The influence of cobalt oxide–graphene hybrids on thermal degradation, fire hazards and mechanical properties of thermoplastic polyurethane composites

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ARTICLE INFO

ABSTRACT

In this work, cobalt oxide nanoparticles decorated on graphene nanosheets was firstly synthesized by a facile hydrothermal method. The structure and morphology of the synthesized hybrids were characterized by X-ray diffraction, Raman spectrum and Transmission electron microscopy measurements. Subsequently, the hybrids were introduced into thermoplastic polyurethane matrix for acting as reinforcements. The hybrids were well dispersed in thermoplastic polyurethane and no obvious aggregation of graphene nanosheets was observed. The obtained nanocomposites exhibited significant improvements in thermal stability, flame retardancy, mechanical properties and reduced the fire toxicity effectively, compared with those of neat polyurethane. The obvious improvements of these properties were mainly attributed to the "tortuous path" effect of graphene nanosheets, catalytic char formation function of cobalt oxide–graphene hybrids and the synergism between the catalysis effect of cobalt oxide nanoparticles and the adsorption effect of graphene nanosheets.

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1. Introduction

Thermoplastic polyurethane (TPU) is a unique polymeric material with high tensile and flexural fatigue strength, excellent low temperature flexibility, outstanding wear and abrasion resistance, which has been widely used in many fields such as furniture, footwear, ideal cable sheathing and insulation materials, coatings, adhesives and elastomers [1]. However, one of the main drawbacks of TPU is its inherent flammability which burns in a rapid way and generates a large amounts of smoke and toxic gases during combustion. Therefore, it is of great significance to reduce fire hazards of TPU, especially in those fields where a flame retardancy property is grimly demanded.

Nanocomposite technology have been proved to be an effective approach for enhancing the flame retardancy of polymer materials [2–5]. In the past few decades, the addition of nanofillers such as layered silicates, layered double hydroxides, carbon nanotube, fullerene, silica and polyhedral oligomeric silsesquioxanes nanoparticles et al. exhibits favorable effect on improving the flame retardancy, thermal stability, mechanical, and electrical properties

of polymer materials simultaneously at low loading [5,6]. As an emerging 2D material, graphene and its derivatives have attracted great attention in numerous fields due to its high surface area and chemical stability, unique electronic and outstanding mechanical properties [7]. The addition of graphene with very low loadings into a polymeric matrix can significantly improve the mechanical, thermal, electrical, and gas barrier properties of the polymer matrix [8]. More recently, graphene has shown great potential as flame retardant additives to endow polymers with flame retardancy which is similar to the other carbon-based materials, such as expanded graphite and carbon nanotubes [9,10].

However, there are still some problems hindering the application of graphene as a flame retardant. Bear the brunt of the low flame retardant efficiency of bare graphene nanosheets [11]; Secondly, it is worth noting that the improvement of fire safety is only achieved when graphene nanosheets are uniformly dispersed and strongly interacts with the surrounding polymer matrix. But actually, pristine graphene has a tendency to agglomerate and even restack in polymer matrix due to the strong van der Waals force and π–π interactions which limits its dispersion in polymer matrices [12,13]. Moreover, the essential reason for incorporating fire retardants into polymer materials is to reduce the fire hazard which is a combination of flammability and fire toxicity. Therefore,

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the concerns are not only focused on making materials less flammable and low flame spread properties, but also in reducing above fatal toxicity [14]. For the flame retardant polymer/graphene nanocomposites, the previous research works are mainly focused on the flame retardancy of the polymer materials, rarely involved with the fire toxicity properties during combustion. Moreover, Bao et al. has been reported that the modified graphene nanosheets even increased the smoke yield during combustion [9]. Therefore, the use of bare graphene to reduce the fire hazards of polymers remains a challenge.

Recently, polymer nanocomposites based on hybrid nanofillers which comprise two or more heterogeneous nano elementary units with different properties, have been demonstrated to be a more attractive strategy for the enhancement of mechanical, electrical, and thermal conductivity properties of the composites [15,16]. Moreover, it can be expected that the agglomeration of the nanoparticles and weak interfacial interaction problems in polymer nanocomposites are solved simultaneously by using such functional hybrid nanofillers [17]. Fang's research work has revealed that the incorporation of carbon nanotubes and graphene obviously slowed down the whole combustion process [18]. In our previous work, transition metal compounds loaded graphene hybrids have been prepared and incorporated into various polymer matrices for fire safety applications [19–21]. These discoveries convince us that the graphene nanosheets are able to make polymeric materials much safer and the transition metal oxides loaded graphene has higher efficiency in flame retardant polymer nanocomposites compared with the bare graphene.

