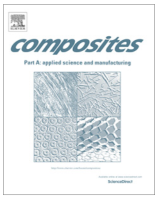
Composites: Part A 100 (2017) 371–380

Contents lists available at ScienceDirect

Composites: Part A

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



Bi_2Se_3 nanosheets: Advanced nanofillers for reinforcing and flame retarding polyethylene nanocomposites

Yanbei Hou [1], Weizhao Hu [1], Zhou Gui *, Yuan Hu *

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

ARTICLE INFO

Article history:
Received 26 March 2017
Received in revised form 24 May 2017
Accepted 29 May 2017
Available online 30 May 2017

Keywords:
Bismuth selenide
Polyethylene
Flame retardancy
Mechanical property

ABSTRACT

Bi_2Se_3 nanosheets with few layers have been successfully synthesized by a practical and mass-producible wet chemical method in this work. as-prepared nanosheets showed excellent compatibility with polyethylene (PE), which was attributed to the polyvinylpyrrolidone (PVP) encapsulated structure, generated during preparation process. The "interface", composed by PVP and PE molecular chains, enhanced the surface interaction between Bi_2Se_3 nanosheets and PE matrix, and thus improved the mechanical properties. Yield modulus of PE increased remarkably even at low loadings of nanofillers. The thermal stability and flame retardancy of PE host were significantly enhanced, including at least 60 °C increase in T_i, 37.6% and 20% decrease in pHRR and THR respectively. Meanwhile, the release of smoke and CO for PE/Bi_2Se_3 nanocomposites was suppressed during combustion. These phenomena mainly caused by the barrier effect of Bi_2Se_3. Thus, Bi_2Se_3 nanosheets could be potentially used to prepare functional polymers for certain applications.

1. Introduction

Two dimensional (2D) nanomaterials have aroused dramatically increasing academic and industrial attention since 2004 when A. K. Geim and K. S. Novoselov achieved the mechanical exfoliation of few-layer and single-layer graphene [1]. Since then, remarkable physicochemical properties of graphene were found one after another with enormous efforts made by scientists [2–4]. The outstanding integration of physical, optical and electronic properties of graphene sparked the exploration for the other 2D nanomaterials that posses similar layered structure, such as transition metal dichalcogenides (TMDs), carbon nitride, boron nitride and black phosphorus nanosheets [5–8]. Driven by the extraordinary properties of 2D nanomaterials, a variety of preparation methods have been developed, e.g., mechanical (micromechanical and ball-milling) exfoliation, chemical synthesis, chemical vapor deposition, electrochemical exfoliation, etc. [9–12] However, there are some drawbacks potentially limit the wide applications of 2D nanomaterials, including low preparation efficiency and severe processing conditions [13,14]. Therefore, it is necessary to modify the existing preparation methods to meet the requirements from commercial applications, or find new materials to replace them in some fields.

Bismuth selenide (Bi_2Se_3), as a class of layered nanomaterials, has been intensively explored in recent years [15–17]. Bi_2Se_3 is layered in a quintuple layer (QL) sequence of Se-Bi-Se-Bi-Se along the c axis and constructs planar. Similar with graphene-like nano layered materials, covalently bonded Bi_2Se_3 sheets are linked together principally via van der Waals interactions, which intrinsically facilitates the preparation of Bi_2Se_3 nanoplates [18]. The wet chemical synthesis is a practical and high-efficiency method to prepare ultrathin Bi_2Se_3 sheets, which produces relatively high yields and proceed under mild conditions [19].

2D nanomaterials have been widely used to modify polymeric materials in many works, which play multiplier roles in improving physical and chemical properties of matrix [20–22]. Due to layered structure, Bi_2Se_3 nanosheets hold extremely large surface-to-volume ratio, similar with graphene-like nanomaterials. Different from the high electronic conductivity of graphene-based nanomaterials, Bi_2Se_3 nanosheets, as a class of semiconductor, could theoretically satisfy some applications that require maintaining the electrical insulation property and high dielectric constant of polymer. In summary, layered Bi_2Se_3 nanomaterials can be used as advanced nanofillers to functionalize raw polymer. To our knowledge, there are no reports on application of Bi_2Se_3 nanosheets as modifier to improve properties of polymers. As a kind of inorganic nanofillers, the inherent attribute of Bi_2Se_3 determines the inferior

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

[1] These authors contributed equally to this work and should be considered co-first authors.

http://dx.doi.org/10.1016/j.compositesa.2017.05.034

compatibility between the fillers with polymeric materials. It's well known that dispersion state of nanofillers in matrix markedly influences the properties of polymer composites. Therefore, a feasible design scheme of organic modification for Bi_2Se_3 nanosheets should be proposed to improve its dispersion in matrix.

To validate the presumption, few-layer Bi_2Se_3 nanoplates are synthesized by a wet chemical method and subsequently incorporated into linear low density polyethylene (PE) matrix to prepare nanocomposites by a simple solvent blending-precipitation method. The surface of as-prepared Bi_2Se_3 nanoplates is covered by polyvinylpyrrolidone (PVP), which acts as stabilizer during synthetic process and promotes the compatibility between nanofillers and polymer by "interfaces". The thermal stability, flame retardancy, and mechanical property of PE/Bi_2Se_3 nanocomposites were measured and analyzed.

2. Experimental

2.1. Materials

Bismuth nitrate pentahydrate ($Bi(NO_3)_3{\cdot}5H_2O$), selenium (Se), sodium borohydride ($NaBH_4$), polyvinylpyrrolidone (PVP), ethylene glycol (EG), acetone, and xylene were all of analytical reagent grade quality and used without further purification. They were provided by Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). PE (8320) was supplied by China Petroleum & Chemical Corp. (China). Deionized water was used throughout this study.

