Polymer Degradation and Stability 134 (2016) 1–9

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Preparation of carbon microspheres coated magnesium hydroxide and its application in polyethylene terephthalate as flame retardant

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A R T I C L E I N F O

Article history:
Received 26 May 2016
Received in revised form
2 September 2016
Accepted 18 September 2016
Available online 20 September 2016

Keywords:
Carbon microspheres
Magnesium hydroxide
Polyethylene terephthalate
Flame retardant

A B S T R A C T

A novel flame retardant, carbon microspheres coated magnesium hydroxide ($Mg(OH)_2$@CMSs) was synthesized. The morphology and structure of $Mg(OH)_2$@CMSs was characterized by scanning electron microscope (SEM) and fourier transform infrared spectroscopy (FTIR). Then, $Mg(OH)_2$@CMSs was added into polyethylene terephthalate (PET) to improve the flame retardancy of PET. The prepared composite ($Mg(OH)_2$@CMSs/PET) with only 1 wt% $Mg(OH)_2$@CMSs obtained a LOI value of 27.5% and reached UL94 V-0 rating. The flame retardant mechanism was studied by cone calorimeter measurement, thermogravimetric analysis (TGA), SEM and FTIR. The results showed that $Mg(OH)_2$ and CMSs had synergistic flame retardant effect on PET. And there were two effects for $Mg(OH)_2$@CMSs to improve the flame retardancy of PET. On one hand, CMSs and MgO as the bridge supporting points were dispersed into the basic framework of char layer in order to further strengthen the three-dimensional network structure of char layer. Thus a continuous and compact protective layer was formed, resulting in the decrease of pk-HRR and pk-MLR. On the other hand, the FTIR spectra of $Mg(OH)_2$@CMSs/PET char residues showed that $Mg(OH)_2$@CMSs induced PET degrading into small molecules with C=C, which prevented PET from further decomposition, thus increased the amount of residue and decreased the THR value.

1. Introduction

Polyethylene terephthalate (PET) is widely used in polyester fibers, engineering plastics, organic film and many other areas, due to its excellent fatigue resistance, frictional resistance and processing properties [1]. However, the shortcoming of flammability has also brought great potential safety hazard for its application [2]. Traditionally, halogenated compounds and phosphate flame retardants have been widely used to endow PET with flame resistance, and then the halide antimony synergetic flame-retardant system, such as bromine diphenyl oxide and antimony trioxide, phosphorus halide synergetic flame-retardant system like dibromo phenyl phosphate ester, and other synergetic flame-retardant system gradually appeared [3–6]. In recent years, some nanoparticles such as the montmorillonite [7], layered silicate [8], inorganic oxide [9] and carbon nanotubes have come into view [10,11]. Though these flame retardants mentioned above improved the limiting oxygen index (LOI) of PET to some extent, most of them have the defects like massive smoke, corrosive gases release and low flame retardant efficiency.

As an emerging carbon nanomaterials, carbon microspheres (CMSs) have low density, good conductivity, chemical stability and thermal stability [12,13], mainly used as photoelectric material, catalyst carrier and adsorption materials at present [14–18]. The previous works of our group [19–21] verified that CMSs enhanced the flame retardancy of PET significantly. However, when added into PET as the single flame retardant, CMSs made the composites release heavy black smoke during burning. In addition, CMSs were easy to gather together in the polymer matrix because of their large specific surface area and high surface energy [22], so CMSs were generally modified before using.

Magnesium hydroxide ($Mg(OH)_2$), because of its good thermal stability, non-toxic and smoke suppression properties [23], was added into a variety of polymer as a kind of environmentally

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http://dx.doi.org/10.1016/j.polymdegradstab.2016.09.019
0141-3910/

friendly flame retardant [24–26], but its flame retardant efficiency is low, requiring the content of $Mg(OH)_2$ up to 40%–60% to achieve good flame retardancy [26,27]. Therefore, it is a preferred method for $Mg(OH)_2$ using other flame retardants to form synergetic flame-retardant system to improve the flame retardant efficiency.

In this work, a novel flame retardant additive, carbon microspheres coated by magnesium hydroxide ($Mg(OH)_2$@CMSs) was synthesized by the chemical deposition reaction, aiming to make full use of the advantages of CMSs and $Mg(OH)_2$, and achieve the superior flame retardancy with good smoke-suppressant property and high flame retardant efficiency. Moreover, core-shell structure of $Mg(OH)_2$@CMSs can reduce agglomerate phenomenon of CMSs and relieve the loss of mechanical properties of PET composites. $Mg(OH)_2$@CMSs was characterized by scanning electron microscope (SEM) and fourier transform infrared spectroscopy (FTIR). And the flame retardancy of $Mg(OH)_2$@CMSs in PET was estimated by means of limiting oxygen index (LOI), UL-94 vertical burning and cone calorimeter tests. Furthermore, thermogravimetric analysis (TGA) coupled with SEM and FTIR were used to discuss the flame retardant mechanism of $Mg(OH)_2$@CMSs in PET.

2. Experimental

2.1. Materials

Carbon microspheres (CMSs) was homemade by hydrothermal method [28]. Ammonia ($NH_3 \cdot H_2O$, analytical grade) was purchased from Tianjin Fuyu Chemical co., Ltd. (China). Magnesium chloride ($MgCl_26H_2O$, analytical grade) was bought from Tianjin Letai Chemical co., Ltd. (China). Anhydrous ethanol was provided by Tianjin Hengxing Chemical co., Ltd. (China). PET chips (SD500) with a viscosity index (VI) of 0.68 dL/g were produced by Sinopec Yizheng co., Ltd. (China). All of these materials were used as received without any further purification.