Inspired by this, it may be an efficient method to improve the thermal stability and reduce the fire hazards of TPU nanocomposites by the combination of graphene with typical transition metal oxides. As well known, the cobalt oxide has been widely applied in accelerating oxidation of CO and organic volatiles which is most appealing for decreasing toxic gases released from the fire accidents [22–24]. As an exfoliated 2D material, graphene can be used as a perfect supporter to ameliorate the dispersion of cobalt oxide nanoparticles in the polymer matrix. In addition, the restacking of the graphene nanosheets can be effectively prevented by the tightly decorated cobalt oxide nanoparticles, which is beneficial for improving the dispersibility of graphene in polymer matrices [11]. Moreover, various improvements have been obtained with TPU/graphene nanocomposites, such as thermal stability, electrical conductivity, mechanical properties, thermal conductivity, bacterial antiadhesive property, gas barrier and dielectric properties [25–29]. Nevertheless, to the best of our knowledge, scarcely any attention has been paid to investigate the influence of graphene on the fire hazards of TPU nanocomposites since the discovery of graphene.

In present study, graphene supported cobalt oxides hybrids (Co_3O_4–GNS) are firstly synthesized by a facile hydrothermal method and then TPU nanocomposites are prepared by solvent blending method. The thermal degradation, fire hazards and mechanical properties of the TPU nanocomposites are investigated seriatim. Furthermore, mechanisms of the improved properties are discussed. This work attempts to provide a promising strategy to reduce the fire hazards of TPU, thus promoting the development of a new class of graphene-based flame retardant additives for polymers.

2. Experimental

2.1. Materials

All starting materials used in this work were of analytical grade and used as received without further purification which were purchased from Sinopharm Chemical Reagent Co. TPU granules were kindly provided by Hefei KeYan Chemical Materials Company (Hefei, China).

2.2. Synthesis of graphite oxide (GO)

GO nanosheets were synthesized from expanded graphite by a modified Hummers' method [19,30].

2.3. Synthesis of Co_3O_4–GNS hybrids

The Co_3O_4–GNS hybrids were prepared by a facile hydrothermal method which was shown in Scheme 1a. In a typical procedure, 200 mg of GO was added to 400 mL of distilled water with the assistance of sonication for 2 h. Then, an appropriate amount of $Co(NO_3)_2 \cdot 6H_2O$, followed by ammonia solution ($NH_3 \cdot H_2O$, 25 wt %) and hydrazine, were slowly added into the above dispersed GO solution. The mixture was then stirred for 30 min and sealed in a 500 mL Teflon-lined autoclave and maintained at 100 °C for 4 h. After cooled to room temperature, the precipitates were collected by centrifugation, washed with ethanol for several times, and dried at 80 °C for 6 h. Finally, the resulting precipitates precursor was calcined at 450 °C in muffle furnace for 2 h to obtain the Co_3O_4–GNS hybrids [31].

The pure GNS samples were prepared under the same synthesis conditions without the addition of $Co(NO_3)_2 \cdot 6H_2O$.

2.4. Preparation of TPU/Co_3O_4–GNS nanocomposites

TPU/Co_3O_4–GNS nanocomposites were prepared by a solvent blending method which was presented in Scheme 1b. In a typical experiment, 0.1 g Co_3O_4–GNS hybrids were firstly dispersed in DMF in a three necked round-bottom flask with several hours of ultrasonication and strong mechanical stirring to obtain homogeneous suspension. Then 5.0 g TPU granules were incorporated into the above homogeneous suspension. After 2 h of ultrasonication and strong mechanical stirring, the black slurry obtained was dried in an oven at 100 °C for 24 h, and further dried at 130 °C for 12 h. Then the obtained samples were hot pressed at 180 °C to form specimens for test.

2.5. Characterization

X-ray diffraction (XRD) patterns were taken on a Japan Rigaku D/Max-Ra rotating anode X-ray diffractometer equipped with a Cu-Kα tube and Ni filter ($\lambda = 0.1542$ nm). Laser Raman spectroscopy (LRS) measurements were carried out at room temperature with a SPEX-1403 laser Raman spectrometer (SPEX Co., USA). Transmission electron microscopy (TEM, JEM-2100F, Japan Electron Optics Laboratory Co., Ltd.) was employed to investigate the morphology of GO, GNS, Co_3O_4–GNS hybrids. Scanning electron microscopy (SEM) (JSM-6800F, JEOL) was used to observe the fracture surface structure of TPU nanocomposites. Thermogravimetric analysis (TGA) was carried out using a Q5000 thermoanalyzer instrument (TA Instruments Inc., New Castle, DE) under N_2 flow of 60 mL min^{-1}. In each case, the samples were heated from room temperature to 800 °C at a linear heating rate 20 °C min^{-1}. Microscale combustion colorimeter (MCC-2) was used to investigate the flammability characteristics of TPU and its nanocomposites according to ASTM D7309-07. The fire toxicity was further assessed using a steady state tube furnace (ISO TS 19700). The thermogravimetric analysis/infrared spectrometry (TG-IR) of the samples was performed using a TGA Q5000 IR thermogravimetric analyzer that was interfaced to the Nicolet 6700 FTIR spectrophotometer. The tensile strength and elongation at breaking of TPU nanocomposites were measured according to the Chinese standard of GB 13022-91