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In-situ synthesized CNTs/Bi_2Se_3 nanocomposites by a facile wet chemical method and its application for enhancing fire safety of epoxy resin

Yanbei Hou, Weizhao Hu, Longxiang Liu, Zhou Gui*, Yuan Hu**

State Key Laboratory of Fire Science, University of Science and Technology of China, Hefei, Anhui 230026, PR China

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ABSTRACT

In this work, a flowering-branch like CNTs/Bi_2Se_3 hybrids was synthesized by a facile in-situ method. CNTs as carrier could provide low agglomeration of layered Bi_2Se_3. As-prepared nanomaterials were added into epoxy resin (EP) to enhance its fire safety. Compared with neat EP, there were more than 44% and 23% decrease in the value of peak heat release and total heat release with 2 wt% content of CNTs/Bi_2Se_3, respectively, confirmed the enhancement of flame retardancy of EP composites. Meanwhile, the release of smoke and CO were also suppressed during EP combustion. From results of thermogravimetric analysis-infrared spectrometry, the addition of CNTs/Bi_2Se_3 obviously reduced the release of organic gaseous products, which contributed to the improved fire safety of EP matrix. Based on the analysis of gas and condensed phases, the possible enhancement mechanisms can be mainly concluded as the barrier effect of as-synthesized binary hybrids and enhanced char layers. Meanwhile, the addition of CNTs/Bi_2Se_3 enhanced the mechanical performance of EP composites. This work broadens the application fields of Bi_2Se_3 and enriches the membership of CNTs-based binary compounds, which were used as flame retardants.

1. Introduction

Two dimensional (2D) nanomaterials have been scientifically studied for more than 150 years [1]. Graphene is the most highly studied 2D materials, due to its exceptional electronic, physical, and optical properties [2]. Beyond graphene, other ultrathin 2D nanomaterials that possess similar layered structure features also have versatile properties, such as 2D hexagonal boron nitride (hBN) [3], graphitic carbon nitride (g-C3N4) [4], and layered double hydroxides (LDHs) [5]. Transition metal dichalcogenides (TMDs) also have been explored in recent years for their unique structural features and outstanding properties [6,7]. These extraordinary properties further ignited the interests of synthetic methods, such as micromechanical cleavage [8], ion-intercalation and exfoliation [9], chemical vapor deposition [10], etc. However, there are some drawbacks in these methods, including low-efficiency and potential hazards. Some active or corrosive substances, such as strong acid and butyl lithium, are used to prepare nanosheets, which could be adverse to experimenter. An efficient method to obtain ultrathin 2D nanomaterials is still on the scientific schedule.

2D nanomaterials, as functional fillers, have been widely applied in polymeric materials to improve their inherent defects [11,12], such as low-strength, inflammability, easy aging, etc. With the increasing applications of polymers in daily life, the fire safety of polymeric materials urgently need to be enhanced. As efficient halogen flame-retardants (FRs) are not on the list for the potential environmental hazards [13], new kinds of halogen-free FRs were explored, such as organic FRs [14,15], inorganic FRs [16], and polymeric FRs. Among them, layered nanomaterials show promising applications as FRs for enhancing fire safety of polymers, such as layered montmorillonite [17], graphene [18], molybdenum disulfide [19], LDHs [20], and so on.

Bismuth selenide (Bi_2Se_3) is a kind of A_2B_3 (A = Sb; B = Se, Te) chalcogenide materials, which share the same layered rhombohedral crystal structure [21]. The synthesis methods of Bi_2Se_3 nanomaterials generally required high temperature [22–24]. However, a facile wet-chemical method as an efficient way to synthesize ultrathin Bi_2Se_3 nanosheets has been recently proposed, which will

* Corresponding author.
** Corresponding author.
E-mail addresses: zgui@ustc.edu.cn (Z. Gui), yuanhu@ustc.edu.cn (Y. Hu).

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prosper the application fields of the nanosheets in the future [25]. Bi_2Se_3 has a promising application as FRs to enhance fire safety of polymers, confirmed by our previous report [26]. To improve the flame-retardant efficiency of Bi_2Se_3, a further modification should be treated.

To further modify Bi_2Se_3 nanosheets, a flowering-branch like CNTs/Bi_2Se_3 hybrids was synthesized by a facile wet-chemical method in this work. The thermal stability, flame retardancy, smoke and CO release behaviors of as-synthesized EP/CNTs/Bi_2Se_3 nanocomposites were all investigated to evaluate the effect of fillers on the fire safety of EP composites. The related mechanisms were provided by the analysis of gas and condensed phases of EP matrix.

2. Experimental section

2.1. Materials

Selenium (Se), Bismuth nitrate pentahydrate ($Bi(NO_3)_3\cdot 5H_2O$), sodium borohydride ($NaBH_4$), polyvinylpyrrolidone (PVP), ethylene glycol (EG), acetone and diaminodiphenylmethane (DDM) were all of analytical reagent grade quality and were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). The acidulated carbon nanotubes (CNTs) were purchased from Beijing DK Nano technology Co., Ltd. Epoxy resin (DGEBA, commercial name: E−44, epoxy value: 0.44) was supplied by Hefei Jiangfeng Chemical Industry Co. Ltd (Anhui, China).