2.2. Preparation of $Mg(OH)_2$@CMSs

CMSs and anhydrous ethanol were introduced into a three-neck flask provided with mechanical stirring. Then a moderate amount of ammonia was added into the mixture to make PH $\geq$ 12, followed by $MgCl_2$ solution (0.5 mol/L) dropwise addition at a rate of 3 mL/min until PH = 10. The mixture was heated to 40 °C under stirring for 1 h, and then let it standing for 10 h. The solids were washed and filtrated with anhydrous ethanol till the PH value of the filtrate was 7. Finally the products were dried at 120 °C for 4 h.

2.3. Preparation of FR-PET composites

PET and flame retardants(CMSs, $Mg(OH)_2$ and $Mg(OH)_2$@CMSs) were previously dried in a vacuum oven at 120 °C overnight before use. The FR-PET composites were prepared by melt blending in a twin-screw extruder (CET35-40D). The temperature of each section was 270 °C, 2720 °C, 273 °C, 276 °C, 287 °C, 280 °C, 282 °C and 285 °C, and the feed rate was 15 rpm. The test specimens were prepared using an injection molding machine (JH600). The temperature of each section for injection molding was 255 °C, 254 °C, 253 °C and 250 °C. To compare the flame retardancy of CMSs, $Mg(OH)_2$ and $Mg(OH)_2$@CMSs, the CMSs/PET and $Mg(OH)_2$/PET composites were also prepared. The formulations of FR-PP composites are described in Table 1.

2.4. Characterization

The morphology of CMSs and $Mg(OH)_2$@CMSs was observed by MIRA-3 Scanning Electron Microscope (SEM) at high vacuum conditions with a voltage of 7 kV. The surface of samples was sputter-coated with gold layer before examination.

Fourier Transform Infrared (FTIR) spectra were obtained using FTIR-1730 infrared spectrometer. The powdered samples were thoroughly mixed with KBr and then pressed into pellets.

The limiting oxygen index (LOI) values were measured at room temperature by a TM606 oxygen index meter according to ISO 4589-2:2006 standard with specimen dimension of $130 \times 6.5 \times 3$ mm^3. Vertical burning (UL-94) tests were performed on a CZF-5-type instrument according to ANSI/UL94-2013 test standard with specimen dimension of $130 \times 13 \times 3.2$ mm^3. UL-94 testing results were carried out for burning ratings V-0, V-1, or V-2. V-0 rating corresponds to the best flame retardancy of polymeric materials.

Cone calorimeter measurements were performed on an FTT cone calorimeter according to ISO 5660 under an external heat flux of 50 kW/m^2. The dimension of samples was $100 \times 100 \times 10$ mm^3. The measurement for each specimen was repeated three times, and the error values of the typical cone calorimeter data were reproducible within ±5%.

Thermogravimetric analysis (TGA) was performed using TG209F1 thermogravimetric analyzer at a heating rate of 10 °C/min under nitrogen atmosphere from 30 °C to 900 °C.

The digital photos of samples after UL94 and cone calorimeter test were taken by the 700D Canon camera. The micromorphology images of the residues after cone calorimeter test were obtained using a MIRA-3 Scanning Electron Microscope (SEM) at high vacuum conditions with a voltage of 20 kV. The element contents of residues from cone calorimeter test were investigated via an AMETEK Quanta 250 FEG/EDS Energy Dispersive Spectrometer. The tested specimens were obtained from the surface of residues with sufficiently mixed and grinded, and the results were the average of the three times repeated tests which were all reproducible within ±5%.

3. Results and discussion

3.1. Characterization of the structure of $Mg(OH)_2$@CMSs

The morphologies and structures of CMSs and $Mg(OH)_2$@CMSs were examined by SEM. Fig. 1a shows that original CMSs have a smooth surface, with a uniform particle size of approximately 600 nm. In contrast, it is observed that the surface of $Mg(OH)_2$@CMSs in Fig. 1b becomes rough, and there is an evident coating layer with several nanometer thickness on the CMSs surface. In addition, the EDS spectrum of $Mg(OH)_2$@CMSs shows that the surface of particles not only contains C and O elements, but that there is also Mg, which suggests that the material coated on the surface of CMSs is likely to be $Mg(OH)_2$.

The FTIR spectra give the evidence to this assumption (Fig. 2). As shown in Fig. 2, the characteristic absorptions at 3410 cm^{-1}, 2125 cm^{-1}, 1634 cm^{-1} and 660 cm^{-1} are assigned to the absorbance peak of H_2O. There are several characteristic absorption peaks of CMSs: the peaks at 3550 cm^{-1} and 3480 cm^{-1} are corresponding to the stretching vibration of -OH; the peak at 1620 cm^{-1} is attributed to the stretching vibration of -COO in carboxyl. By contrast, $Mg(OH)_2$@CMSs retain the characteristic peaks of CMSs, and a new peak at 3698 cm^{-1} appears due to the stretching vibration of -OH in $Mg(OH)_2$. Moreover, the peak at 480 cm^{-1} is associated with the stretching vibration of O-Mg, which further confirms that material coating on the surface of CMSs is $Mg(OH)_2$.

3.2. Flame-retardant behaviors of PET composites

3.2.1. LOI and UL94 vertical tests

The flame retardancy of PET and PET composites was detected