2.2. Synthesis of Bi_2Se_3 nanosheets

The Bi_2Se_3 was prepared by a modified wet-chemical method [19]. Generally, stoichiometric Se was added into $NaBH_4$ aqueous solution to obtain NaHSe (0.35 mM) under inert and ice-bath conditions. 2.33 mmol $Bi(NO_3)_3{\cdot}5H_2O$ and 2 g PVP were added into 200 mL EG under magnetic agitation at room temperature for 0.5 h, and then heated to 160 °C. The freshly prepared NaHSe solution (5 mL) was rapidly added into the mixture. The reaction system was maintained at 160 °C for another 10 min before cooling to room temperature. An acetone (160 mL) and water (40 mL) mixture was poured into the obtained dark-brown solution and shook well. The as-synthesized Bi_2Se_3 was collected and washed with acetone/water mixture several times, and dried at 80 °C overnight.

2.3. Preparation of PE/Bi_2Se_3 nanocomposites

The PE/Bi_2Se_3 nanocomposites with different content of Bi_2Se_3 (0.2, 0.5, and 1 wt%) were prepared by a simple solvent blending-precipitation method, named as PE/Bi_2Se_3−0.2, PE/Bi_2Se_3−0.5, PE/Bi_2Se_3−1, respectively. The calculated Bi_2Se_3 was dispersed in a certain volume of xylene with ultrasonication. The PE solution, obtained by dissolving PE grains in xylene at 90 °C, was added into the mixture and further treated under sonication-assisted stirring for 1 h. Then, the hot mixture was poured into water to precipitate PE/Bi_2Se_3 nanocomposites. Thus-obtained nanocomposites were dewatered by drying at 80 °C overnight, followed by melt blending. For comparison, the neat PE sample was processed with the same procedure.

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 ($\lambda = 1.54178$ Å). Fourier transform infrared (FTIR) spectrum was obtained using a Nicolet 6700 FTIR (Nicolet Instrument Company, USA) with scanning from 1000 to 4000 cm^{-1}. Morphology of Bi_2Se_3 was studied by a PHILIPS XL30E scanning electron microscope (SEM). Transmission electron microscopy (TEM) (JEM-2100F, Japan Electron Optics Laboratory Co., Ltd.), with a 200 kV accelerating voltage, was employed to characterize the shape of Bi_2Se_3 and its dispersed state in PE matrix. Thermogravimetric analysis (TGA) was performed by a Q5000 thermoanalyzer instrument (TA Instruments Inc., USA) under air flow of 25 $mL{\cdot}min^{-1}$ and heated from room temperature to 700 °C at a linear heating rate of 20 $°C{\cdot}min^{-1}$. Flammability of the samples was characterized using a cone calorimeter (Fire Testing Technology, UK) according to ISO 5660. Square specimens ($100 \times 100 \times 3$ mm^3) were irradiated at a heat flux of 35 $kW{\cdot}m^{-2}$, corresponding to a mild fire scenario. All the measurements were repeated three times and the results were averaged. The SSTF tests were measured according to ISO TS 19,700 [23]. Typically, 20 g of samples were spread evenly over a quartz boat, which was fed into the furnace at 650 °C at around 40 $mm{\cdot}min^{-1}$. 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 test curves were obtained by a WD-20D electronic universal testing instrument (Changchun Intelligent Instrument Co. Ltd., China) at a tensile velocity of 50 $mm{\cdot}min^{-1}$. Dynamic mechanical analysis (DMA) of samples was conducted on a DMA Q800 at a fixed frequency of 1 Hz from −100 °C to 150 °C at a linear heating of 10 $°C{\cdot}min^{-1}$.

3. Results and discussion

3.1. Structure and morphology characterization

The XRD pattern of synthesized Bi_2Se_3 is illustrated in Fig. 1a. All the peaks can be indexed to that of reported Bi_2Se_3 [24], implying the sample with rhombohedral structure was successfully obtained. To detect the presence of PVP on the surface of plate, FTIR was utilized and the result was displayed in Fig. 1b. It was found that these peaks revealed a typical molecular structure of PVP, where absorption bands at 3413, 2954, 1658, and 1286 cm^{-1} were attributed to stretching vibration of —OH, —C—H, C=O, and C—N group respectively [25,26]. The strong adsorption bands of C=O and C—N stretching indicated the existing of PVP in the obtained Bi_2Se_3 after excluding the effects of free PVP molecules [27]. As a nontoxic stabilizer and surfactant, PVP-encapsulated Bi_2Se_3 nanosheets potentially perform superior compatibility with polymeric materials.

The micro-morphologies and structure of as-synthesized Bi_2Se_3 was investigated by TEM, as observed in Fig. 2. The single Bi_2Se_3 sheet exhibited regular-hexagon structure and was seemingly covered by some organic compound, which resulted in the rough selvedges and uneven surface. The results of energy dispersive spectrometer (EDS) revealed the elementary composition and the ratio of Bi to Se. The presence of C, O and N elements further confirmed the presence of PVP on the surface of Bi_2Se_3 nanoplates, which was agreement with FTIR results. Based on the high resolution TEM (HRTEM) image in Fig. 2b, the Bi_2Se_3 nanosheets showed clear lattice fringes of 2.083 Å, ascribed to the (1 1 0) plane of the crystal, corresponding to previous report [28]. As shown in Fig. 2c, there are many clear Bi_2Se_3 nanosheets in sight. The lateral dimension of a large number of flakes was measured and the statistical analysis is plotted in Fig. 2c. The observation reveals that size distribution of Bi_2Se_3 nanosheets predominantly ranges from 150 to 250 nm. From the vertical growth section, as shown in Fig. 2c-d, few-layered Bi_2Se_3 nanosheets with a thickness that was several nanometers were prepared.