2.2. Preparation of CNTs/Bi_2Se_3 hybrids

In this work, Bi_2Se_3 nanosheets were in-situ synthesized on the surface of CNTs. Typically, 0.1 g CNTs dispersed in 100 mL EG with sonication for 0.5 h, and then 1.0 g PVP slowly added into the above solution under intense agitation. As PVP was fully dissolved, 0.93 mmol $Bi(NO_3)_3\cdot 5H_2O$ was mixed into the solution, followed by sonication for 0.5 h (solution A). The synthesis process of Bi_2Se_3 was similar with previous report by a wet chemical reaction. To prepare NaHSe solution, 3.4 mmol Se and 7 mmol $NaBH_4$ were reacted in the 11 mL distilled water under N_2 atmosphere until the mixed solution became transparent (solution B). The solution A was heated to 160 °C under N_2 condition, and then 2 mL solution B quickly injected into it. After 15 min reaction, the black products were collected by centrifugation with 10000 r/min rotate speed, washing with acetone for several times, and drying in 50 °C oven. The Bi_2Se_3 nanosheets were prepared by the same process without CNTs.

2.3. Preparation of EP/CNTs/Bi_2Se_3 nanocomposites

EP/CNTs/Bi_2Se_3 nanocomposites were prepared by a facile solution method. Briefly, the preparation of EP composites with 0.5, 1, and 2 wt% CNTs/Bi_2Se_3 were performed as follow: to obtain homogeneous dispersed additives in matrix, a given mass of CNTs/Bi_2Se_3 hybrids dispersed in acetone with sonication for 0.5 h. The corresponding mass of EP resins were added to the suspension and stirred for another 0.5 h. Assisted with stirring, the mixtures were heated to 95 °C and kept overnight to remove acetone. Then melting DDM poured into the system and stirred several minutes. The viscous EP pre-polymers cured at 100 °C for 2 h and post cured at 150 °C for another 2 h, and thus the EP/CNTs/Bi_2Se_3 nanocomposites were obtained. To further characterize the performances of EP/CNTs/Bi_2Se_3 nanocomposites, EP/CNTs and EP/Bi_2Se_3 composites were both prepared in the same method with the 2 wt% content of the additives, respectively.

2.4. Characterization

X-ray diffraction (XRD) patterns were conducted by a Japan Rigaku Dmax X-ray diffractometer which is equipped with graphite monochromatized high-intensity Cu-Kα radiation (λ = 1.54178 Å).

Morphologies of CNTs, Bi_2Se_3, and CNTs/Bi_2Se_3 were studied by a PHILIPS XL30E scanning electron microscope (SEM) and transmission electron microscopy (TEM) (JEM-2100F, Japan Electron Optics Laboratory Co., Ltd.), which was also employed to characterize the dispersion state of CNTs/Bi_2Se_3 in PE matrix.

Thermogravimetric analysis (TGA) was performed to test the thermal stability of EP composites by a Q5000 thermoanalyzer instrument (TA Instruments Inc., USA) under air flow of 25 mL min^{-1} and heated from room temperature to 750 °C at a linear heating rate of 20 °C·min^{-1}.

Flammability of the samples was characterized using a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. Square specimens (100 × 100 × 3 mm^3) were irradiated at a heat flux of 35 kW m^{-2}, corresponding to a mild fire scenario.

The steady-state tube furnace (SSTF) tests were measured according to ISO TS 19700 [27]. Typically, 20 g of samples were spread evenly over a quartz boat, which was fed into the furnace at 650 °C at around 40 mm min^{-1}. Oxygen depletion and yields of carbon dioxide, carbon monoxide were determined using standalone detectors.

Glass transition behavior was investigated by a Q2000 differential scanning calorimetry (DSC) (TA Instruments Inc., USA). Dynamic mechanical analysis (DMA) was performed with the PerkinElmer Pyris Diamond DMA from −100 to 250 °C at a heating rate of 5 °C/min, at a frequency of 1 Hz in the tensile configuration.

Thermogravimetric analysis-infrared spectrometry (TG-IR) was conducted using a TGA Q5000IR thermogravimetric analyzer that was linked to a Nicolet 6700 FTIR spectrophotometer. About 5–10 mg of the sample was put in an alumina crucible and heated from 30 to 750 °C. The heating rate was 20 °C·min^{-1} (nitrogen atmosphere, flow rate of 50 ml min^{-1}).

Laser Raman spectroscopy (LRS) was performed with a SPEX-1403 laser Raman spectrometer (USA) at room temperature. The scanning scope was from 100 to 1800 cm^{-1}.

Tensile testing was measured by an electronic universal testing instrument (WD-20D, Changchun Intelligent Instrument Co. Ltd., China) at a tensile speed of 5 mm min^{-1}.

3. Results and discussion

It has reported that Bi_2Se_3 nanosheets can be synthesized in a facile wet chemical method [25]. As-synthesized nanosheets were coated with PVP, which was widely used in polymers. Meanwhile, CNTs, as a class of inorganic compounds, show inferior compatibility with polymeric matrix without organic modification. PVP has been used to modify CNTs for absorbing metallic ions or enhancing the compatibility with polymers [28,29]. Therefore, PVP can potentially promote the compatibility between EP matrix and the hybrids, as illustrated in Scheme 1.

3.1. Characterization of CNTS/Bi_2Se_3 nanocomposites

XRD patterns are usually applied to characterize the crystal structure of materials. The XRD curves of CNTS, Bi_2Se_3 and the nanocomposites prepared in this work are plotted in Fig. 1a. The characteristic (002) diffraction peak of CNTs can be clearly identified at 26.1°, which generates from the graphite-like tube-wall of CNTs [30,31]. For Bi_2Se_3, all peaks are well agreement with the previous reports, implying the successful preparation of the nanosheets with rhombohedral structure [32]. The XRD curve of CNTS/Bi_2Se_3