The influence of manganese–cobalt oxide/graphene on reducing fire hazards of poly(butylene terephthalate)

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HIGHLIGHTS

- $MnCo_2O_4$–GNS hybrids are synthesized by a two-stage liquid phase method.
- $MnCo_2O_4$–GNS/PBT composites were prepared via a masterbatch-melt blending method.
- Fire hazards are monitored and evaluated by cone calorimeter and TG-IR.
- $MnCo_2O_4$–GNS hybrids decrease thermal hazards and smoke hazards of PBT composites.
- $MnCo_2O_4$–GNS hybrids perform better catalytic oxidation of CO and organic volatile.

ARTICLE INFO

ABSTRACT

By means of direct nucleation and growth on the surface of graphene and element doping of cobalt oxide (Co_3O_4) nano-particles, manganese–cobalt oxide/graphene hybrids ($MnCo_2O_4$–GNS) were synthesized to reduce fire hazards of poly(butylene terephthalate) (PBT). The structure, elemental composition and morphology of the obtained hybrids were surveyed by X-ray diffraction, X-ray photoelectron spectrometer and transmission electron microscopy, respectively. Thermogravimetric analysis was applied to simulate and study the influence of $MnCo_2O_4$–GNS hybrids on thermal degradation of PBT during combustion. The fire hazards of PBT and its composites were assessed by the cone calorimeter. The cone test results had showed that peak HRR and SPR values of $MnCo_2O_4$–GNS/PBT composites were lower than that of pure PBT and Co_3O_4–GNS/PBT composites. Furthermore, the incorporation of $MnCo_2O_4$–GNS hybrids gave rise to apparent decrease of pyrolysis products containing aromatic compounds, carbonyl compounds, carbon monoxide and carbon dioxide, attributed to combined impact of physical barrier for graphene and cat O_4 for organic volatiles and carbon monoxide.

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1. Introduction

As is well known, Fire hazards of polymer materials are thermal hazards and smoke hazards. Thermal hazards are that polymer materials during combustion generate a large amount of heat that drives people trapped in the fire into a tremendous threat and encourages the spread of fire. Heat release rate (HRR), total heat release (THR), time to ignition, fire performance index and fire growth index are all evaluation index of thermal hazards [1,2]. Among these, HRR is the most important parameter to estimate seriousness of thermal hazards, especially peak heat release rate (PHRR) [3]. Smoke hazards are polymer materials during combustion generate a large amount of pyrolysis products composed of smoke particles, organic volatiles, carbon dioxide (CO_2), carbon monoxide (CO) and so on [4]. The hazards of organic volatiles exhibit on three aspects: firstly, organic volatiles could be condensed and aggregated to form smoke particles, which would

greatly increase the difficulty of fire rescue by reducing the visibility of fire scenes; secondly, various kinds of organic volatiles including aromatic hydrocarbons [5] and carbonyl compounds [6] are harmful for humans body; finally, organic volatiles can act as "fuel" to support burning. Hence, the reduction of organic volatiles would increase the visibility of fire scenario, lower the damage to people's health and decrease HRR of materials. Moreover, CO, the most dangerous killer for casualties in fire accidents, is the deadliest threat to persons fell into fire [7]. Therefore, decrease of organic volatiles and CO yield to reduce smoke hazards of materials, has been more and more active [4,8]. Based on the previous work, it can be seen that it is an effective and green way to catalyze organic volatiles and CO to non-flammable and non-toxic carbon dioxide (CO_2) [9–11].

Due to good dimensional stability, high thermal resistance, prominent mechanical properties and excellent electrical insulation, Poly(butylene terephthalate) (PBT) has been broadly applied in electronic industries [12]. Similar to other polymer materials, PBT has high fire hazards in the applications when fire accidents happen. PHRR of pure PBT would reach up to 1404 kW/m^2 [13], indicating that large amount of heat will be released during combustion. Yang *et al.* have demonstrated that plentiful aromatic compounds and carbonyl compounds are liberated during burning [14], which harm human's health. In addition, aromatic compounds tend to form smoke particles because of high content of carbon, thus reducing the visibility of fire scenes. Therefore, it is important to reduce fire hazards of PBT, which is in favor of enlarging its application.

As the most studied class of layered materials, graphene nanosheets (GNSs) have attracted attention in numerous fields covering catalysts, energy devices, transistor, nanocomposites [15–17]. Due to the superior barrier effect resulting from its peculiar two-dimensional (2D) structure, GNSs have aroused continuous studies on fire safety in last several years [18–20]. Kim et al. have proved that graphene nanosheets show remarkable flame resistance [21]. Besides, our previous reports have demonstrated that GNS can significantly inhibit the release of heat and pyrolysis outcomes during burning of polymer materials [22]. Whereas, flame retardant efficiency of graphene alone could not reach anticipant result. To enhance the inflaming retarding efficiency of graphene, it is essential to modify graphene with other flame retardants. Because of high efficiency in catalytic carbonization and catalytic oxidation, transition metal oxide is a nice choice [23].

