation of MH coating CMSs (MCMSs): $MgCl_2 \cdot 6H_2O$ (1.02 g) was added into 50 mL solution of ethanol and water (1:1, volume ratio) and stirred until it was dissolved completely. This solution was added with 0.58 g ionized CMSs, then stirred and sonicated for 1 h. The solution was named S1. 0.1 mL PEG6000 was added into the S1. NaOH (0.4 g) was added into 50 mL of ethanol/distilled water (1:1, volume ratio) and stirred until it was dissolved completely. The solution was named S2. S1 was added into a three-necked flask, followed by S2 dropwise addition at a rate of 2 mL/min under stirring with the speed of 1500 r/min. After dropping, reaction was kept at 45 °C for 18 h. Finally, the mixture was filtered, washed several times with distilled water and absolute ethyl alcohol, and dried at 120 °C for 5 h to obtain the product, named as MCMSs.

2.3. Preparation of APTS grafted on the surface of MCMSs (Si-MCMSs)

A three-necked flask was charged with 1 g MCMSs and 100 mL of absolute ethanol. 0.05 mL of APTS was added into 10 mL distilled water, and sonicated for 30 min. The APTS solution was added into the three-necked flask. The above mixture was reacted at 80 °C for 7 h under the conditions of condenser. The solids were washed, filtered and dried in vacuum. The product was defined as Si-MCMSs.

2.4. Preparation of microencapsulated Si-MCMSs (PMCMSs)

Certain amounts of Si-MCMSs was added into 500 mL four-necked flask with 100 mL of EG under ultrasonic vibration for 40 min. Then an amount of DMT was added into the above-mentioned solution. After preheating at elevated temperature, the transesterification catalyst $Zn(Ac)_2$ (accounting for 0.02% of DMT mass) was added with the stirring. By heating to 180 °C gradually and controlling the temperature of fractionation column (about 65 °C), when the amount of distilled methanol was about 95% of the theoretical amount, the ester interchange reaction was completed. Then the stabilizer TMP (0.03% of DMT mass) was added by dropwise. After about 5 min, the polycondensation catalyst Sb_2O_3 (0.04% of DMT mass) was added into the solution. With the increase of temperature, the temperature of the column top rose to 198 °C. After the removal of excess EG, when the temperature rose to about 240 °C, the material was bis- β -hydroxyethyl terephthalate (BHET) coating MCMSs (BHET@MCMSs). When the reaction temperature reached 255 °C, the polycondensation reaction was carried out under vacuum to obtain the PET coating MCMSs (PET@MCMSs), which is microencapsulated MCMSs, and named as PMCMSs.

2.5. Fabrication of PMCMSs/PET flame retardant composites

In the fabrication process of flame retardant composites, MCMSs and PMCMSs were mixed with PET pellets separately. All materials were dried in a vacuum oven at 120 °C for 12 h before use. After high speed mixing, the PET and flame retardants were melt-extruded in a CET35-40D type twin-extruder. The melt temperature range was from 263 °C to 270 °C, and the rotation speed of the twin-screw was 180 rpm. Then the products were cooled by flowing water and cut into pellets, named PMCMSs/PET composites. Finally, the pellets were processed for flame retardancy testing by injection-molding at the temperature from 255 °C to 275 °C. The whole scheme of the material preparation was shown in Fig. 1.

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