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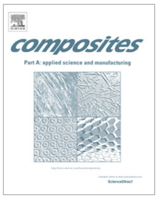

The influence of graphene based smoke suppression agents on reduced fire hazards of polystyrene composites

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ABSTRACT

In this work, typical smoke suppression agent particles decorated on graphene nanosheets were facilely synthesized by a solvothermal method for reducing the fire hazards of polymer composites. The structure, elemental composition and morphology of the hybrids were characterized by X-ray diffraction, Raman spectroscopy, X-ray photoelectron spectroscopy and transmission electron microscopy measurements. Subsequently, the hybrids were incorporated into polystyrene for improvement of the thermal stability and reduction of fire hazards. The hybrids were well dispersed in PS matrix and no obvious aggregation of graphene nanosheets was observed. The obtained nanocomposites exhibited significant improvements in thermal stability, flame retardancy and reduced the fire toxicity, compared with those of neat polystyrene. This dramatically reduced fire hazard was mainly ascribed to the combined effects of smoke suppression agent particles and graphene nanosheets, containing good dispersion of hybrids, catalytic char function of hybrids and physical barrier effects of graphene nanosheets.

1. Introduction

In the past few decades, polymeric materials have been widely used in our life due to the incomparable advantages over traditional materials. However, many potential applications are limited by serious fire hazards of the polymer materials, which cause the loss of life and property, attracting considerable attention from governments and society. It mainly contains thermal hazards and non-thermal hazards. Thermal hazards are defined as that polymer materials generate a large amount of heat during combustion and lead to melt dripping which further encourages the spread of fire [1,2]. The non-thermal hazards means the emitting a great deal of toxic gases and smoke, such as CO, HCN, NO_x, organic volatiles and smoke particles. It has been reported that most fire deaths are due to toxic gases, oxygen deprivation and smoke inhalation [3,4]. The smoke produced in the fire is even the most important factor which directly puts people to death by poisoning and suffocation [5]. In addition, the impairing visibility and narcotic irritating effect of fire gases are regarded as the decisive factor which prevents many fire victims from perceiving their possibilities of escape [6].

Polystyrene (PS) is a general-purpose thermoplastic which has been extensively used in many fields due to its outstanding properties [7]. However, like many synthetic polymers, the inherent flammability, severe melt-dripping and release a large amount of smoke during combustion severely restricts its application. Therefore, it is of significance to improve the thermal stability and reduce the fire hazards of PS simultaneously. As a general rule, polymers with aliphatic backbones tend toward low smoke generation, while polyenic polymers and those with pendant aromatic groups produce more smoke [8], which means that PS is easy to produce large amounts of smoke. As a consequence, reducing the overall fire hazards requires consideration of flammability, toxic gases and smoke from PS.

According to previous research works, even incorporation of a small amount of 2D layered inorganic nanofillers, such as molybdenum disulfide (MoS_2) [9–15], clay and layered double hydroxides (LDH) [16–19], could significantly improve the thermal stability and flame retardancy of polymers. As an emerging 2D material, graphene and its derivatives had attracted world-wide attention in numerous fields covering catalysts, energy devices, transistors, nanocomposites due to their unrivalled properties [2]. It has demonstrated that graphene is very thermally stable even after being exposed to a flame, clearly indicating the high intrinsic flame resistance of graphene [20]. According to recent reports, graphene shows great potential as flame retardant

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additives to endow polymers with high flame retardancy [21,22], which is similar to the other carbon-based materials, such as expanded graphite and carbon nanotubes. However, there are still some problems hindering the application of graphene widely as a flame retardant. Bear the brunt of the low flame retardant efficiency [23]; secondly, it is worth noting that the improvement in fire safety is only achieved when graphene nanosheets are uniformly dispersed and strongly interacts with the polymer matrix. But actually, pristine graphene has a tendency to agglomerate and even restack in polymer matrices due to the strong van der Waals force and π–π interactions which limits the dispersion of graphene in polymer matrix [24,25]. 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 smoke toxicity. Therefore, the concerns are not only focused on making materials less flammable and low flame spread properties, but also in reducing above fatal toxicity [26]. For the polymer/graphene nanocomposites, the previous research works are mainly focused on the fire resistance properties, rarely involved with the smoke suppression properties during combustion. Moreover, Bao et al. has been reported that the modified graphene nanosheets even increased the smoke yield during combustion [27]. Therefore, the use of graphene alone to reduce the fire hazards of polymers remains a challenge.