As a result of high catalytic activity of tricobalt tetraoxide (Co_3O_4), it has been applied in facilitating hydrogen (H_2) production [24], promoting oxygen reduction reaction (ORR) [25], accelerating deep oxidation of CO [26] and organic volatiles [27], and so on. Among these, catalytic oxidation of CO and organic volatiles is most appealing for decreasing toxic gases. In order to improve catalytic activity of Co_3O_4, doping other transition metal element in Co_3O_4 is a more effective method. Zhao et al. show MnO_3 has better catalytic oxidation of phenol than Co_3O_4 [28]. Furthermore, substituted Co_3O_4 with Mn has shown more excellent catalytic activity for ORR [29]. As a consequence, it is reasonable to expect that doping Mn into tricobalt tetraoxide may perform better catalytic oxidation of CO and organic volatiles during the combustion of polymers. Furthermore, manganese sub-group compounds could tremendously improve flame retardance of intumescent polymer systems via increasing char residues and forming more compact char layer [30–32], which demonstrates the importance of Mn on reducing fire hazards of polymer.

In this work, the covalently coupled $MnCo_2O_4$–GNS hybrids were synthesized by the nucleation and crystallization of $MnCo_2O_4$ nanoparticles on graphene and were added into PBT to prepare $MnCo_2O_4$–GNS/PBT composites via a masterbatch-melt blending method. It is anticipated that $MnCo_2O_4$–GNS hybrids could show better catalytic oxidative activity of generated CO and organic volatiles than Co_3O_4/GNS hybrids, thus leading to lower fire hazards of PBT.

2. Experimental

2.1. Materials

Poly(butylene terephthalate) was purchased from BASF Chemical Company, Germany. Powdered graphite, oil of vitriol (98%), $NaNo_3$, $KMnO_4$, H_2O_2 solution (30%), hydrochloric acid, $Co(OAc)_2·4H_2O$, $Mn(OAc)_2·4H_2O$ and NH_4OH were all bought from Sinopharm Chemical Reagent Co., Ltd.

2.2. Synthesis of $MnCo_2O_4$–GNS hybrid

Graphite oxide (GO) was originated from graphite by means of modified Hummers' method. $MnCo_2O_4$–GNS hybrids were synthesized via two-stage liquid phase method, as shown in Scheme 1a. Firstly, 8 ml of 0.3 M cobalt acetate aqueous solution and 4 ml of 0.3 M manganese acetate aqueous solution were mixed with 200 ml GO ethanol suspension ($\sim$ 0.5 mg/ml), accompanied by adding 200 ml of water and 8 ml $NH_3·H_2O$. The reaction was held at 80 °C for the whole day with mild stirring. Secondly, the above mixture was shifted to an autoclave and kept at 150 °C for 4 h. Since then, the resultant products were collected by centrifugal separation, then cleaned with deionized water, and completely dried.

Co_3O_4–GNS hybrids were synthesized through the same procedure expect 4 ml of 0.3 M manganese acetate aqueous solution was replaced by 2 ml of 0.6 M cobalt acetate aqueous solution.

2.3. Preparation of $MnCo_2O_4$–GNS/PBT nanocomposites

Scheme 1b displays that $MnCo_2O_4$–GNS/PBT nanocomposites were processed by a masterbatch-melt blending method. 0.5 g $MnCo_2O_4$–GNS hybrids were dispersed in a certain amount of the mixed solvent composed by phenol and tetrachloroethane (the mass ratio was 1:1) with several hours of ultrasonication and mechanical agitation, and homogeneous suspension was obtained. 4.5 g PBT was dissolved in proper amount of the above-mentioned solvents and the mixture was added to the above suspension. After 2 h of ultrasonication and mechanical stirring, this homogenous mixture was obtained and dried in a vacuum oven overnight to remove excess solvents. Then the masterbatch (10% $MnCo_2O_4$–GNS hybrids and 90% PBT) was obtained and mixed with neat PBT by the melting method to prepare the samples containing 1% $MnCo_2O_4$–GNS hybrids.

Co_3O_4–GNS/PBT composites were prepared via the same step expect only $MnCo_2O_4$–GNS hybrids were replaced by the same amount of Co_3O_4–GNS.

2.4. Characterization

X-ray diffraction (XRD) measurements were implemented on a Japan Rigaku D Max-Ra rotating anode X-ray diffractometer. The scanning speed and range were 4°/min and 10°–70° respectively.

X-ray photoelectron spectrometer (XPS) spectra were recorded using a Kratos Axis Ultra DLD spectrometer employing a monochromatic Al Kα X-ray source ($h\nu$ = 1486.6 eV).

The morphology of manganese–cobalt oxide/graphene hybrid was observed by transmission electron microscopy (TEM, JEM-2100F, Japan Electron Optics Laboratory Co., Ltd., Japan).

Thermogravimetric analysis (TGA) was implement with the aid of a Q5000 IR (TA Instruments) thermal analyzer in range between indoor temperature and 800 °C. The heating speed is 20 °C/min.