In previous work, transition metal compounds such as CuO, MoO_3 and FeOOH have been widely used to act as flame retardants and smoke suppressants for organic polymers [28]. As a typical smoke suppression agent, ferrocene and a range of substituted ferrocene have been synthesized and incorporated into polymer matrices which can improve the thermal stability, fire resistance and smoke suppression properties [29,30]. The most optimistic results is that the addition of 2% substituted ferrocene leads to 50% decrease in smoke suppression property of the PVC [29]. However, in our previous work, the incorporation of the ferrocene into PS can improve the smoke suppression properties, but exhibiting a combustion-supporting effect simultaneously [13]. Therefore, the use of ferrocene alone as flame retardants to reduce the fire hazards of PS composites remains unsatisfactory.

It is well-known that the combination of two or more components can present a synergistic effect and offer an excellent flame resistance to polymers. Fang's group has revealed that the incorporation of graphene and carbon nanotubes obviously slowed down the whole combustion process [31]. Tang's group has demonstrated that dramatically improved fire retardancy of polyolefin by combination of 2D clay and Ni_2O_3 [32]. Inspired by this, it may be an efficient method to improve the thermal stability and reduce the fire hazards of PS composites by the combination of graphene and commonly used smoke suppression agent ferrocene (Fc). As an exfoliated two-dimensional material, graphene can be used as a perfect supporter to ameliorate the dispersion of Fc nanoparticles in the polymer matrix. In addition, the restacking of the graphene nanosheets can be effectively prevented by the tightly decorated nanoparticles, which is beneficial for increasing the dispersibility of graphene in polymer matrices [23].

In this work, graphene based smoke suppression agent hybrids (Fc-GNS) are synthesized and incorporated into PS matrix. The thermal stability, fire resistance and smoke suppression properties of the PS composites are investigated. The mechanism of the enhanced thermal stability and the reduction of fire hazards is proposed. It is anticipated that graphene based smoke suppression agent hybrids will provide a promising solution to reduce the fire hazards of PS, 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. PS (158 K) was obtained from BASF-YPC Co., Ltd (China).

2.2. Synthesis of graphite oxide (GO)

GO single layers were synthesized from expanded graphite using a modified Hummers'method [33,34].

2.3. Synthesis of Fc-GNS hybrids

The Fc-GNS hybrids were prepared by a simple solvothermal process [35] which was shown in Scheme 1a. In a typical procedure, 0.3 g GO was dispersed uniformly into 400 mL anhydrous ethanol by sonication. Then, 0.3 g Fc was added into the solution under sonication. The mixture was then stirred for 20 min and sealed in a 500 mL Teflon-lined autoclave and maintained at 170 °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 10 h.

The pure GNS samples were obtained under the same synthesis conditions without the addition of Fc.

2.4. Preparation of Fc-GNS/PS nanocomposites

Fc-GNS/PS nanocomposites were prepared by a masterbatch-melt blending method which was presented in Scheme 1b. The formulations of the PS nanocomposites were listed in Table 1. In a typical experiment, 1.0 g Fc-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 10.0 g PS particles 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 masterbatch was mixed with neat PS particles by melting method to prepare PS nanocomposites.

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). X-ray photoelectron spectroscopy (XPS) spectra were performed on VG ESCALB MK-II electron spectrometer. Transmission electron microscopy (TEM) images were carried out to observe the morphology of GO, GNS, Fc-GNS hybrids and the dispersibility of Fc-GNS hybrids in PS matrix using a Hitachi model H-800 TEM. Thermogravimetric analysis (TGA) was carried out using a Q5000 thermoanalyzer instrument (TA Instruments Inc., New Castle, DE) under air flow of 25 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}. Flammability of the samples was characterized using a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. The fire toxicity was further assessed using a steady state tube furnace (ISO TS 19700) which was shown in Scheme 2. The